OXYGEN TRANSPORT MEMBRANES FOR POWER GENERATION WITH CARBON CAPTURE

RIAN RUHL

OXYGEN TRANSPORT MEMBRANES FOR POWER
GENERATION WITH CARBON CAPTURE

ZUURSTOFTRANSPORTMEMBRANEN VOOR
ELEKTRICITEITSPRODUCTIE MET CO₂-AFVANG

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SUMMARY

This thesis focuses on materials science related to Oxygen Transport Membranes (OTMs). The general aim is to characterize and improve the structural and oxygen transport properties of candidate OTM materials for application in power generation with carbon capture.

In short, OTMs can be applied as a technology to produce pure oxygen which can be used for the combustion of a fuel. Compared with air, burning with oxygen should lead to a relatively pure stream of gaseous combustion products. The composition of that stream should limit the number and complexity of separation steps required for carbon capture. To obtain commercially viable OTMs, some of the most important properties to be improved are the magnitude of the oxygen flux and the chemical stability of the membrane material in atmospheres containing steam and acidic gases. In the introduction, **Chapter 1**, detailed accounts of materials, basic concepts and process aspects are given.

In **Chapter 2**, a new route for the synthesis of perovskite-type oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ is described. This route permits to prepare titanium-containing oxides via a modified Pechini route. It is optimized by the combined use of EDTA and citric acid as chelating and gelating agents, as well as by balancing the amounts of fuel and oxidizing agents in the reaction mixture. The method produces almost phase-pure perovskite oxide powder, with an ultra-fine crystallite size of 20-40 nm, and with a low level of organic residues. Highly sinter-active powders are obtained after calcination and ball-milling of the powders.

Chapter 3 discusses the influence of yttrium dopant concentration on performance and stability of perovskite-type oxides $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Y}_x\text{O}_{3-\delta}$. Without yttrium doping, the material exhibits the highest oxygen flux through a MIEC membrane

reported to date. However, the parent material is subject to degradation when operated below ~ 840 °C. The oxygen transport properties at different yttrium dopant concentrations are assessed *in situ*, at 700 °C and 800 °C, over 200 h using automated electrical conductivity relaxation (ECR) measurements. Detailed phase analysis is performed after the long-term annealing experiments by scanning electron microscopy (SEM). The combined results show that yttrium doping markedly improves the structural and performance stability, and that a substitution level of 10 mol% yttrium suffices to obtain a material with virtually no degradation during annealing for 200 h at the assessed temperatures.

Chapter 4 continues on the subject of tailoring material properties by partial substitution. The perovskite-structured calcium manganite exhibits fast oxygen transport and excellent stability in reducing environments, and therefore holds promise for application as an oxygen storage material in chemical looping combustion processes. In this chapter, partial substitution was applied to explore its possible use as an oxygen transport membrane. A main finding of the work is that partial substitution of the manganese ions by iron and/or titanium ions affects the onset temperatures of phase transitions occurring in the host material as confirmed by high-temperature X-ray diffraction studies at typical membrane operation temperatures. Electrical conductivity relaxation experiments demonstrate that the oxygen transport properties are correlated with these structural transformations.

Chapter 5 describes routes to enhance the oxygen flux through NiFe_2O_4 - $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$ (NFO-CTO) composite membranes. It is found that the oxygen flux increases by a factor of 2-4 by coating a porous NFO-CTO layer on both sides of the membrane, and by a factor of 6 –12 relative to the bare membrane after activating the porous layers with Pr_6O_{11} catalyst nanoparticles.

The subject of **Chapter 6** is fundamental, being focused towards carbonation of Sr-containing perovskite oxides. As the applied sweep gases for OTMs in industrial processes often contain acidic gases such as carbon dioxide or sulphur dioxide, it is of

utmost importance to understand the reaction of the perovskite oxide with these gases leading to the formation of carbonates and/or sulfates. To this end, thermogravimetric and temperature-programmed desorption experiments on different perovskite oxides and mixtures of oxides and carbonates are performed. The results reveal that carbonation is governed by both kinetics and thermodynamics. The apparent activity of strontium oxide in the perovskite oxide, at given partial pressure of CO_2 , plays a crucial role in determining the onset temperature of carbonation.

In **Chapter 7**, the story moves on to the application of OTMs. Oxyfuel combustion and pre-combustion carbon capture based processes with a combined cycle layout are designed to efficiently incorporate OTMs into these processes. Using either a coal/pet-coke mixture or natural gas as the fuel, both processes are benchmarked against an existing and comparable process in which no carbon capture is performed. The applied methods and assumptions are considered with care, to make both processes directly comparable to the reference and to each other. The electricity price and the energy efficiency are taken as the main issues for comparison. Next to that, the obtained data is analyzed in detail to gain insight in the most critical points for implementing OTMs into power plants.

Finally, **Chapter 8** gives reflections to the work described in this thesis, and to the field in general. Some directions and opportunities for future work are suggested.

SAMENVATTING

Dit proefschrift gaat over de chemische materiaalkunde van zuurstoftransportmembranen (Engels: *Oxygen Transport Membranes* (OTMs)). Het beschrijft wetenschappelijk onderzoek met het doel de structuur en zuurstoftransporteigenschappen van deze materialen voor toepassing als OTM te karakteriseren en te verbeteren.

OTMs kunnen worden ingezet in energiecentrales om CO₂-afvang mogelijk te maken. Kortgezegd kunnen deze membranen worden geïntegreerd in een thermische energiecentrale om de verbranding van pure zuurstof te voorzien, waardoor de ontstane rookgassen slechts geringe hoeveelheden onzuiverheden bevatten. Daardoor kunnen het aantal zuiveringsstappen om CO₂ te kunnen afvangen en de daarmee samenhangende complexiteit worden verminderd. Om CO₂-afvang met deze technologie efficiënt en kostentechnisch interessant te maken, moet er evenwel nog een flink aantal stappen gezet worden. De zuurstofflux en de chemische stabiliteit in een atmosfeer met stoom en zure gassen zijn hierbij twee van de meest belangrijke eigenschappen. In de introductie van het proefschrift, **Hoofdstuk 1**, worden de materialen voor membranen, de benodigde eigenschappen, en de processen waarin ze gebruikt kunnen worden in detail beschreven.

In **Hoofdstuk 2** wordt een nieuwe route voor de synthese van SrTi_{1-x}Fe_xO_{3-δ} perovskieten beschreven. Deze syntheseroute maakt het mogelijk om titaanhoudende oxiden te bereiden via een gemodificeerde Pechini-route. De synthese is geoptimaliseerd door het gecombineerde gebruik van EDTA en citroenzuur als complexvormende en gelerende middelen, en tevens door de hoeveelheden brandstof en oxidator in het reactiemengsel in de juiste verhouding te brengen. Poeders van perovskietoxiden die op deze manier bereid zijn hebben een zeer fijne kristallietgrootte (20 - 40 nm) en bevatten weinig organische residuen. Na calcinatie en malen in een kogelmolen worden zeer sinteractieve perovskietoxidepoeders verkregen.

Hoofdstuk 3 beschrijft de invloed van yttriumdoting op de stabiliteit en prestaties van perovskietoxiden $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Y}_x\text{O}_{3-\delta}$. Het basismateriaal zonder yttrium is het perovskietmateriaal met de hoogste zuurstofflux tot op heden vermeld in de literatuur. Echter, bij afkoelen tot temperaturen lager dan $\sim 840^\circ\text{C}$ is het materiaal niet stabiel. In dit hoofdstuk wordt bekeken hoe de concentratie van yttrium in het materiaal de zuurstofflux beïnvloedt over een tijdsduur van 200 uur bij 700°C en bij 800°C . Dit wordt gedaan door middel van geautomatiseerde metingen van de relaxatie van de elektrische geleiding. Een gedetailleerde analyse van de gevormde fasen is gedaan met een rasterelektronenmicroscop. De gecombineerde resultaten laten zien dat dotering met yttrium de structurele stabiliteit en de transporteigenschaften verbetert, en dat dotering van 10 mol% yttrium voldoende is voor verkrijging van een materiaal dat nagenoeg geen degradatie meer laat zien gedurende 200 uur bij de bovengenoemde temperaturen.

Hoofdstuk 4 gaat eveneens over de beïnvloeding van materiaaleigenschappen door partiële substitutie. Calciummanganiet is een perovskietverbinding met een hoge zuurstofflux en een uitstekende stabiliteit in een reducerende omgeving. Om deze reden is het een zeer beloftevol materiaal om voor zuurstofopslag gebruikt te worden in *chemical looping combustion* processen. In dit hoofdstuk wordt partiële substitutie toegepast om de mogelijke toepassing van het materiaal als zuurstoftransportmembraan te bestuderen. Een belangrijke waarneming in het gedane onderzoek is dat de partiële substitutie van de mangaanionen door ijzer- en/of titaanionen de temperatuur van faseovergangen in de gastheerstructuur beïnvloedt, zoals bevestigd door röntgendiffractiemetingen bij hoge temperatuur. ECR-metingen laten zien dat de zuurstoftransporteigenschaften gecorreleerd zijn met deze structurele overgangen.

Hoofdstuk 5 beschrijft methodes om de zuurstofflux door $\text{NiFe}_2\text{O}_4 - \text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$ (NFO-CTO) composiet-membranen te verbeteren. Gevonden wordt dat de zuurstofflux een factor 2 – 4 toeneemt door coating van een poreuze laag van hetzelfde materiaal aan beide zijden van het membraan. Activering van de poreuze lagen met Pr_6O_{11} katalysator-

nanodeeltjes verhoogt de zuurstofflux verder met een factor 6 – 12 ten opzichte van die van het oorspronkelijke membraan.

Het onderwerp van **Hoofdstuk 6** is fundamenteel van aard en gaat over de carbonaatvorming op strontiumhoudende perovskietoxiden. Aangezien dikwijls zure gassen aanwezig zullen zijn in de spoelgassen van OTMs gebruikt in verschillende industriële processen is het van groot belang om de reacties tussen de oxiden en deze gassen die leiden tot carbonaat- en/of sulfaatvorming te begrijpen. Om deze reden zijn thermogravimetrische en temperatuur-geprogrammeerde desorptie-metingen uitgevoerd aan verschillende perovskieten en mengsels van oxiden en carbonaten. De resultaten laten zien dat de carbonatiereacties bepaald worden door zowel thermodynamica als reactiekinetiek. De activiteit van strontiumoxide in de perovskietoxiden, bij gegeven partiële spanning van CO_2 , is bepalend voor de temperatuur waarbij carbonatie plaatsvindt.

In **Hoofdstuk 7** wordt naar de toepassing van OTMs gekeken. *Oxyfuel combustion* en *pre-combustion* gebaseerde koolstofafvangprocessen worden ontworpen om op een efficiënte manier OTMs in deze processen te integreren in een elektriciteitscentrale met een gecombineerde cyclus. Deze processen, waarin aardgas of een mengsel van pet-coke en kolen wordt gebruikt als brandstof, worden vergeleken met een bestaand, vergelijkbaar proces waarin geen koolstofafvang wordt toegepast. Veel aandacht gaat uit naar de toegepaste methodes en aannames, zodat directe vergelijking met elkaar en met de referentie mogelijk is. De elektriciteitsprijs en de energie-efficiëntie van het proces zijn de belangrijkste aspecten die gebruikt worden in de vergelijkingen tussen processen. Aan de hand van de verkregen data en de verkregen inzichten wordt besproken welke punten kritisch zijn bij de implementatie van OTMs in energiecentrales.

Ten slotte geeft **Hoofdstuk 8** een reflectie op het onderzoek beschreven in dit proefschrift, en meer in het algemeen, op het gebied van het onderzoek. Een aantal richtingen en mogelijkheden voor verder onderzoek worden gegeven.

CHAPTER 1

Introduction: Oxygen Transport Membranes and
their applications

1.1 Electricity production and carbon capture

In the modern world, most people feel disarmed when their access to electricity is limited. Lighting, cooking, communication, and transportation all heavily rely on electricity. Figure 1.1 shows how the total worldwide energy consumption and electricity use have gone hand in hand since the start of the current millennium. Although the future cannot be predicted exactly, nothing currently points at a sudden decrease of the electricity demand. Actually, with the quickly growing world population and the similarly swift growing access to electricity, a further increase in the electricity demand could be expected.

Figure 1.1. Historical overview of total worldwide energy consumption ¹ and electricity consumption ². Data for the total worldwide electricity consumption starts in 1960.

Figure 1.2 shows that fossil sources represent the largest share in the amount of energy consumed worldwide during the last century. The amount of energy generated from renewable sources accounts for less than five percent of the total energy consumption. Due to the nature of renewable-based power plants, most of this energy is used for the production of electricity. In the year 2015, 14.4% of the total amount of primary energy was converted into electricity³. Taking into account the limited efficiency of thermal power plants, one can understand that electricity generation is responsible for much of the fossil fuel use, and therefore for a large share in the CO₂ emissions. In fact, according to the 2014 report of the Intergovernmental Panel on Climate Change (IPCC), the production of electricity and heat was responsible for 25% of the global greenhouse gas emissions, and with that it represents the largest economic sector in terms of emissions⁴.

Figure 1.2. Total worldwide energy consumption per primary energy source. Data adapted from Ref. 1.

Fossil-fueled plants are typically industrial-size plants with a lifespan of 40 – 60 years ⁵. Even though many of the recently built units are wind farms or solar power based facilities, their share in the total electricity production is still small. It is likely that fossil-fuelled plants will be used for generation of electricity for decades to come, thereby emitting large amounts of CO₂ into the atmosphere.

In the Paris climate accord, 175 countries agree to keep the global temperature rise well below two degrees Celsius ⁶. Among many measures that can be taken, one that comes to the mind quickly is to significantly increase the share of renewable and low-carbon energy sources. To reach a 100% share of renewables by 2050, the growth in installed capacity should continue at the same rate as the last decade for another decade, after which it suffices to grow with 4-5% ⁷. This, of course, only holds when the capacity of non-renewable electricity generation decreases with time, to have it nullified by 2050. Alternative electricity-related measures to reach the goal include, for example, to increase the efficiency of electrical apparatuses and that of existing and new-built power plants, to improve the insulation of buildings, and to increase the share of electricity in the energy used for heating and transport purposes.

Next to these options, technologies directly targeting CO₂ are considered. Two different categories of technologies exist. The first is known as carbon capture and storage (CCS) or carbon capture and utilization (CCU), sometimes being merged under the name ‘carbon capture’. These technologies prevent CO₂ from entering the atmosphere after being generated. The second type known as carbon dioxide removal (CDR) technologies actively remove CO₂ from the atmosphere. Both categories of technologies are probably required to meet the two-degrees target. In most of the scenarios presented by the IPCC that likely lead to a temperature increase of less than 2 °C (probability >66%), the amount of CO₂ offset by CCS and CCU needs to increase to a value equivalent to the current production rate (around $4 \cdot 10^{10}$ t year⁻¹) ⁸. Meanwhile, up to $2 \cdot 10^{10}$ t CO₂ year⁻¹ needs to be removed by CDR technologies to compensate for the emission of other gases that contribute to the greenhouse effect ⁸. Whereas quite a few

CCS/CCU technologies are commercially available or are close to that point ⁹, CDR approaches – apart from enhanced ecosystem stewardship – are still far below the level of readiness ⁷. Bioenergy with CCS, abbreviated as BECCS, is considered as one of the most promising negative emission technologies ^{7,10}. Being a combination of two existing technologies, CCS and the combustion of biological matter to produce heat, the technological readiness of BECCS depends on that of the underlying technology as well as on the speed with which optimizing and upsizing is performed. Further information about the implementation of CCS technology into the electricity generation system can be found in recent review by Bui *et al.* ¹¹.

Power plants, cement plants, and steel plants are examples of industrial processes in which combustion plays a major role. Heat is typically generated by the combustion of fuels from a fossil origin. Due to the localized nature of the emissions from industrial plants, these are called point sources of carbon dioxide (and other gases). Point sources are excellent places to capture CO₂, due to the high concentration of carbon dioxide in flue gases as compared to that in the atmosphere. The industrial processes mentioned at the beginning of this paragraph all comprise of different process schemes, and therefore require differentiated approaches.

This thesis is written in the context of the GREEN-CC (Graded Membranes for Energy Efficient New Generation Carbon Capture Process) project, which was an EU-funded research program in which a consortium of universities, research institutes, and companies aimed to improve a wide range of carbon capture technologies based on oxygen transport membranes (OTMs). The GREEN-CC project focused on application of carbon capture technology in cement plants and various types of power plants. This thesis focuses on power plants, but as the process conditions and the required properties for membrane materials are roughly similar, much of the work could be valuable for both applications.

1.2 Separation processes for carbon capture

Carbon capture requires the separation of CO₂ from other gases. For storage and utilization, as well as for pipeline transport, maximum concentrations of impurities in CO₂ streams have been defined .

1.2.1 CO₂ separation processes

A broad range of processes to separate carbon dioxide from flue gases or hydrogen from carbon dioxide has been developed over the years. The main constituents of the flue gas stream obtained after combusting fuels such as coal, natural gas, or biomass are – next to CO₂ – are nitrogen, water, and oxygen. Since both the physical (boiling point, vapor pressure, size of molecule) and chemical properties (reactivity with other materials) of CO₂ are considerably different compared with the other three gases, multiple separation processes have been developed. These can be categorized in absorption, adsorption, cryogenic, and membrane-based processes ¹², and are briefly discussed below.

Absorption and adsorption

Amine-solution based absorption processes for flue gas scrubbing can be considered as mature technologies, as illustrated by their widespread use in natural gas sweetening for decades ¹³. Nonetheless, absorption processes continue to be optimized by researchers ^{14,15}. Adsorption processes for the same application, using for example carbon-based materials, metal-organic frameworks, solid amine sorbents, or zeolites are still less mature ^{14,16,17}. The amine-solution based absorption processes are based on the formation of a carbonate in one reactor, after which the carbonate is decomposed and the sorbent regenerated in a second reactor. Adsorption processes also use a dual-reactor setup, but instead of reaction of the sorbent with the CO₂, the gas is physically or chemically adsorbed. As the amount of energy required for desorption is much below that required for the decomposition of carbonates, adsorption-based processes are typically less energy-intensive than absorption-based processes ¹².

Separation processes categorized as ‘other processes’ in Ref. 14 include for example chemical looping combustion ^{18,19}, calcium carbonate looping ²⁰, CO₂ hydrates ²¹, and electrochemical oxidation/reduction cycles of chemicals that react with CO₂ ¹⁹. Apart from chemical looping combustion, these processes are based on controlled formation and decomposition of carbonates, and can therefore be considered as absorption processes as well. All these ‘other processes’ are still far from commercial use ¹¹.

Cryogenic distillation

Cryogenic distillation is a process to separate liquefied gases from each other. This works well if the boiling point of the gas to be separated from the mixture and those of the other gases in the mixture are dissimilar. On the one hand, the required investments are relatively low and the reliability is high, but on the other hand, cooling of gases to the liquid state requires a lot of energy ¹². Furthermore, if the flue gas stream or H₂/CO₂ mixture contains less than 90% of CO₂, dry ice could be formed in the cryogenic process which may block the piping. Typically, streams for carbon capture contain less than 50% of CO₂ ²², thereby making cryogenic distillation a less attractive separation method for this application.

Membrane separation*

Membrane-based processes, including gas separation membranes and membrane contactors, are relative newcomers to the separation of carbon dioxide from flue gas ²³ or

* A membrane could be defined as a barrier which allows certain components of a mixture to pass and retains others. Using this principle, materials can be separated from each other. A few requirements can be defined for any membrane to work. First, the barrier should be selective towards the species to be separated. Second, the membrane should not impose a high resistance to the permeating species. Third, a driving force is required to direct transport in the desired direction. When these conditions are fulfilled, thermodynamics and kinetics act on the species to be transported to drive the system to a new equilibrium. In a non-steady state situation, for example when the membrane feed and sweep fluids are replaced continuously, the system strives to reach equilibrium but is

the separation of hydrogen from carbon dioxide ²⁴. Polymeric membranes are industrially applied for the production of hydrogen ¹⁶, but are not ideally suited for carbon capture processes due to limited thermal, mechanical, and chemical stability, as well as the typically observed trade-off between selectivity and permeability ^{25,26}. Dense palladium or palladium composite membranes have been applied commercially for the production of hydrogen with high purity, but this technology may be less well suited to carbon capture processes due to the associated costs ²⁷. In addition, porous ceramic membranes can separate hydrogen from CO₂ based on the size of the molecules. Porous membranes based on functionalized silica, zeolites, and metal-organic frameworks are subject of intensive research ²⁵. These membranes did not yet find commercial application in the field of carbon capture. More research directed to improve selectivity, permeability, and stability as well as towards upscaling of defect-free membrane production is necessary to bring these membranes closer to commercial application ²⁵. Finally, mixed-matrix membranes are promising class of membranes for the separation of CO₂ ²⁶. This type of membranes consists of a polymer and inorganic fillers, trying to combine the less demanding production process of the polymeric membranes with the advantageous separation properties of the porous inorganic membranes. However, based on a recent review article ²⁶, the maturity of mixed matrix membranes technology seems to be behind that of polymeric and porous inorganic membranes.

1.2.2 O₂ production processes

As discussed in Sections 1.3.3 and 1.3.2, oxyfuel combustion combined cycle processes always require pure oxygen for each combustion step, while in pre-combustion processes pure oxygen may be only required for gasification or reforming. Using pure oxygen instead of air for the combustion limits the concentration of species other than

never given the chance to reach that. In this way, a membrane can be operated continuously to selectively separate one species from another.

CO₂ and H₂O in the process, which renders the separation of CO₂ more easy and efficient. The amount of oxygen required in a power plant is large. As discussed in Chapter 7 of this thesis, an hourly oxygen feed of 77,200 kg is required to generate a moderate 238 MW of electricity in a pre-combustion.

Table 1.1. Comparison of industrial oxygen production processes ³⁰.

Process	Status	Economic range [short ton per day]	Purity limit [vol.%]
Cryogenic distillation	Mature	>20	99+
Adsorption	Semi-mature	<40	95
Polymeric membranes	Semi-mature	<20	~40
Oxygen Transport Membranes	Developing	Undetermined	99+
Molten salt	Developing	Undetermined	99+

Oxygen is among the top five of industrially produced chemicals in terms of yearly sold volume ²⁸. Typical applications include its use in the production of cement, steel, polymers, and in the preparation of a wide variety of other chemicals and petrochemicals ²⁹, while highly pure oxygen finds application in some smaller-scale industrial processes as well as for medical purposes. According to the open literature, the most economically attractive way to produce oxygen depends strongly on the flowrate and purity which are required. Table 1.1 gives some insight into the market segments in which the various oxygen production methods operate, as well as on the maturity of the technology. Among the different methods used for oxygen production, cryogenic distillation and OTM technology are briefly discussed below.

Cryogenic distillation

As seen from Table 1.1, the only mature and economically viable oxygen production process for a demand as large as that of a power plant is cryogenic distillation ³¹. Cryogenic distillation has been used industrially to separate air into oxygen and nitrogen since the beginning of the 20th century ³². Figure 1.3 shows a photo of such an industrial plant. In

this process, ambient air is compressed, slightly cooled, and impurities such as water and CO_2 are removed. After further cooling to a temperature of approximately -175°C , at which the remaining gases are in a liquid state at the used pressure, the species are separated by distilling. Distillation is most suited for separating large quantities of liquids with different boiling points. Since the boiling points of oxygen and nitrogen (90 and 77 K at atmospheric pressure) are close to each other, many stages are required in a distillation column to achieve a separation with sufficiently pure products³².

Figure 1.3. Cryogenic air separation to produce oxygen and nitrogen[†].

Oxygen transport membranes (OTMs)

Even though methods exist to make cryogenic distillation less energy-intensive^{33,34}, it is expected that OTM-based processes could gain an advantage over cryogenic distillation in terms of efficiency due the better heat integration possibilities into processes where large quantities of heat are available³¹. This is the case in power plants: the low

[†] Picture reused from <https://commons.wikimedia.org/wiki/File:Coldbox.JPG> under CC BY-SA 3.0 license.

temperature of the produced oxygen and nitrogen is not directly beneficial to the remainder of the process, while gas streams with the high temperature required to operate OTMs are present in the power plant. OTM-based processes therefore offer better heat integration options. Before discussing OTMs in more detail (See Section 1.4), different process schemes of power plants with carbon capture are introduced.

1.3 Carbon capture process schemes

Three main routes to capture CO_2 from point sources have been developed: post-combustion, pre-combustion and oxyfuel combustion carbon capture. Hereafter, a concise overview of the working principle of each of these technologies is given.

1.3.1 Post-combustion carbon capture

Processes that capture CO_2 by separating it from other gaseous combustion products are called post-combustion carbon capture processes. This could be considered as a traditional approach in chemical engineering: first, the combustion reaction takes place, after which the side products are separated from the main product. In the case of traditional fossil fuel-based electricity production, the main product is the heat released by combustion which is used to produce steam. The reaction products are partly and fully oxidized gases which are released into the atmosphere. When post-combustion carbon capture is integrated into such an electricity generation process, CO_2 is separated from other combustion products as depicted in Figure 1.4. Compared to other pre-combustion and oxyfuel combustion processes used to separate CO_2 from flue gases, amine-based

Figure 1.4. Simplified scheme of a post-combustion carbon capture process.

post-combustion processes are the most mature ³⁰. However, regeneration of the solvent is highly energy-intensive ^{30,35}, thereby penalizing the net energy output of the power plant.

1.3.2 Pre-combustion carbon capture

In pre-combustion carbon capture processes, of which a simplified scheme is given in Fig. 1.5, CO₂ is captured before full completion of the combustion. Typically, a solid feedstock (coal, biomass, pet-coke) or gaseous feedstock (natural gas) is partially oxidized using oxygen or air, reformed with steam, or oxidized and reformed at the same time. Afterwards, the ratio of gases in the produced syngas is modified in the water gas shift (WGS) reaction (Eq. 1.1).

To steer the ratio of components, the equilibrium in the water gas shift reaction is forced towards the right side. Addition of steam or adsorption of CO₂ (sorption-enhanced water gas shift, SEWGS) are ways to tune the equilibrium ²². The remaining species are a mixture of hydrogen and CO₂, which are the desired products, and some unused oxygen, and nitrogen and argon if air was used for oxidation.

Figure 1.5. Simplified scheme of a pre-combustion carbon capture process.

CO₂ can be separated from the other gases by similar means as those employed in post-combustion processes. Pilot scale tests have been concluded successfully for pre-combustion carbon capture with an amine sorbent ³⁶, therefore pre-combustion carbon capture could be regarded as an almost mature technology ¹¹. Absorbents that perform ‘physical absorption’, a term used to describe a single-step absorption process without any chemical reaction afterwards, are most common for pre-combustion processes ²². Separation of CO₂ from hydrogen in a pre-combustion process is less energy-intensive than separation of CO₂ from flue gases in post-combustion processes ³⁷, mainly due to the high concentration of CO₂ in the product stream of the WGS section (~15% – 40% ^{22,38}) compared with that in flue gas (~5% – 15% ^{30,38}).

If pure oxygen is used in the gasification or reforming section of a pre-combustion based process, the amounts of nitrogen and NO_x which are present in produced syngas are much lower than when gasification or reforming is performed using air. With lower amounts of impurities, separation of CO₂ from hydrogen becomes more efficient ³⁸. Oxygen transport membranes can be integrated into a pre-combustion power plant to supply the required oxygen, an example and a detailed analysis of such a process are given in Chapter 7.

1.3.3 Oxyfuel combustion carbon capture

In an oxyfuel combustion carbon capture process (cf. Fig. 1.6), the fuel is burnt with pure oxygen rather than air. Only two gaseous compounds (CO₂ and steam) are present in large quantities after the combustion. Steam is easily liquefied by lowering the temperature of the combustion products to a temperature at which the water vapor condenses out. The concentrations of impurities such as carbon sulfide (CS₂), carbonyl sulfide (COS), SO_x, and NO_x depend on the gasification and combustion process characteristics, gas cleanup is done to absorb these acidic species from the CO₂. The remaining CO₂ is pressurized and can be transported to another facility for utilization or storage. The oxyfuel combustion process does not require a large-scale gas separation process after the combustion, unlike post-combustion and pre-combustion processes. This would increase the efficiency of oxyfuel combustion carbon capture as compared to

post-combustion and pre-combustion carbon capture processes. However, the production of pure oxygen from air is costly and increases the amount of energy required for the process³⁸. Furthermore, combustion of syngas with pure oxygen would lead to too high temperatures in the gas turbine, hence another gas that acts as a diluting agent (CO_2 or steam) is mixed with oxygen.

Figure 1.6. Simplified scheme of an oxyfuel combustion carbon capture process.

1.3.4 Alternative process schemes

In the last years, process schemes for power plants have been continuously redesigned in order to improve their efficiency, reliability, flexibility, and carbon capture ability. Most of these process designs can still be classified into one of the three categories mentioned above, although some of the newer designs do not resemble the traditional ones. Most notably, chemical looping combustion (CLC) – a promising process in terms of efficiency – could be regarded as an oxyfuel combustion process, but is often not listed among the three traditional CCS technologies^{11,18,39}. Research and upscaling of all three technologies are being carried out^{37,40}. Looking at the lists of advantages and disadvantages of each of the process schemes, it is not a settled matter which of the three is the most promising.

1.4 Materials and oxygen transport properties of OTMs

Two main types of OTMs are single-phase and dual-phase mixed ionic-electronic conducting (MIEC) membranes as shown in Fig. 1.7. The driving force for oxygen permeation is the oxygen chemical potential gradient across the ceramic membrane. The selectivity is 100% provided that there are no cracks or connected-through porosity. As oxygen is transported in the ionic form, at least one of the components in the dual-phase membrane must have a high-enough ionic conductivity.

To fulfill the criterion of charge neutrality, a simultaneous flux of electrons occurs in the opposite direction. The latter implies that to sustain transport of both charge carriers both phases in the dual-phase membrane must be continuous, i.e., having volume fractions exceeding the percolation threshold. The highest oxygen fluxes are generally found for single-phase ABO_3 perovskite-structured ceramic membranes, typically operating at temperatures in excess of 800°C . Well-studied examples include $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF)⁴¹⁻⁴⁶ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF)⁴⁷⁻⁵². Also mixed conductors with a brownmillerite ($\text{A}_2\text{B}_2\text{O}_5$) and K_2NiF_4 -type (first member of the Ruddlesden-Popper series ($\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$)) structure are being investigated. Their structures may be classified as perovskite-related intergrowth structures. One of the core requirements for use of OTM's in power plants is that the membrane exhibits a long-life

Figure 1.7. Schematic view on ceramic mixed ionic-electronic conducting membranes; single-phase membrane (left), and dual-phase membrane (right).

performance and reliability under the severe operating conditions. Dual-phase membranes have been developed with improved stability over the single-phase perovskite membranes, especially in CO₂-containing environments, referring the vulnerability of the earth-alkaline earth containing perovskite oxides in CO₂ ambients. In general, however, the dual-phase membranes exhibit lower fluxes compared with their single-phase counter-parts. Typical examples of dual-phase membranes with a separate ionic and electronic conducting phase are NiFe₂O₄-Ce_{0.8}Tb_{0.2}O_{2-δ}⁵³⁻⁵⁵ and FeCo₂O₄-Ce_{0.8}Gd_{0.2}O_{2-δ}⁵⁶⁻⁵⁸, and examples of dual-phase membranes containing a mixed-conducting phase are Ce_{0.9}Gd_{0.1}O_{2-δ}-LSCF⁵⁹ and Ce_{0.8}Sm_{0.2}O_{2-δ}-LSCF⁶⁰. For industrial-scale usage, aspects such as process and materials costs, reliability of the technology, and integration with existing processes are obvious and important.

Because of the importance for the work conducted in this PhD study, a brief introduction is given towards structure and oxygen transport properties exhibited by single-phase perovskite-structured MIEC membranes. In the perovskite-structured mixed conductors, the A-site is occupied by an alkali, alkaline earth or rare earth cation, whereas the B-site is occupied by a late-transition metal or rare earth cation. The ideal cubic perovskite structure is shown in Figure 1.8 . In practice, however, many distorted perovskite structures are found due to tilting of the BO₆ octahedra. Goldschmidt proposed a tolerance factor t , which defines the degree of distortion of the perovskite lattice⁶¹

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (1.2)$$

where r_A , r_B , and r_O are the radii of the constituent ions. The parameter t has been widely used to assess the formation and stability of perovskite structures. The perovskite structure is preserved if t is between 0.8 and 1. Structures with a lower symmetry, e.g. orthorhombic or rhombohedral, may appear when the distortion becomes too large, i.e., when $t < 0.8$, whereas hexagonal phases may appear for $t > 1$. It is noteworthy that also other factors such as the lattice free volume and oxygen nonstoichiometry may affect

Figure 1.8. Schematic representation of the cubic perovskite structure. Figure made with Vesta.⁶⁵

formation of the ideal cubic perovskite structure. An excellent review about perovskite and perovskite-related structures is given by Zhu *et al.*⁶²

Pioneering studies of oxygen permeation through perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ membranes were conducted by Teraoka *et al.*^{63,64}. The partial substitution of A-site La^{3+} ions by Sr^{2+} ions is charge compensated by the formation of oxygen vacancies and/or valence changes of the B-site cations. The degree of oxygen non-stoichiometry exhibited by perovskite oxides is not only affected by the extent of aliovalent substitution, but also by temperature and ambient oxygen partial pressure. Oxygen ion migration in the perovskite lattice is mediated by the presence of oxygen vacancies (vacancy diffusion mechanism). For a relatively thick membrane, at given temperature, the oxygen flux is given by the well-known Wagner equation⁶⁶

$$J_{\text{O}_2} = \frac{RT}{4^2 F^2 L} \int_{\ln p''_{\text{O}_2}}^{\ln p'_{\text{O}_2}} \frac{\sigma_e \sigma_i}{\sigma_e + \sigma_i} d \ln p_{\text{O}_2} \quad (1.3)$$

where L is the membrane thickness, σ_i and σ_e are the partial ionic and electronic conductivities, and p'_{O_2} and p''_{O_2} the oxygen partial pressures maintained at the feed and permeate sides of the membrane, respectively. Other parameters in Eq. 1.4 have their usual significance. Eq. 1.4 is simplified to

$$J_{O_2} = \frac{RT}{4^2 F^2 L} \frac{\sigma_e \sigma_i}{\sigma_e + \sigma_i} \ln \left(\frac{p'_{O_2}}{p''_{O_2}} \right) \quad (1.4)$$

for small p_{O_2} gradients across the membrane or when the partial conductivities appear to be invariant with oxygen partial pressure.

The Wagner equation, predicting that the oxygen flux is inversely proportional to membrane thickness, no longer holds if surface exchange rate limitations come into play. These may become apparent upon reducing membrane thickness in an attempt to increase the oxygen flux. The overall exchange reaction can be written as, in Kröger-Vink notation,

where $V_O^{\bullet\bullet}$ denotes a doubly positively charged oxygen vacancy, e' an electron, and $O_O^{\times}$ a regular lattice oxygen. This reaction can be broken down in a number of elementary steps, each of which may be rate determining. To date, however, our understanding of the exchange kinetics between oxygen in the gas phase and oxygen in the oxide lattice is rather rudimentary. This is, at least in part, due to the difficulties in measuring oxygen surface exchange at elevated temperature, where these reactions are most pertinent. Assuming linear kinetics for the surface exchange reactions at both sides of the membrane, and in the limit of small p_{O_2} gradients, Bouwmeester *et al.* derived for the oxygen flux under mixed control of oxygen diffusion and surface exchange ⁶⁷

$$J_{O_2} = \frac{RT}{4^2 F^2 (L + 2L_c)} \frac{\sigma_e \sigma_i}{\sigma_e + \sigma_i} \ln \left(\frac{p'_{O_2}}{p''_{O_2}} \right) \quad (1.6)$$

where L_c is the characteristic membrane thickness below which the oxygen flux is predominantly controlled by oxygen surface exchange. Using the Nernst-Einstein

equation while assuming $\sigma_e \gg \sigma_i$ (valid for most of the perovskite-type mixed conductors), it can be shown that ⁶⁷

$$L_c = \frac{D_s}{k} \quad (1.7)$$

where D_s is the self-diffusion coefficient and k the surface exchange coefficient. Both parameters can be extracted simultaneously from data of ^{18}O - ^{16}O isotope exchange experiments, followed by ex-situ depth profiling (IEDP), usually by scanning ion mass spectroscopy (SIMS) ⁶⁸. Techniques used for measurement of these parameters include amongst others the pulse ^{18}O - ^{16}O isotope exchange (PIE) technique (for measurement of k only) ⁶⁹ and chemical relaxation measurements such as the electrical conductivity relaxation (ECR) technique ^{47,70,71}, in which the electrical conductivity is monitored after a step-wise change in the ambient p_{O_2} . For evaluation of D_s and k from experimental data, the latter technique requires supplementary data of the dependence of the oxygen non-stoichiometry of the perovskite oxide with oxygen partial pressure. The oxygen non-stoichiometry of the perovskite oxide relative to the initial condition can be investigated by thermogravimetry, neutron diffraction, or coulometric titration ^{43,72}. A detailed descriptions of the ECR technique as employed in this PhD study is given in Appendix A3.

One strategy to improve the oxygen flux is to reduce membrane thickness, provided that the oxygen flux is limited by bulk-diffusion. Below a thickness of approximately 150 μm , a porous support is needed to provide sufficient mechanical robustness. The rate of the surface exchange reactions can be promoted by depositing a porous activation layer onto the dense and crack-free thin film membrane, effectively enhancing the available surface area for oxygen exchange, and/or by coating the surface with an appropriate catalyst, e.g., by infiltration of the porous activation layer. To avoid compatibility issues, such as thermal expansion differences, which may cause stress at elevated temperatures ultimately leading to cracks and mechanical instability, the porous support, thin film and activation layers are preferably made from the same perovskite composition. Different

ceramic methods have been exploited to fabricate the asymmetric membranes (see below). It is obvious that the porous support layer must facilitate fast gas transport, while being coated with a dense oxygen-permeable film layer. Recent observations made in a joint research effort of researchers of the Forschungszentrum Jülich and our group at the University of Twente made apparent that the support layer of asymmetric membranes of mixed ionic-electronic conducting perovskite-type oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF; $x=0.3, 0.5$ and 0.7), BSCF and LSCF imposes a non-negligible resistance on the oxygen fluxes. From the results it is evident that more research needs to be done to optimize the gaseous transport path ways in the microporous support layers.

1.5 Scope and outline of this thesis

This thesis focuses on materials science aspects of OTMs such as synthesis, characterization and optimization of transport properties, and (chemical) stability of membrane materials. In addition, attention is devoted to design considerations and optimization of power plant processes in which OTMs are integrated.

In Chapter 2, an improved auto-combustion method for the synthesis of powders of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ is presented.

The performance of the state-of-the-art mixed ionic-electronic conducting perovskite oxide $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) is known to degrade with time due to (partial) decomposition. In **Chapter 3**, the thermal stability and oxygen transport properties of Y-doped BSCF, $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Y}_x\text{O}_{3-\delta}$, are assessed by long-term electrical conductivity relaxation (ECR) measurements and microstructural investigations

Chapter 4 investigates structure and oxygen transport of perovskite-type $\text{CaMnO}_{3-\delta}$ after partial substitution of the manganese ions with either iron or titanium, or both.

Chapter 5 focuses on improvement of the oxygen reduction reaction kinetics of the $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}\text{-NiFe}_2\text{O}_4$ dual-phase membrane material. The surface area was increased by deposition of a porous scaffold on the membrane, which was subsequently infiltrated with Pr_6O_{11} catalyst nanoparticles.

Chapter 6 deals with the thermodynamics and kinetics of carbonation of perovskite oxides. Thermogravimetry and temperature-programmed desorption experiments were carried out to investigate carbonation and decarbonation behavior .

The integration of OTMs in different power plant scenarios is discussed in **Chapter 7**. The different process designs are evaluated in terms of efficiency, leveled cost of electricity, carbon capture performance, and suitability for application of OTMs.

Chapter 8 provides a summary of the results described in this thesis and recommendations for future research.

References

1. H. Ritchie, M. Roser. OurWorldInData.org. Energy Production & Changing Energy Sources. 2018; <https://ourworldindata.org/energy-production-and-changing-energy-sources>. Accessed February 18, 2018.
2. International Energy Agency. Electric power consumption (kWh per capita). <https://data.worldbank.org/indicator/EG.USE.ELEC.KH.PC?end=2014&start=1960&vi ew=chart>. Accessed February 18, 2018.
3. *Key world energy statistics*. International Energy Agency; 2017, <https://www.iea.org/publications/freepublications/publication/KeyWorld2017.pdf>
4. I.P.o.C. Change. *Climate change 2014: mitigation of climate change*. Vol 3: Cambridge University Press; 2015.
5. D.M. Andrew, H.W. Ryan, S. Joachim. *Power Plant Retirements: Trends and Possible Drivers*. Lawrence Berkeley National Laboratory 2017, <https://emp.lbl.gov/publications/power-plant-retirements-trends-and>
6. United Nations Framework Convention on Climate Change. The Paris Agreement. http://unfccc.int/paris_agreement/items/9485.php. Accessed 5 March 2018.
7. T. Kuramochi, N. Höhne, M. Schaeffer, *et al.* *Ten key short-term sectoral benchmarks to limit warming to 1.5 °C*. Climate Policy. 2018; 18(3), pp. 287-305.
8. G.P. Peters. *The 'best available science' to inform 1.5 °C policy choices*. Nat. Clim. Change. 2016; 6, pp. 646-649.

9. J.C. Abanades, B. Arias, A. Lyngfelt, T. Mattisson, D.E. Wiley, H. Li, M.T. Ho, E. Mangano, S. Brandani. *Emerging CO₂ capture systems*. Int. J. Greenh. Gas Con. 2015; 40, pp. 126-166.
10. J. Rogelj, G. Luderer, R.C. Pietzcker, E. Kriegler, M. Schaeffer, V. Krey, K. Riahi. *Energy system transformations for limiting end-of-century warming to below 1.5 °C*. Nat. Clim. Change. 2015; 5, pp. 519-527.
11. M. Bui, C.S. Adjiman, A. Bardow, et al. *Carbon capture and storage (CCS): the way forward*. Energy Environ. Sci. 2018; 11(5), pp. 1062-1176.
12. S.-Y. Lee, S.-J. Park. *A review on solid adsorbents for carbon dioxide capture*. J. Ind. Eng. Chem. 2015; 23, pp. 1-11.
13. M. Voldsund, K. Jordal, R. Anantharaman. *Hydrogen production with CO₂ capture*. Int. J. Hydrogen Energy. 2016; 41(9), pp. 4969-4992.
14. X. Chen, G. Huang, C. An, Y. Yao, S. Zhao. *Emerging N-nitrosamines and N-nitramines from amine-based post-combustion CO₂ capture – A review*. Chem. Eng. J. 2018; 335, pp. 921-935.
15. I.M. Bernhardsen, H.K. Knuutila. *A review of potential amine solvents for CO₂ absorption process: Absorption capacity, cyclic capacity and pKa*. Int. J. Greenh. Gas Con. 2017; 61, pp. 27-48.
16. J.A. Ritter, A.D. Ebner. *State-of-the-Art Adsorption and Membrane Separation Processes for Hydrogen Production in the Chemical and Petrochemical Industries*. Sep. Sci. Technol. 2007; 42(6), pp. 1123-1193.
17. E.E. Ünveren, B.Ö. Monkul, Ş. Sarioğlu, N. Karademir, E. Alper. *Solid amine sorbents for CO₂ capture by chemical adsorption: A review*. Petroleum. 2017; 3(1), pp. 37-50.
18. J. Li, H. Zhang, Z. Gao, J. Fu, W. Ao, J. Dai. *CO₂ Capture with Chemical Looping Combustion of Gaseous Fuels: An Overview*. Energy & Fuels. 2017; 31(4), pp. 3475-3524.
19. E.J. Granite, T. O'Brien. *Review of novel methods for carbon dioxide separation from flue and fuel gases*. Fuel Processing Technology. 2005; 86(14), pp. 1423-1434.
20. J. Blamey, E.J. Anthony, J. Wang, P.S. Fennell. *The calcium looping cycle for large-scale CO₂ capture*. Prog. Energy Combust. Sci. 2010; 36(2), pp. 260-279.
21. P. Babu, P. Linga, R. Kumar, P. Englezos. *A review of the hydrate based gas separation (HBGS) process for carbon dioxide pre-combustion capture*. Energy. 2015; 85, pp. 261-279.
22. D. Jansen, M. Gazzani, G. Manzolini, E.v. Dijk, M. Carbo. *Pre-combustion CO₂ capture*. Int. J. Greenh. Gas Con. 2015; 40, pp. 167-187.

23. X. He, M.-B. Hägg. *Energy Efficient Process for CO₂ Capture from Flue gas with Novel Fixed-site-carrier Membranes*. Energy Procedia. 2014; 63, pp. 174-185.
24. N. Norahim, P. Yaisanga, K. Faungnawakij, T. Charinpanitkul, C. Klaysom. *Recent Membrane Developments for CO₂ Separation and Capture*. Chem. Eng. Tech. 2018; 41(2), pp. 211-223.
25. M. Pera-Titus. *Porous Inorganic Membranes for CO₂ Capture: Present and Prospects*. Chem. Rev. 2014; 114(2), pp. 1413-1492.
26. M. Vinoba, M. Bhagiyalakshmi, Y. Alqaheem, A.A. Alomair, A. Pérez, M.S. Rana. *Recent progress of fillers in mixed matrix membranes for CO₂ separation: A review*. Sep. Purif. Technol. 2017; 188, pp. 431-450.
27. K. Atsonios, K. Panopoulos, A. Doukelis, A. Koumanakos, E. Kakaras, T. Peters, Y. van Delft. *Introduction to palladium membrane technology*. In: Doukelis A., Panopoulos K., Koumanakos A., Kakaras E., eds. *Palladium Membrane Technology for Hydrogen Production, Carbon Capture and Other Applications: Principles, Energy Production and Other Applications*. Woodhead Publishing; 2015.
28. P.J. Chenier. *Survey of industrial chemistry*. Springer Science & Business Media; 2012.
29. J.G. Hansel, S. Updated by. *Oxygen*. *Kirk-Othmer Encyclopedia of Chemical Technology*: John Wiley & Sons, Inc.; 2000.
30. A.S. Bhowan, B.C. Freeman. *Analysis and Status of Post-Combustion Carbon Dioxide Capture Technologies*. Environ. Sci. Technol. 2011; 45(20), pp. 8624-8632.
31. A.R. Smith, J. Klosek. *A review of air separation technologies and their integration with energy conversion processes*. Fuel Processing Technology. 2001; 70(2), pp. 115-134.
32. J.G. Weisend. *Cryogenic Technology*. *Kirk-Othmer Encyclopedia of Chemical Technology*: John Wiley & Sons, Inc.; 2000.
33. Y. Kansha, A. Kishimoto, T. Nakagawa, A. Tsutsumi. *A novel cryogenic air separation process based on self-heat recuperation*. Sep. Purif. Technol. 2011; 77(3), pp. 389-396.
34. Q. Fu, Y. Kansha, C. Song, Y. Liu, M. Ishizuka, A. Tsutsumi. *An elevated-pressure cryogenic air separation unit based on self-heat recuperation technology for integrated gasification combined cycle systems*. Energy. 2016; 103, pp. 440-446.
35. A.-M. Cormos, C.-C. Cormos. *Techno-economic evaluations of post-combustion CO₂ capture from sub- and super-critical circulated fluidised bed combustion (CFBC) power plants*. Appl. Therm. Eng. 2017; 127(Supplement C), pp. 106-115.

36. P. Casero, F.G. Peña, P. Coca, J. Trujillo. *ELCOGAS 14MWth pre-combustion carbon dioxide capture pilot. Technical & economical achievements*. Fuel. 2014; 116(Supplement C), pp. 804-811.
37. T. Lockwood. *A Compararitive Review of Next-generation Carbon Capture Technologies for Coal-fired Power Plant*. Energy Procedia. 2017; 114, pp. 2658-2670.
38. B.P. Spigarelli, S.K. Kawatra. *Opportunities and challenges in carbon dioxide capture*. J. CO₂ Util. 2013; 1, pp. 69-87.
39. A. Bhave, R.H.S. Taylor, P. Fennell, *et al.* *Screening and techno-economic assessment of biomass-based power generation with CCS technologies to meet 2050 CO₂ targets*. Applied Energy. 2017; 190, pp. 481-489.
40. M. Kanniche, Y. Le Moullec, O. Authier, H. Hagi, D. Bontemps, T. Neveux, M. Louis-Louisy. *Up-to-date CO₂ Capture in Thermal Power Plants*. Energy Procedia. 2017; 114(Supplement C), pp. 95-103.
41. S. McIntosh, J.F. Vente, W.G. Haije, D.H.A. Blank, H.J.M. Bouwmeester. *Structure and oxygen stoichiometry of SrCo_{0.8}Fe_{0.2}O_{3-δ} and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}*. Solid State Ionics. 2006; 177(19-25), pp. 1737-1742.
42. Z. Shao, W. Yang, Y. Cong, H. Dong, J. Tong, G. Xiong. *Investigation of the permeation behavior and stability of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} oxygen membrane*. J. Membr. Sci. 2000; 172(1-2), pp. 177-188.
43. D.N. Mueller, R.A. De Souza, H.-I. Yoo, M. Martin. *Phase Stability and Oxygen Nonstoichiometry of Highly Oxygen-Deficient Perovskite-Type Oxides: A Case Study of (Ba,Sr)(Co,Fe)O_{3-δ}*. Chem. Mater. 2012; 24(2), pp. 269-274.
44. L.-S. Unger, M. Meffert, V. Wilde, H. Störmer, C. Niedrig, W. Menesklou, S.F. Wagner, D. Gerthsen, E. Ivers-Tiffée. *Influence of a La_{0.6}Sr_{0.4}CoO_{3-δ} Functional Layer on (Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-δ} Oxygen Transport Membranes (OTMs)*. ECS Transactions. 2016; 72(7), pp. 37-45.
45. X. Li, T. Kerstiens, T. Markus. *Oxygen permeability and phase stability of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} perovskite at intermediate temperatures*. J. Membr. Sci. 2013; 438, pp. 83-89.
46. S. Baumann, J.M. Serra, M.P. Lobera, S. Escolástico, F. Schulze-Küppers, W.A. Meulenbergh. *Ultrahigh oxygen permeation flux through supported Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membranes*. J. Membr. Sci. 2011; 377(1-2), pp. 198-205.
47. H.J.M. Bouwmeester, M.W. Den Otter, B.A. Boukamp. *Oxygen transport in La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-δ}*. J Solid State Electrochem. 2004; 8(9), pp. 599-605.

48. M. Kuhn, Y. Fukuda, S. Hashimoto, K. Sato, K. Yashiro, J. Mizusaki. *Oxygen Nonstoichiometry and Thermo-Chemical Stability of Perovskite-Type $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($y = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$)* Materials. J. Electrochem. Soc. 2013; 160(1), pp. F34-F42.
49. L. Zhao, J. Drennan, C. Kong, S. Amarasinghe, S.P. Jiang. *Insight into surface segregation and chromium deposition on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathodes of solid oxide fuel cells*. J. Mater. Chem. A. 2014; 2(29), pp. 11114-11123.
50. F. Schulze-Küppers, S. Baumann, F. Tietz, H.J.M. Bouwmeester, W.A. Meulenbergh. *Towards the fabrication of $\text{La}_{0.98-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite-type oxygen transport membranes*. J. Eur. Ceram. Soc. 2014; 34(15), pp. 3741-3748.
51. J. Oishi, J. Otomo, Y. Oshima, M. Koyama. *The effects of minor elements in $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ cathodes on oxygen reduction reaction*. J. Power Sources. 2015; 277, pp. 44-51.
52. S. Saher, S. Naqash, B. Boukamp, B. Hu, C. Xia, H.J.M. Bouwmeester. *Influence of ionic conductivity of the nano-particulate coating phase on oxygen surface exchange of $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$* . J. Mater. Chem. A. 2017, pp.
53. C. Gaudillere, J. Garcia-Fayos, M. Balaguer, J.M. Serra. *Enhanced Oxygen Separation through Robust Freeze-Cast Bilayered Dual-Phase Membranes*. ChemSusChem. 2014; 7(9), pp. 2554-2561.
54. J. Garcia-Fayos, V.B. Vert, M. Balaguer, C. Solís, C. Gaudillere, J.M. Serra. *Oxygen transport membranes in a biomass/coal combined strategy for reducing CO_2 emissions: Permeation study of selected membranes under different CO_2 -rich atmospheres*. Catal. Today. 2015; 257(2), pp. 221-228.
55. M. Balaguer, J. Garcia-Fayos, C. Solis, J.M. Serra. *Fast Oxygen Separation Through SO_2 - and CO_2 -Stable Dual-Phase Membrane Based on NiFe_2O_4 - $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$* . Chem. Mater. 2013; 25(24), pp. 4986-4993.
56. M. Ramasamy, S. Baumann, J. Palisaitis, et al. *Influence of Microstructure and Surface Activation of Dual-Phase Membrane $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ - FeCo_2O_4 on Oxygen Permeation*. J. Am. Ceram. Soc. 2016; 99(1), pp. 349-355.
57. Y. Lin, S. Fang, D. Su, K.S. Brinkman, F. Chen. *Enhancing grain boundary ionic conductivity in mixed ionic-electronic conductors*. Nat Commun. 2015; 6, pp. 6824.
58. W. Deibert, M.E. Ivanova, S. Baumann, O. Guillon, W.A. Meulenbergh. *Ion-conducting ceramic membrane reactors for high-temperature applications*. J. Membr. Sci. 2017; 543, pp. 79-97.

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59. J.H. Joo, K.S. Yun, Y. Lee, J. Jung, C.Y. Yoo, J.H. Yu. *Dramatically Enhanced Oxygen Fluxes in Fluorite-Rich Dual-Phase Membrane by Surface Modification*. Chem. Mater. 2014; 26(15), pp. 4387-4394.
 60. B. Hu, K. Guo, M. Li, Y. Li, C. Xia. *Effect of SDC Grain Size on the Oxygen Incorporation at the LSCF-SDC-Gas Three-Phase Boundary*. J. Electrochem. Soc. 2016; 163(3), pp. F190-F195.
 61. V.M. Goldschmidt. *Die Gesetze der Krystallochemie*. Naturwissenschaften. 1926; 14(21), pp. 477-485.
 62. Z. Liang, R. Ran, T. Moses, W. Wei, S. Zongping. *Perovskite materials in energy storage and conversion*. Asia-Pacific Journal of Chemical Engineering. 2016; 11(3), pp. 338-369.
 63. Y. Teraoka, T. Nobunaga, N. Yamazoe. *Effect of Cation Substitution on the Oxygen Semipermeability of Perovskite-type Oxides*. Chem. Lett. 1988; 17(3), pp. 503-506.
 64. Y. Teraoka, H.-M. Zhang, S. Furukawa, N. Yamazoe. *Oxygen Permeation through Perovskite-type Oxides*. Chem. Lett. 1985; 14(11), pp. 1743-1746.
 65. K. Momma, F. Izumi. *VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data*. J. Appl. Crystallogr. 2011; 44(6), pp. 1272-1276.
 66. H.J.M. Bouwmeester, A.J. Burggraaf. *Dense ceramic membranes for oxygen separation*. In: Gellings P.J., Bouwmeester H.J.M., eds. *The CRC handbook of solid state electrochemistry*. Boca Raton: CRC Press; 1997:481.
 67. H.J.M. Bouwmeester, H. Kruidhof, A.J. Burggraaf. *Importance of the surface exchange kinetics as rate limiting step in oxygen permeation through mixed-conducting oxides*. Solid State Ionics. 1994; 72, pp. 185-194.
 68. J.A. Kilner, S.J. Skinner, H.H. Brongersma. *The isotope exchange depth profiling (IEDP) technique using SIMS and LEIS*. J Solid State Electrochem. 2011; 15(5), pp. 861-876.
 69. H.J.M. Bouwmeester, C. Song, J. Zhu, J. Yi, M.v.S. Annaland, B.A. Boukamp. *A novel pulse isotopic exchange technique for rapid determination of the oxygen surface exchange rate of oxide ion conductors*. PCCP. 2009; 11(42), pp. 9640-9643.
 70. A. Falkenstein, D.N. Mueller, R.A. De Souza, M. Martin. *Chemical relaxation experiments on mixed conducting oxides with large stoichiometry deviations*. Solid State Ionics. 2015; 280, pp. 66-73.
 71. F. Ciucci. *Electrical conductivity relaxation measurements: Statistical investigations using sensitivity analysis, optimal experimental design and ECRTTOOLS*. Solid State Ionics. 2013; 239, pp. 28-40.

-
72. A.A. Yaremchenko, D.D. Khalyavin, M.V. Patrakeev. *Uncertainty of oxygen content in highly nonstoichiometric oxides from neutron diffraction data: example of perovskite-type $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$* . J. Mater. Chem. A. 2017; 5(7), pp. 3456-3463.

CHAPTER 2

Auto-combustion synthesis of perovskite-type oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

Abstract

A versatile one-pot auto-combustion method for the synthesis of powders of iron doped strontium titanate, $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, has been developed. The synthesis is optimized by the combined use of EDTA and citric acid as chelating agents, and an appropriate balance between fuel and oxidising elements in the reaction mixture. The method produces immediately an almost phase-pure perovskite oxide powder, with an ultra-fine crystallite size of 20-40 nm, and with a low level of organic residues. Highly sinter-active powders are obtained after calcination and ball-milling of the powders.

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2.1 Introduction

The non-stoichiometric perovskite oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF) are presently extensively investigated. The STF materials are good mixed ionic-electronic conductors¹⁻³, while other functional properties such as stability in reducing atmospheres, creep, and stability in CO_2 -containing atmospheres can be tuned by the Ti/Fe ratio. Especially the compositions with high Fe concentrations exhibit fast oxygen surface exchange and transport kinetics, which render them as viable candidates for use as cathode for solid oxide fuel cells (SOFCs)⁴, and as dense ceramic membrane for oxygen separation².

STF is known⁵ to form a continuous solid solution between the two end members $\text{SrFeO}_{3-\delta}$ and SrTiO_3 over the whole composition range $0 < x < 1$. At high temperatures, all compositions in the series $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ adopt the cubic perovskite structure (space group $\text{Pm}\bar{3}\text{m}$). While the end-member $\text{SrFeO}_{3-\delta}$ undergoes a structural phase transition to the ordered orthorhombic brownmillerite $\text{SrFeO}_{2.5}$ phase below $\sim 800\text{-}900^\circ\text{C}$ ⁶, substitution of as little as 1% Fe by Ti is sufficient to prevent this transition from happening⁵.

STF powders are typically synthesized by a solid state reaction, in which a stoichiometric mixture of solid reactants, e.g. carbonates, hydrates, oxalates or nitrates, is calcined at elevated temperature^{1,7-9}. Multiple grinding and calcination steps are necessary to improve chemical homogeneity of the powder. The wide particle size distribution of the powder obtained via solid-state reaction often leads to poor sintering characteristics¹. Intimate mixing of reactants on a molecular level on the other hand is a key benefit of wet synthesis methods. Examples of wet synthesis methods include co-precipitation⁹⁻¹¹, hydrothermal synthesis^{12,13}, solvent vaporization (spray drying, spray pyrolysis, and freeze drying), and combustion synthesis methods¹⁴⁻¹⁶. In general, these methods yield powders with higher compositional uniformity, smaller particle size and larger surface area than those prepared by solid-state reaction.

Combustion synthesis routes are inspired by the work of Pechini ¹⁶, in which citric acid and ethylene glycol are added to an aqueous solution of suitable metal salts or oxides, taken in appropriate proportions. Gelation occurs upon solvent evaporation due to polycondensation of the citric acid and ethylene glycol. Immobilisation of the metal citrate complexes in the gel prevents precipitation of the cations, ensuring that the chemical homogeneity is retained in the precursor solution during drying ¹⁷. After drying, the gel is fired at elevated temperature to obtain a finely dispersed powder of metal oxides and/or metal carbonates ¹⁸. A phase-pure ceramic powder is obtained after calcination at a suitable temperature.

Alternatively, in modified Pechini synthesis routes, different chelating or combined chelating agents are employed ¹⁹. The synthesis typically consists of four steps: (i) formation of organometallic complexes in solution, (ii) solvent evaporation and gel formation, (iii) auto-combustion (pyrolysis) followed by (iv) a heat treatment of the obtained powder ^{20,21}. Among several chelating agents, ethylene-diamine-tetra-acetic acid (EDTA) and citric acid (CA) are used most frequently ^{11,20}. Due to its higher chelating power, a far more extensive range of cations can be chelated with EDTA compared to CA ²². Possessing three carboxyl groups and one hydroxyl group, however, CA is the chelating agent with the stronger gelation ability ²³. The sole use of CA as chelating agent, however, may result in a highly exothermic, non-uniform combustion reaction, adversely affecting the morphology of the powder ²⁴. For these reasons CA and EDTA are often employed as combined chelating agents ^{20,23,25,26}.

In this chapter, a versatile one-pot auto-combustion route for the preparation of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF) powders is described, using EDTA and citric acid as combined chelating agents. The synthesis is exemplified by the preparation of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ with $x = 0.3$, $x = 0.5$ and $x = 0.7$ (abbreviated as STF30, STF50, and STF70, respectively). Water-soluble nitrates are used as precursors for strontium and iron, while titanium (IV) n-propoxide dissolved in ethanol is used as precursor for titanium.

2.2 Experimental

Synthesis of STF powders was carried out following the scheme as depicted in Fig. 2.1. High purity (> 99%) $\text{Sr}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, citric acid (CA, $\text{C}_6\text{H}_8\text{O}_7$), ethylene-diamine-tetra-acetic acid (EDTA, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$), and titanium (IV) n-propoxide, $(\text{Ti}(\text{OC}_3\text{H}_7)_4)$ were purchased from Sigma-Aldrich. In beaker 1, $\text{Ti}(\text{OC}_3\text{H}_7)_4$ was dissolved in dry ethanol in a glove box under dry N_2 conditions. Beaker 2 contained a solution of EDTA in Q_2 -distilled water brought to a pH of 5.5 by the addition of concentrated NH_4OH (30 vol%, Sigma-Aldrich). In beaker 3, stoichiometric proportions of strontium and iron nitrates were dissolved in Q_2 -distilled water. The EDTA solution (beaker 2) was added to the titanium (IV) n-propoxide solution (beaker 1) under vigorously stirring followed by the addition of the metal nitrate solution (beaker 3). Next, CA powder was added to beaker 1 up to a CA /total metal molar ratio of 1.5. In selected experiments only EDTA or CA was used as chelating agent. In all cases the total chelating agent : total metal molar ratio was maintained at 2.5 : 1. The pH of the precursor solution was re-adjusted to a value of 7 with NH_4OH (30 vol%, Sigma-Aldrich) before splitting of the solution into smaller batches.

The solution was divided in batches; each batch comprised an amount equivalent to produce approximately 3.5 gram of powder, and was transferred to a tall glass beaker (2 L borosilicate 3.3). The amount of oxidizer NH_4NO_3 (Sigma-Aldrich) added to the precursor solution was varied in different experiments to study its influence on combustion characteristics. After addition of NH_4NO_3 , the precursor solution was heated on a ceramic hot plate, set to 350 °C, until a vigorously boiling gel was obtained. Upon further heating, a foam-like structure developed which eventually self-ignited. The temperature of the gel and that of the gas phase just above the gel during combustion were monitored using K-type thermocouples. These were positioned just below and ~10 cm above the (initial) surface of the precursor solution, respectively, and were connected to a data logging device with a measuring frequency of 1 Hz. The beaker containing the precursor solution was covered with a stainless steel wire screen (100 mesh) to prevent

undesired powder loss during combustion. The obtained flakes were crushed with a single zirconia ball ($\varnothing$ 52 mm) to obtain a raw powder with a high pouring density.

The powders were heat treated in air for 12 h either at 300, 500, 700, 900, or 1100 °C, using heating and cooling rates of 5 °C·min⁻¹. Powder X-ray diffraction patterns were obtained using a Bruker D2 Phaser with Cu-K α radiation (λ = 1.54184 Å). The XRD patterns were fitted by a Monte Carlo and grid search using the X'Pert Highscore Plus software package (PANalytical, version 3.0e). Powder samples were imaged using a JEOL JSM-6010LA analytical scanning electron microscope (SEM), operated at an acceleration voltage of 5 kV.

Raw powders obtained from synthesis were studied by thermogravimetric analysis (TGA) using a Netzsch STA 449 F3 Jupiter. The measurements were performed on 10 mg of the sample enclosed in an α -Al₂O₃ crucible under a flow of synthetic air (70 ml·min⁻¹ (STP)), using heating and cooling rates of 10 °C·min⁻¹.

To investigate the sintering activity of the powder, dilatometric measurements (Netzsch dilatometer 402 C) were performed on green rectangular bars in the temperature range 25 - 1400 °C, using heating and cooling rates of 2 °C·min⁻¹. Prior to these measurements, the powders were calcined at 950 °C for 12 h in stagnant air and ball-milled in ethanol for 48 h. Green rectangular bars (15 × 4 × 4 mm³) were obtained by uniaxial pressing at 50 MPa followed by isostatic pressing at 400 MPa.

2.3 Results and discussion

2.3.1 Precursor solution

Metal nitrates are widely used as precursors in aqueous synthesis routes²⁷. Due to its high volatility at room temperature, however, titanium nitrate is less suitable as precursor²⁸. For this reason, titanium (IV) n-propoxide dissolved in dry ethanol (beaker 1) was used in this study as precursor for titanium. After addition of the content of beaker 2, containing the aqueous solution of the EDTA with a pH of 5.5, a white

turbidity (due to precipitation of $\text{Ti}(\text{OH})_2$) appeared in the solution, disappearing within less than about 10 s, after which the solution became colourless and transparent again.

Condensation of metal alkoxides following hydrolysis by water can occur via two basic processes: (i) *via* the formation of hydroxy-bridges between the metal centres (olation) or (ii) *via* the formation of more stable oxo-bridges (oxolation)²⁹. Whether ololation or oxolation occurs will depend strongly on the pH of the solution. In a test experiment, first Q₂-distilled water with a pH of 11.8 was added to the solution of titanium (IV) propoxide in dry ethanol (beaker 1). Immediately, a white precipitate was formed. Next, EDTA in the form of powder was added to the solution, but the precipitation persisted even after stirring at 65°C for 24 h. This simple experiment demonstrates that it is important to control the pH of the solution in which hydrolysis and condensation of the titanium (IV) n-propoxide precursor occurs.

Some precipitation was observed after the addition of the aqueous solution of iron and strontium nitrates (beaker 3). Addition caused a drop in the pH of the solution, lowering the EDTA solubility. Readjusting the pH to ~7 by adding NH_4OH dissolved EDTA again, upon which a dark brownish solution was obtained. Unless specified otherwise, the CA : EDTA molar ratio during synthesis was 1.5 : 1, while the total chelating agent : total metal molar ratio was 2.5. After addition of CA, NH_4OH was again used to readjust the pH to ~7 (Fig. 2.1). Subsequently, the precursor solution was divided into smaller batches for further processing.

2.3.2 Combustion characteristics

Traditionally, the constitution of a combustion reaction mixture is expressed in terms of the oxidizer-to-fuel ratio, ϕ , which quantity is referred to as the equivalence ratio³⁰. This concept is however less useful when the fuel molecules contain oxidizer elements and/or the oxidizer molecules contain fuel elements. Combustion reactions are redox reactions and, hence, oxidation numbers can be used to determine which elements in the reactant mixture act as an oxidizer, and which act as a fuel (i.e., reducing agent).

Figure 2.1. Scheme for synthesis of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF) powder.

In this study, the method proposed by Jain *et al.*³⁰ was pursued by calculation of the so-called elemental stoichiometric coefficient for a given combustion reaction mixture:

$$\phi_e = \frac{\sum_1^i z_i n_{O,i}}{\sum_1^j z_j n_{R,j}} \quad (2.1)$$

where $n_{O,i}$ and $n_{R,j}$ are the number of moles of oxidizing and reducing (fuel) elements in the reaction mixture, respectively, whilst z_i and z_j are their corresponding valences. Under stoichiometric conditions, the total number of oxidizing elements, i.e., oxygen, and reducing elements, such as carbon, hydrogen, and iron, in the reaction mixture are balanced, i.e., $\phi_e = 1$. In calculation, the following valences were taken: $z(\text{O}) = -2$, $z(\text{H}) = 1$; $z(\text{C}) = 4$, $z(\text{Sr}) = +2$; $z(\text{Ti}) = +4$; $z(\text{Fe}) = +3$; $z(\text{N}) = 0$. These correspond to the valences in the products of the combustion reaction. It was further assumed that ethanol in the precursor solution was evaporated before the actual combustion reaction took place.

Assuming complete combustion to CO_2 , H_2O and N_2 , the overall stoichiometric reaction for the formation of, for example, $\text{SrTi}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (STF50) at a CA : EDTA ratio of 1.5 can be written as

Hence, in this case 76.5 moles of oxidizer NH_4NO_3 per mole of product are required to achieve a stoichiometric balance of fuel and oxidizer. For a fuel-rich composition of the reaction mixture, O_2 from the gas phase will be required to achieve complete combustion. To ensure complete combustion during synthesis of the different STF compositions an overstoichiometric amount of oxidizer NH_4NO_3 was added to the reaction mixture corresponding to a value for ϕ_e of 1.25. Gelation occurred after evaporation of the water, and in all cases the dried nitrate-citrate gels exhibited self-propagating combustion. Figure 2.2 shows the typical evolution of the temperature in the gel core and just above the gel with time during combustion synthesis of STF50. The results show that under

the conditions of the experiment the onset of ignition occurs at a gel temperature of $\sim 220^\circ\text{C}$, while the combustion is completed within about 50 s. The temperature in the core and above the gel reaches as high as $\sim 800^\circ\text{C}$ and $\sim 1100^\circ\text{C}$, respectively. The data will depend on the exact positioning of the thermocouples in the glass beaker and the extent of swelling of the gel, and therefore should be taken with some care. The combustion was found to propagate like a wave through the gel. A video recording

Figure 2.2. Typical evolution of the temperature in the core of the gel and in the gas phase just above the gel with time during combustion synthesis of STF50.

showing the auto-combustion reaction is available on-line³¹. High local temperatures are maintained only for a short time and may lead to incomplete combustion. Some non-combusted gel was indeed observed at the wall of the glass beaker after the combustion reaction when only EDTA was used as chelating agent, while the combustion was considered too violent when only CA was used as chelating agent.

Figure 2.3a shows TGA patterns of the as-synthesized STF50 powder or ash obtained from synthesis using either EDTA or CA as chelating agent or using them as combined

Figure 2.3. TGA patterns during heating and cooling of as-synthesized STF50 powder prepared by using (A) CA, EDTA or (EDTA + CA) as chelating agents (at $\phi_e = 1.25$), and (B) at different values for ϕ_e (at EDTA : CA molar ratio of 1.5). Regions I-V are explained in the main text.

chelating agents (in a ratio of CA : EDTA of 1.5). Data of mass spectroscopic analysis of the evolved gases in the effluent of the TGA indicates that up to ~ 150 °C (region I) mainly desorption of water and some organic species takes place, whilst the burn out of remaining organics occurs between 150 °C and 650 °C (region II). The temperature regions III-V are dominated by reversible oxygen non-stoichiometry changes of STF50³². It is clear from Fig. 2.3a that the smallest fraction of organics in the as-synthesized powder remains when during its synthesis CA is used as chelating agent, which is followed by the powder obtained from synthesis using EDTA and CA as combined chelating agents, and that using solely EDTA as chelating agent.

In additional synthesis experiments, the amount NH_4NO_3 added to the reaction mixture was lowered to values for ϕ_e of 1 and 0.4, maintaining the CA : EDTA molar ratio at 1.5. The lower amount of oxidizer expectedly decreased the intensity of the combustion process, and led to a more incomplete combustion as quantified by subsequent TGA analysis of the powders obtained. As can be judged from the

corresponding weight losses in Fig. 2.3b, the combustion efficiency is found to decrease with lowering ϕ_e .

Based on above observations, it was decided to prepare powders of the other STF compositions using combustion reaction mixtures having a ϕ_e of 1.25, while using CA and EDTA as combined chelating agents (in a ratio of CA : EDTA of 1.5). Although the lowest organic residue in this work was found in the ash produced using solely CA as chelating agent, the combustion reaction with CA was considered too violent. TGA registered a weight loss of 8%-9% for the powder obtained from the synthesis using CA and EDTA as combined chelating agents (Fig. 2.3a). This value is favourably low when compared with weight losses between 22% and 50% as reported for powders from combustion syntheses of related perovskites oxides^{14,25,33-35}.

Figure 2.4. XRD patterns of as-synthesized STF50 powder (A) before, and after 12 h of calcination in air at (B) 300 °C, (C) 500 °C, (D) 700 °C, (E) 900 °C, and (F) 1100 °C. The peak labelled with * is assigned to an impurity phase.

2.3.3 Powder characteristics and sintering behavior

XRD patterns were recorded for as-synthesized STF powders before and after calcination in air at different temperatures, as shown for STF50 in Fig. 2.4. A small peak at $2\theta = 25^\circ$ is assigned to an unknown impurity phase. It is no longer found to be present in the XRD pattern of the powder obtained after calcination at 700°C . Similarly low calcination temperatures were required to obtain phase pure powders of STF30 and STF70.

Figure 2.5. SEM micrographs of as-synthesized STF50 powder calcined at (a) 500°C , (b) 700°C , (c) 900°C , and (d) 1100°C .

Indexing of the XRD patterns confirms that all STF compositions adopt the cubic perovskite structure with cell parameters $3.8936(8) \text{ \AA}$, $3.8910(2) \text{ \AA}$ and $3.8831(2) \text{ \AA}$ for

STF30, STF50 and STF70, respectively, in good agreement with literature data ^{2,36}. Typical SEM micrographs of the ceramic powders obtained after calcination at different temperatures are given in Fig. 2.5. These show porous, agglomerated structures with an estimated particle size between 10 and 100 μm . The pictures clearly evidence densification of the grains in the temperature range between 700 and 900 $^{\circ}\text{C}$ along with pore coarsening. The crystallite size, d_c , of the STF powders after calcination at different temperatures was estimated from the (110) reflection at 2θ of about 32.3° , using the Scherrer equation

$$d_c = \frac{k\lambda}{\beta \cos \theta} \quad (2.3)$$

where k ($= 0.94$) is the Scherrer constant, λ ($= 1.54184 \text{ \AA}$) is the wavelength of Cu-K α radiation, θ is the Bragg angle, and β is the full width at half maximum of the (110) reflection. Corresponding results are displayed in Fig. 2.6.

Figure 1.6. Apparent crystallite size of STF powders as a function of temperature. Data calculated by means of the Scherrer equation (Eq. 3) using the (110) reflection of STF powders calcined at different temperatures. The dashed lines are a guide to the eye.

The results confirm that nano-sized crystallites (20–40 nm) are obtained from synthesis, and that densification and grain growth is initiated around 800 °C. The sintering behaviour of STF was further examined by dilatometric measurements. Figure 2.7 shows the densification behaviour for the three STF compositions. The results confirm that sintering starts around 800 °C, which is consistent with the SEM observations and the results obtained from the Scherrer equation. As shown in Fig. 2.7b,

Figure 2.7. A) Linear shrinkage, and B) linear shrinkage rate as a function of temperature during sintering of green compacts of STF in air. The dashed vertical lines in (b) denote the maximum shrinkage rate temperature.

maximum sintering rates are between 1120 °C (STF70) and 1180 °C (STF30). These temperatures are 120–150 °C lower than those observed for STF powders prepared by the method of solid-state reaction³⁷. For STF70 some swelling is observed in the final stage of the sintering process. The swelling is related with oxygen nonstoichiometry changes with increase of temperature, and is due to the building up of high pressures in sub-micron pores³⁸. As this is beyond the scope of this research, the observation was not further investigated.

2.4 Conclusions

In this work, combustion synthesis has been successfully employed for the preparation of powders of the perovskite oxide $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (STF). This synthesis method represents an alternative to the solid-state reaction method conventionally used for the preparation of STF powders. The synthesis is optimised by the combined use of EDTA and citric acid as chelating agents, and an appropriate balance between fuel and oxidising elements in the reaction mixture. Combustion is found to produce an almost phase-pure perovskite oxide powder with an ultra-fine crystallite size (20–40 nm), and with a low level of organic residues. Highly sinter-active powders are obtained after calcination and ball-milling of the powders.

References

1. S. Molin, W. Lewandowska-Iwaniak, B. Kusz, M. Gazda, P. Jasinski. *Structural and electrical properties of $\text{Sr}(\text{Ti}, \text{Fe})\text{O}_{3-\delta}$ materials for SOFC cathodes*. J Electroceram. 2012; 28(1), pp. 80–87.
2. F. Schulze-Küppers, S.F.P. ten Donkelaar, S. Baumann, P. Prigorodov, Y.J. Sohn, H.J.M. Bouwmeester, W.A. Meulenbergh, O. Guillon. *Structural and functional properties of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($0 < x < 1$) for the use as oxygen transport membrane*. Sep. Purif. Technol. 2015; 147, pp. 414–421.
3. W.C. Jung, H.L. Tuller. *Impedance study of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.05$ to 0.80) mixed ionic-electronic conducting model cathode*. Solid State Ionics. 2009; 180(11–13), pp. 843–847.

4. W. Jung, H.L. Tuller. *Investigation of Cathode Behavior and Surface Chemistry of Model Thin Film $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ Electrode*. ECS Trans., 2009; 25(2), pp. 2775-2782.
5. L.H. Brixner. *Preparation and properties of the $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-x/2}/\text{O}_{x/2}$ system*. Mater. Res. Bull. 1968; 3(4), pp. 299-308.
6. J.-C. Grenier, N. Ea, M. Pouchard, P. Hagenmuller. *Structural transitions at high temperature in $\text{Sr}_2\text{Fe}_2\text{O}_5$* . J. Solid State Chem. 1985; 58(2), pp. 243-252.
7. X. Chen, Q. Luo, M. Han, O.K. Tan, M.S. Tse, H. Huang. *Mechanochemical synthesis of nanostructured $\text{Sr}(\text{Ti}_{1-x}\text{Fe}_x)\text{O}_{3-\delta}$ solid-solution powders and their surface photovoltage responses*. J. Solid State Chem. 2012; 189(0), pp. 80-84.
8. M. Ghaffari, H. Huang, P.Y. Tan, O.K. Tan. *Synthesis and visible light photocatalytic properties of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ powder for indoor decontamination*. Powder Technol. 2012; 225(0), pp. 221-226.
9. J. Sunarso, S. Baumann, J.M. Serra, W.A. Meulenbergh, S. Liu, Y.S. Lin, J.C. Diniz da Costa. *Mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation*. J. Membr. Sci. 2008; 320(1-2), pp. 13-41.
10. B. Seyfi, M. Baghalha, H. Kazemian. *Modified LaCoO_3 nano-perovskite catalysts for the environmental application of automotive CO oxidation*. Chem. Eng. J. 2009; 148(2-3), pp. 306-311.
11. S. Nakayama. *LaFeO_3 perovskite-type oxide prepared by oxide-mixing, co-precipitation and complex synthesis methods*. J. Mater. Sci. 2001; 36(23), pp. 5643-5648.
12. C. Chen, J. Cheng, S. Yu, L. Che, Z. Meng. *Hydrothermal synthesis of perovskite bismuth ferrite crystallites*. J. Cryst. Growth. 2006; 291(1), pp. 135-139.
13. L. Yuan, K. Huang, C. Hou, W. Feng, S. Wang, C. Zhou, S. Feng. *Hydrothermal synthesis and magnetic properties of $\text{REFe}_{0.5}\text{Cr}_{0.5}\text{O}_3$ ($\text{RE} = \text{La, Tb, Ho, Er, Yb, Lu and Y}$) perovskite*. New J. Chem. 2014; 38(3), pp. 1168-1172.
14. R.H.E.v. Doorn, H. Kruidhof, A. Nijmeijer, L. Winnubst, A.J. Burggraaf. *Preparation of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ perovskite by thermal decomposition of metal-EDTA complexes*. Journal of Materials Science. 1998; 8(9), pp. 2109-2112.
15. M.G. Rosmaninho, J.C. Tristão, F.C.C. Moura, R.M. Lago, M.H. Araújo, J.L.G. Fierro. *Structural and surface analysis of unsupported and alumina-supported $\text{La}(\text{Mn, Fe, Mo})\text{O}_3$ perovskite oxides*. Anal. Bioanal. Chem., 2010; 396(8), pp. 2785-2795.
16. M.P. Pechini, Inventor; Sprague Electric Co., assignee. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor. US3330967A, 1967.

17. D. Geng, M. Shang, D. Yang, Y. Zhang, Z. Cheng, J. Lin. *Green/green-yellow-emitting $\text{KSrGd}(\text{PO}_4)_2\text{:Ce}^{3+}$, $\text{Tb}^{3+}/\text{Mn}^{2+}$ phosphors with high quantum efficiency for LEDs and FEDs*. Dalton Trans. 2012; 41(46), pp. 14042-14045.
18. A.M. Huízar-Félix, T. Hernández, S. de la Parra, J. Ibarra, B. Kharisov. *Sol-gel based Pechini method synthesis and characterization of $\text{Sm}_{1-x}\text{Ca}_x\text{FeO}_3$ perovskite $0.1 \leq x \leq 0.5$* . Powder Technol. 2012; 229, pp. 290-293.
19. T. Razpotnik, J. Maček. *Synthesis of nickel oxide/zirconia powders via a modified Pechini method*. J. Eur. Ceram. Soc. 2007; 27(2-3), pp. 1405-1410.
20. F. Deganello, G. Marci, G. Deganello. *Citrate-nitrate auto-combustion synthesis of perovskite-type nanopowders: A systematic approach*. J. Eur. Ceram. Soc. 2009; 29(3), pp. 439-450.
21. A. Mali, A. Ataie. *Influence of the metal nitrates to citric acid molar ratio on the combustion process and phase constitution of barium hexaferrite particles prepared by sol-gel combustion method*. Ceram. Int. 2004; 30(7), pp. 1979-1983.
22. G.F. Zou, J. Zhao, H.M. Luo, T.M. McCleskey, A.K. Burrell, Q.X. Jia. *Polymer-assisted-deposition: a chemical solution route for a wide range of materials*. Chem. Soc. Rev. 2013; 42(2), pp. 439-449.
23. W. Zhou, Z. Shao, W. Jin. *Synthesis of nanocrystalline conducting composite oxides based on a non-ion selective combined complexing process for functional applications*. J. Alloys Compd. 2006; 426(1-2), pp. 368-374.
24. M. Marinšek, K. Zupan, J. Maček. *Ni-YSZ cermet anodes prepared by citrate/nitrate combustion synthesis*. J. Power Sources. 2002; 106(1-2), pp. 178-188.
25. F. Deganello, L. Liotta, G. Marci, E. Fabbri, E. Traversa. *Strontium and iron-doped barium cobaltite prepared by solution combustion synthesis: exploring a mixed-fuel approach for tailored intermediate temperature solid oxide fuel cell cathode materials*. Materials for Renewable and Sustainable Energy. 2013; 2(1), pp. 1-14.
26. A.A. Asadi, A. Behrouzifar, M. Iravaninia, T. Mohammadi, A. Pak. *Preparation and Oxygen Permeation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) Perovskite-Type Membranes: Experimental Study and Mathematical Modeling*. Industrial & Engineering Chemistry Research. 2012; 51(7), pp. 3069-3080.
27. A.S. Mukasyan, C. Costello, K.P. Sherlock, D. Lafarga, A. Varma. *Perovskite membranes by aqueous combustion synthesis: synthesis and properties*. Sep. Purif. Technol. 2001; 25(1-3), pp. 117-126.
28. D.W. Amos, D.A. Baines, G.W. Flewett. *Nitration by titanium(IV)nitrate*. Tetrahedron Lett. 1973; 14(34), pp. 3191-3194.

29. C.J. Brinker, G.W. Scherer. *Sol-gel science: the physics and chemistry of sol-gel processing*. San Diego: Academic Press, Inc; 1990.
30. S.R. Jain, K.C. Adiga, V.R. Pai Verneker. *A new approach to thermochemical calculations of condensed fuel-oxidizer mixtures*. Combust. Flame. 1981; 40, pp. 71-79.
31. J.M. Beér. *High efficiency electric power generation: The environmental role*. Prog. Energy Combust. Sci. 2007; 33(2), pp. 107-134.
32. S. Steinsvik, R. Bugge, J.O.N. Gjønnes, J. Taftø, T. Norby. *The defect structure of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-y}$ ($x = 0-0.8$) investigated by electrical conductivity measurements and electron energy loss spectroscopy (EELS)*. Journal of Physics and Chemistry of Solids. 1997; 58(6), pp. 969-976.
33. A. Banerjee, S. Bose. *Free-Standing Lead Zirconate Titanate Nanoparticles: Low-Temperature Synthesis and Densification*. Chem. Mater. 2004; 16(26), pp. 5610-5615.
34. Z. Wang, S. Jiang, G. Li, M. Xi, T. Li. *Synthesis and characterization of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ nanopowders by citric acid gel method*. Ceram. Int. 2007; 33(6), pp. 1105-1109.
35. R.Q. Chu, Z.J. Xu, Z.G. Zhu, G.R. Li, Q.R. Yin. *Synthesis of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ powder and ceramic via auto-combustion of citrate-nitrate gel*. Materials Science and Engineering B. 2005; 122(2), pp. 106-109.
36. C.-Y. Yoo, H.J.M. Bouwmeester. *Oxygen surface exchange kinetics of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ mixed conducting oxides*. Phys. Chem. Chem. Phys. 2012; 14, pp. 11759-11765.
37. S.F.P. ten Donkelaar, F. Schulze-Küppers, S. Baumann, M.J. Wolf, A. Nijmeijer, H.J.M. Bouwmeester. *Oxygen permeation through asymmetric mixed-conducting membranes based on perovskite oxides $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$* . In preparation.
38. K. Wiik, A. Fossdal, L. Sagdahl, et al. *LaFeO_3 and LaCoO_3 Based Perovskites: Preparation and Properties of Dense Oxygen Permeable Membranes*. Paper presented at: Mixed Ionic Electronic Conducting Perovskites for Advanced Energy Systems 2004; Dordrecht.

CHAPTER 3

Oxygen Transport and Phase Stability of Yttrium-Doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$

Abstract

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) in its cubic perovskite phase has attracted much interest for potential use as oxygen transport membrane (OTM) due to its very high oxygen permeability at high temperatures. However, performance degradation due to a sluggish phase decomposition occurs when BSCF is operated below 840 °C. Partial B-site substitution of the transition metal cations in BSCF by larger and redox-stable cations has emerged as a potential strategy to improve the structural stability of cubic BSCF. In this study, the influence of yttrium doping (0 – 10 mol%) on oxygen transport properties and stability of the cubic BSCF phase is assessed by *in situ* electrical conductivity relaxation (ECR) during long-term thermal annealing both at 700 °C and 800 °C. A detailed phase analysis is performed by scanning electron microscopy (SEM) after long-term annealing of the samples in air at four different temperatures to investigate the relation between the presence of non-cubic phases and the transport properties.

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3.1 Introduction

Three decades ago, Teraoka *et al.* drew first attention to fast oxygen transport exhibited by mixed ionic-electronic conducting (MIEC) perovskite-type oxides $\text{La}_x\text{A}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$, where A = Ca, Sr, Ba^{1,2}. Partial A-site substitution of lanthanum by divalent earth-alkaline cations serves to create oxygen vacancies, and thereby to enhance oxygen ionic conductivity. In recent years, in particular, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) has attracted much interest for potential use as oxygen transport membrane (OTM) due to its very high oxygen permeability at high temperatures³⁻⁵. Baumann *et al.* reported an oxygen flux as high as $67.7 \text{ ml (STP) min}^{-1} \text{ cm}^{-2}$ through an asymmetric BSCF membrane, measured at 1000°C , using pure oxygen as feed and argon as sweep gas⁶. Being prone to significant performance degradation when exposed to even the smallest concentrations of acidic impurity gases such as CO_2 and SO_x , BSCF can only be used in environments free of these gases^{7,8}. Furthermore, performance degradation due to a sluggish decomposition of the cubic BSCF phase will occur when the material is operated at intermediate temperatures^{3,9-15}.

Shao *et al.* showed the oxygen fluxes through BSCF membranes to decline over time when operated below $\sim 850^\circ\text{C}$ ³, and Li *et al.* reported more than 50% degradation of the oxygen flux through undoped BSCF membranes after operation for 2000 h at 800°C ¹⁶. Detailed structural studies, using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD), have demonstrated that BSCF undergoes a partial transformation to a Fe-depleted hexagonal phase during long-term annealing at intermediate temperatures. The hexagonal phase is preferably formed at the grain boundaries, indicating that the latter act as nucleation sites^{10,12,13}. In addition to the hexagonal phase, the formation of cobalt oxide precipitates¹⁷⁻¹⁹, $\text{Ba}_{n+1}\text{Co}_n\text{O}_{3n+3}(\text{Co}_8\text{O}_8)$ ($n \geq 2$) (BCO) particles, and a phase with a plate-like morphology are commonly observed^{11,20}. The latter has been identified as a lamellar intergrowth between cubic and hexagonal BSCF and BCO^{20,21}.

The relative stability of the perovskite structure is often rationalized in terms of the Goldschmidt tolerance factor

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (3.1)$$

where r_A , r_B , and r_O are the radii of the A- and B-site cations in the appropriate coordination, and that of the oxygen anions, respectively. For cubic perovskites, t lies between 0.8 and 1²². The cubic perovskite structure is formed for $t = 1$, whilst for $t < 1$ lower symmetry arrangements with tilted BO_6 octahedra are commonly seen. For $t > 1$, hexagonal structures with near hexagonal close-packed layers of the A cations and O^{2-} anions are formed. Indeed, partial B-site substitution of the transition metal cations in BSCF by larger and redox-stable cations such as Y^{3+} ^{23,24}, Zr^{4+} ²⁵⁻³⁰, or Nb^{5+} ^{31,32} has emerged as a strategy to improve the structural stability of BSCF.

This study consists of two parts, in part I the influence of yttrium doping on the evolution of the lattice parameters, stability under reducing conditions, electrical conductivity, and oxygen permeation has been studied³³. Here, we report our results from *in situ* electrical conductivity relaxation (ECR) and electrical conductivity measurements on undoped BSCF in comparison to different yttrium-dopant concentrations (1 mol%, 3 mol% and 10 mol%) during long-term thermal annealing both at 700 °C and 800 °C. The work is complemented by a detailed phase analysis of the materials after long-term annealing in air at 640 °C, 760 °C, 880 °C, and 1100 °C by SEM.

3.2 Experimental

3.2.1 Preparation of samples

Powders of $\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-x}\text{Y}_x\text{O}_{3-\delta}$, with $x = 0, 0.01, 0.03$ and 0.10 (BSCF:100xY), were prepared via solid state reaction. BaCO_3 and SrCO_3 (Merck KGaA, Darmstadt, Germany), Co_3O_4 (chemPUR, Karlsruhe, Germany), and Fe_2O_3 and Y_2O_3 (Alfa Aesar, Karlsruhe, Germany) were used as starting materials. Multiple grinding and

calcination steps were carried out to achieve homogeneous powders. The final calcination temperatures were 900 °C for BSCF, BSCF:1Y, and BSCF:3Y and 950 °C for BSCF:10Y. The d_{50} values of the powders obtained after ball milling for 24 h were around 2 μm as determined by dynamic laser scattering (CILAS 1064L, Orléans, France). The calcined powders were granulated and uniaxially pressed at 10 kN cm^{-2} into rectangular bars. Subsequently, these were annealed in ambient air for 1 h at 500 °C (heating rate 1 K min^{-1}), and sintered for 2 h at 1050 °C, 1100 °C, 1100 °C and 1150 °C for BSCF, BSCF:1Y, BSCF:3Y and BSCF:10Y, respectively, using heating and cooling rates of 5 K min^{-1} . The sintered ceramics were polished with three diamond slurries, in sequence, with grain sizes 9 μm , 3 μm , and 1 μm , respectively, down to dimensions of approximately $17 \times 6 \times 1 \text{ mm}^3$ for ECR measurements and $17 \times 6 \times 2 \text{ mm}^3$ for long-term electrical conductivity measurements. The relative density of all sintered samples was above 96 %. X-ray diffraction (XRD) analysis (Siemens D8-ADVANCE A25 spectrometer, Bruker-AXS, Karlsruhe, Germany) of the sintered ceramics revealed no indications of impurities or secondary phases (see Ref. 33).

For microstructural analysis, sintered samples were annealed in air at 1100 °C for 12 h, and subsequently subjected to long-term annealing at temperatures in the range 640 – 880 °C for 10 d. Heating and cooling rates were 5 K min^{-1} . After the long-term annealing, samples were quenched in water to room temperature. Reference samples were obtained after annealing in air at 1100 °C for 24 h, and quenching to room temperature.

3.2.2 Electrical Conductivity Relaxation

ECR measurements were performed during long-term thermal annealing of the samples at either 800 °C or 700 °C and at a $p\text{O}_2$ of 0.215 bar. The transient conductivity following $p\text{O}_2$ step changes between 0.215 bar and 0.316 bar was measured at regular intervals during the annealing procedure. Prior to use, the ceramics were cleaned with MilliQ water, followed by ethanol. A four-probe dc technique was used to collect conductivity data. Gold wires (0.25 mm in diameter, Alfa Aesar) were wrapped around each bar end. Two additional gold wires were wrapped around the bar 0.2 – 0.4 cm remote

from each bar end. Sulphur-free gold paste (MaTeck GmbH, Juelich, Germany) was used to ensure good electrical contact, and to completely cover both bar ends. The gold wire ends were wrapped around gold contacts present on the sample holder. The holder with sample was then placed inside an alumina cell with an internal volume of about 2.6 cm³ for measurement. Care was taken to ensure a free gas flow around the sample. A K-type thermocouple was used to measure the temperature at a position a few millimeters beneath the sample. Two gas flow pathways with different pO_2 values were maintained in the system, one of which was fed through the cell. The pO_2 of the gas streams (300 ml min⁻¹) was adjusted by mixing nitrogen and oxygen, using Brooks GF40 mass flow controllers, and monitored by an oxygen sensor (Systech Model ZR893/4). A pneumatically-operated 4-way valve was used to rapidly switch between both pathways to achieve an instantaneous step change in pO_2 . The flush time constant calculated assuming idealized continuous flow stirred tank reactor (CSTR) conditions was typically less than 0.15 s. Two Keithley 2400 SourceMeters® were used for electrical measurements. One was used to supply a constant current of 300 mA through the sample, the other for voltage measurements.

A LabVIEW program was used to monitor and control the temperature and pO_2 during ECR measurements, as well as for data acquisition. As visualized in Fig. 3.1, each

Figure 3.1. Schematics of the temperature and pO_2 steps during ECR measurements.

measurement started by ramping the temperature up to 900 °C at a rate of 10 K min⁻¹, at which hexagonal phase formation does not occur, followed by a dwell at this temperature for 1 h (denoted by regions I and II in Fig. 3.1, respectively).

Next, the sample was rapidly cooled to 800 °C (region III), at which the measurements started. Within every 30 min interval of the 200 h lasting thermal treatment, three subsequent oxidation and reduction runs were performed, after which the annealing at a $p\text{O}_2$ of 0.215 bar was continued (region IV). A similar procedure was followed for the measurements at 700 °C.

Fundamental descriptions of the ECR technique and the model used for data fitting have been given elsewhere^{34,35}. Appendix A2 contains a more detailed description of the methodology used for ECR experiments in this thesis.

3.2.3 Microstructural investigations

The samples annealed for microstructural investigations, prepared as described in Section 3.2.1, were polished using diamond lapping film with grit sizes starting at 30 µm down to 0.5 µm followed by an etching process involving a colloidal silicon dioxide suspension (MasterMet2, ITW Test & Measurement GmbH, Düsseldorf, Germany). Different secondary phases in BSCF exhibit characteristic contrast after etching which can be visualized by secondary electron (SE) SEM imaging. Details of this method can be found elsewhere¹¹. Images were recorded using the Everhart-Thornley detector in a FEI Quanta 650 FEG scanning electron microscope operated at 15 kV.

3.3 Results and discussion

3.3.1 Electrical Conductivity Relaxation (ECR)

ECR measurements were performed on BSCF and Y-doped BSCF samples to evaluate whether the oxygen transport kinetics are subject to degradation during prolonged thermal annealing. Typical normalized conductivity transients for BSCF and BSCF:10Y recorded during annealing at 700 °C and 800 °C are presented in Fig. 3.2.

Figure 3.2. Normalized conductivity relaxation transients measured during long-term annealing at $pO_2 = 0.215$ bar. At the top row, transients recorded at 800 °C after annealing for the indicated amount of time for BSCF (A), and BSCF:10Y (B) are shown. Likewise, at the bottom row the transients recorded at 700 °C for BSCF (C), and BSCF:10Y (D). For clarity reasons, only data from oxidation runs are shown.

Shown in this figure is how the conductivity transients evolve over time under the thermal annealing treatments. Note that the x-axis scales of the top row figures is different than that of the bottom row figures, as the relaxation rate is much faster at 800 °C than at 700 °C. The initial relaxation rate of both materials is comparable. However, BSCF ceramics show a clear increase in the re-equilibration time with increased time of annealing at both temperatures. For BSCF:10Y, the conductivity transients remain virtually unaltered

during annealing at 800 °C, whilst at 700 °C the equilibration time increases with increased annealing time, albeit in a much less pronounced way than pure BSCF during annealing at this temperature. To further quantify the observed increase in equilibration time, the transient conductivity data were fit to Eqs. 3.3-3.5 to obtain D_{chem} and k_{chem} . A typical fit and the related error plot are shown in Fig. 3.3. As the critical length scales L_c are found in the range $2.5 \mu\text{m} < L_c < 40 \mu\text{m}$ for all materials and temperatures, the re-equilibration kinetics at given sample thicknesses ($\sim 1 \text{ mm}$) are under almost pure diffusion control³⁴. For this reason it was impossible to extract significant values of k_{chem} from curve fitting.

Figure 3.4 shows the values of D_{chem} as a function of annealing time for each of the compositions obtained from fitting. Because similar trends were observed for oxidation and reduction runs, only data obtained from oxidation runs are presented. It is seen that D_{chem} for BSCF, BSCF:1Y and BSCF:3Y decreases with the time of annealing, whilst

Figure 3.3. A) Normalized conductivity relaxation transient obtained in an ECR measurement (orange symbols), and typical curve fit (blue line) of the according to Eqs. 3-5. Grey dots indicate the difference in the value of the measured data and the calculated value for each datapoint. Data were obtained using undoped BSCF with dimensions $11.17 \times 6.08 \times 0.89 \text{ mm}^3$, at a temperature of 800 °C, and after annealing for approximately 20 h. B) Error plot showing value of $1/\chi^2$, calculated at a 50×50 grid around the best fitting values of D_{chem} and k_{chem} . The highest value of $1/\chi^2$, which indicates the lowest deviation of the values from the measured values, is found at the middle point by definition. The shape of the graph indicates the sensitivity of the fit for both parameters.

Figure 3.4. Chemical diffusion coefficients D_{chem} for BSCF, BSCF:1Y, BSCF:3Y, and BSCF:10Y as a function of the annealing time at 800 °C. For clarity reasons, 1 out of 7 data points and only data from oxidation runs are shown.

for BSCF:10Y it remains virtually constant over the duration of the measurement. Note that doping BSCF with 10 mol% yttrium lowers the initial value of D_{chem} . At the onset of the annealing procedure, the value for BSCF:10Y is about 30 % lower than that for pure BSCF. After 200 h of annealing, however, the ratio of D_{chem} for both compositions is almost reversed.

In agreement with previously reported results²⁸, the lowering in D_{chem} of BSCF during annealing is observed to be much more pronounced at 700 °C than at 800 °C. This behavior is attributed to a decrease of the thermodynamic stability of the cubic phase

Figure 3.5. Chemical diffusion coefficient of BSCF and BSCF:10Y as a function of the annealing time at 700 °C. For clarity reasons, 1 out of 7 data points and only data from oxidation runs are shown.

relative to that of hexagonal BSCF as well as impurity phases upon cooling from 800 °C to 700 °C.

The above results confirm that deterioration of oxygen transport in BSCF at 800 °C can be suppressed by doping with yttrium. However, at the lower temperature of 700 °C, where deterioration is found most severe, doping with 10 mol-% yttrium cannot completely inhibit degradation of performance over time. It is noted from Fig.3.5 that the decrease in the magnitude of D_{chem} for BSCF:10Y over the 200 h-lasting anneal at 700 °C is still about 20 %.

3.3.2 Microstructural investigation

Fig. 3.6 shows a representative SEM micrograph with secondary phases that are observed in undoped BSCF after annealing for 240 h at 760 °C in ambient air. Different phases can be distinguished on the basis of the different image intensities (different grey-scale values). As previously established using transmission electron microscopy (TEM), an intermediate intensity represents the cubic phase and dark areas depict the hexagonal phase¹¹. Plate-like regions appear with bright contrast and elongated shape. Cobalt-oxide phases, in this particular case Co_3O_4 , appear with the brightest contrast.

Figure 3.6. SEM micrograph showing the formation of secondary phases in a sintered BSCF sample after annealing for 240 h at 760 °C in air followed by subsequent quenching in water.

Secondary phase formation in undoped and Y-doped BSCF is compared in Fig. 3.7. The samples were subjected to annealing treatments for either 24 h at 1100 °C or 240 h at temperatures in the range 880 – 640 °C in ambient air. Representative SEM images are shown for BSCF and BSCF:10Y (top and bottom row of Fig. 3.7). As most of these SEM micrographs do not show all microstructural features in one image, simplified

Figure 3.7. Comparison of secondary phase formation in undoped and doped BSCF. SEM images in the first and last row for BSCF and BSCF:10Y, respectively, after annealing for 240 h in ambient air. Schematic representation of secondary phase formation for all compositions in rows 2 to 5 at temperatures between 640 °C and 1100 °C.

schemes are presented which summarize the findings from numerous SEM images and TEM studies (rows 2-5 in Fig. 3.7). Undoped BSCF (top two rows) does not contain any hexagonal phase segments after annealing at 1100 °C. Next to the main phase, cubic BSCF, some CoO particles with a diameter of approximately 1 μm are present. The latter precipitates appear with bright SEM contrast that is characteristic for Co_xO_y precipitates. After annealing at 880 °C, the presence of large plate-like precipitates (several μm in length) is observed, which consist of $\text{Ba}_{n+1}\text{Co}_n\text{O}_{3n+3}(\text{Co}_8\text{O}_8)$ ($n \geq 2$) (BCO). Annealing at 760 °C results in the formation of a percolating hexagonal phase along the grain boundaries (in agreement with findings from long-term conductivity measurements ¹⁴), in addition to the plate-like precipitates and Co_3O_4 . The formation of the hexagonal phase is initiated by the increasing concentration of lattice oxygen with decreasing temperature, which results in oxidizing Co^{2+} to Co^{3+} . Due to the resulting change in ionic radius – from ~65 pm (Co^{2+}) to ~55 pm (Co^{3+}) ³⁶ – hexagonal phase formation is encouraged and will occur at suitable nucleation sites, i.e. grain boundaries, Co_xO_y , and plate-like precipitates. We note that the plate-like precipitates at temperatures below ~800 °C may contain a complex substructure consisting of lamellae of BCO, cubic and hexagonal BSCF ²⁰. Secondary phase composition after annealing at 640 °C is similar to that at 760 °C, however, with a significantly smaller volume fraction of secondary phases due to slower formation kinetics.

While the formation of plate-like, BCO, and Co_xO_y precipitates is only slightly reduced in BSCF:1Y, the formation of these secondary phases is completely suppressed at all investigated temperatures in samples with 3 and 10 mol-% Y content (rows 3-6). BSCF:3Y still suffers from the formation of a percolating network of the hexagonal phase along the grain boundaries at 760 °C and – to a lesser extent without percolation – also at the lowest temperature of 640 °C. These findings are in agreement with former phase analyses carried out on BSCF:3Y by Müller *et al.* ³⁷. The suppression of Co_xO_y precipitates is essential, because they serve as nucleation centers for all other secondary phases. Co_xO_y precipitate suppression is related with B-cation deficiency because Y was found not only on the B-site – as intended – but also on the A-cation sites ²⁴.

A dopant concentration of 10 mol-% Y, however, appears to stabilize the cubic BSCF at all investigated temperatures above 760 °C (where small amounts of hexagonal phase can still be detected along some grain boundaries). Additional long-term annealing experiments do not show secondary phases in BSCF:10Y after 1000 h at 800 °C in ambient air³⁸. This may be due to the complete absence of Co_xO_y , plate-like, and BCO precipitates, that would serve as additional nucleation centers for the hexagonal phase, but also due to an increased Goldschmidt tolerance factor. The monovalent Y^{3+} has an ionic radius of ~90 pm which is considerably larger than both Co^{2+} (~65 pm) and Co^{3+} (~55 pm)³⁶. The apparent absence of the hexagonal BSCF phase after annealing at 640 °C is attributed to the slow formation kinetics at this temperature.

These results show improved thermal stability of the cubic phase of BSCF after doping with 10 mol% yttrium. This may be beneficial for the use of OTMs in applications which require membranes with a high oxygen flux as well as an operating temperature below 840 °C, the temperature below which the cubic phase of pure BSCF becomes unstable^{10,13}. A recently published study shows that doping yttrium into BSCF is not only beneficial for the thermal stability of the cubic phase, but also for the chemical stability in atmospheres containing up to 3% of CO_2 ³⁹. This finding may further increase the viability of yttrium-doped BSCF for use as OTM. However, doping with yttrium has a limited effect on the A-site basicity. It could be expected that a concurrent decrease in operating temperature and increase in partial pressure of CO_2 would lead to the formation of carbonates. Hence, long-term tests in the actual operating conditions are required to ensure the stability of the material.

3.4 Conclusions

Yttrium doping is a promising strategy to increase the thermal stability of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). *In situ* long-term electrical conductivity relaxation (ECR) measurements yield stable values for D_{chem} only at the operating temperature of

800 °C for BSCF:10Y. At 700 °C, however, the value of D_{chem} of this material decreases by about 20% during the 200 h measurement. BSCF doped with up to 3% of yttrium did not show a stable value of D_{chem} at any of the two temperatures. BSCF:10Y initially showed the lowest D_{chem} value of all four compositions. However, since it remained much more stable than the samples doped with less or no Y, it outperforms pure BSCF already after 75 hours (800 °C) or 20 hours (700 °C).

Microstructural analyses demonstrate the suppression of all secondary phases except the hexagonal one at all investigated temperatures between 640 °C and 1100 °C for Y-concentrations of at least 3 mol-%. With 10 mol-% of Y in BSCF, a stable cubic system was observed at all investigated temperatures, except for small amounts of non-percolating hexagonal phase formed at 760 °C.

Concluding, doping BSCF with 10 mol-% Y manages to extend the stability range of the cubic perovskite phase towards lower operating temperatures. In the doped material, no secondary phase formation/degradation is observed at 800 °C. Below that temperature, degradation is significantly reduced compared to pure BSCF.

References

1. Yasutake Teraoka, Hua-Min Zhang, Shoichi Furukawa, Noboru Yamazoe. *Oxygen Permeation through Perovskite-type Oxides*. Chem. Lett. 1985; 14(11), pp. 1743-1746.
2. Yasutake Teraoka, Takashi Nobunaga, Noboru Yamazoe. *Effect of Cation Substitution on the Oxygen Semipermeability of Perovskite-type Oxides*. Chem. Lett. 1988; 17(3), pp. 503-506.
3. Zongping Shao, Weishen Yang, You Cong, Hui Dong, Jianhua Tong, Guoxing Xiong. *Investigation of the permeation behavior and stability of a $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ oxygen membrane*. J. Membr. Sci. 2000; 172(1-2), pp. 177-188.
4. Zongping Shao, Guoxing Xiong, Jianhua Tong, Hui Dong, Weishen Yang. *Ba effect in doped $\text{Sr}(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ on the phase structure and oxygen permeation properties of the dense ceramic membranes*. Sep. Purif. Technol. 2001; 25(1), pp. 419-429.

5. J. Sunarso, S. Baumann, J. M. Serra, W. A. Meulenberg, S. Liu, Y. S. Lin, J. C. Diniz da Costa. *Mixed ionic–electronic conducting (MIEC) ceramic-based membranes for oxygen separation*. J. Membr. Sci. 2008; 320(1–2), pp. 13–41.
6. S. Baumann, J. M. Serra, M. P. Lobera, S. Escolástico, F. Schulze-Küppers, W. A. Meulenberg. *Ultrahigh oxygen permeation flux through supported $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes*. J. Membr. Sci. 2011; 377(1–2), pp. 198–205.
7. J. Martynczuk, K. Efimov, L. Robben, A. Feldhoff. *Performance of zinc-doped perovskite-type membranes at intermediate temperatures for long-term oxygen permeation and under a carbon dioxide atmosphere*. J. Membr. Sci. 2009; 344(1–2), pp. 62–70.
8. M. Arnold, H. Wang, A. Feldhoff. *Influence of CO_2 on the oxygen permeation performance and the microstructure of perovskite-type $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ membranes*. J. Membr. Sci. 2007; 293(1–2), pp. 44–52.
9. H. Lu, Y. Cong, W. S. Yang. *Oxygen permeability and stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as an oxygen-permeable membrane at high pressures*. Solid State Ionics. 2006; 177(5), pp. 595–600.
10. Silvie Švarcová, Kjell Wiik, Julian Tolchard, Henny J. M. Bouwmeester, Tor Grande. *Structural instability of cubic perovskite $Ba_xSr_{1-x}Co_{1-y}Fe_yO_{3-\delta}$* . Solid State Ionics. 2008; 178(35–36), pp. 1787–1791.
11. P. Müller, H. Störmer, L. Dieterle, C. Niedrig, E. Ivers-Tiffée, D. Gerthsen. *Decomposition pathway of cubic $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ between 700 °C and 1000 °C analyzed by electron microscopic techniques*. Solid State Ionics. 2012; 206, pp. 57–66.
12. Konstantin Efimov, Qiang Xu, Armin Feldhoff. *Transmission Electron Microscopy Study of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ Perovskite Decomposition at Intermediate Temperatures*. Chem. Mater. 2010; 22(21), pp. 5866–5875.
13. David N. Mueller, Roger A. De Souza, Thomas E. Weirich, Daniel Roehrens, Joachim Mayer, Manfred Martin. *A kinetic study of the decomposition of the cubic perovskite-type oxide $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) ($x = 0.1$ and 0.5)*. PCCP. 2010; 12(35), pp. 10320–10328.
14. Christian Niedrig, Simon Taufall, Mónica Burriel, Wolfgang Menesklou, Stefan F. Wagner, Stefan Baumann, Ellen Ivers-Tiffée. *Thermal stability of the cubic phase in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)*. Solid State Ionics. 2011; 197(1), pp. 25–31.
15. Hui Lu, Jianhua Tong, Zengqiang Deng, You Cong, Weishen Yang. *Crystal structure, oxygen permeability and stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}M_{0.1}O_{3-\delta}$ ($M=Fe, Cr, Mn, Zr$) oxygen-permeable membranes*. Mater. Res. Bull. 2006; 41(4), pp. 683–689.

16. Xiaoyu Li, Thomas Kerstiens, Torsten Markus. *Oxygen permeability and phase stability of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskite at intermediate temperatures*. J. Membr. Sci. 2013; 438, pp. 83-89.
17. S. Baumann, F. Schulze-Küppers, S. Roitsch, M. Betz, M. Zwick, E. M. Pfaff, W. A. Meulenbergh, J. Mayer, D. Stöver. *Influence of sintering conditions on microstructure and oxygen permeation of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) oxygen transport membranes*. J. Membr. Sci. 2010; 359(1), pp. 102-109.
18. C. Buysse, A. Kovalevsky, F. Snijkers, A. Buekenhoudt, S. Mullens, J. Luyten, J. Kretzschmar, S. Lenaerts. *Development, performance and stability of sulfur-free, macrovoid-free BSCF capillaries for high temperature oxygen separation from air*. J. Membr. Sci. 2011; 372(1), pp. 239-248.
19. Matthias Meffert, Lana-Simone Unger, Lukas Grünewald, Heike Störmer, Stefan F. Wagner, Ellen Ivers-Tiffée, Dagmar Gerthsen. *The impact of grain size, A/B-cation ratio, and Y-doping on secondary phase formation in $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$* . J. Mater. Sci. 2017; 52(5), pp. 2705-2719.
20. Philipp Müller, Heike Störmer, Matthias Meffert, Levin Dieterle, Christian Niedrig, Stefan F. Wagner, Ellen Ivers-Tiffée, Dagmar Gerthsen. *Secondary Phase Formation in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ Studied by Electron Microscopy*. Chem. Mater. 2013; 25(4), pp. 564-573.
21. Junliang Sun, Min Yang, Guobao Li, Tao Yang, Fuhui Liao, Yingxia Wang, Ming Xiong, Jianhua Lin. *New Barium Cobaltite Series $\text{Ba}_{n+1}\text{Co}_n\text{O}_{3n+3}(\text{Co}_8\text{O}_8)$: Intergrowth Structure Containing Perovskite and CdI₂-Type Layers*. Inorg. Chem. 2006; 45(23), pp. 9151-9153.
22. V. M. Goldschmidt. *Die Gesetze der Krystallochemie*. Naturwissenschaften. 1926; 14(21), pp. 477-485.
23. P. Haworth, S. Smart, J. Glasscock, J. C. Diniz da Costa. *Yttrium doped BSCF membranes for oxygen separation*. Sep. Purif. Technol. 2011; 81(1), pp. 88-93.
24. Matthias Meffert, Heike Störmer, Dagmar Gerthsen. *Dopant-Site Determination in Y- and Sc-Doped $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ by Atom Location by Channeling Enhanced Microanalysis and the Role of Dopant Site on Secondary Phase Formation*. Microsc. Microanal. 2016; 22(01), pp. 113-121.
25. Pippardt U., Böer J., Kiesel L., Kircheisen R., Kriegel R., Voigt I. *Co-firing technology for the preparation of asymmetric oxygen transporting membranes based on BSCF and Zr-doped BSCF*. AIChE J. 2014; 60(1), pp. 15-21.

26. S. Yakovlev, C.-Y. Yoo, S. Fang, H. J. M. Bouwmeester. *Phase transformation and oxygen equilibration kinetics of pure and Zr-doped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite oxide probed by electrical conductivity relaxation*. Appl. Phys. Lett. 2010; 96(25), pp. 254101.
27. Olga Ravkina, Tobias Klande, Armin Feldhoff. *Investigation of Zr-doped BSCF perovskite membrane for oxygen separation in the intermediate temperature range*. J. Solid State Chem. 2013; 201, pp. 101-106.
28. Saim Saher, Matthias Meffert, Heike Störmer, Dagmar Gerthsen, Henny J. M. Bouwmeester. *Grain-size dependence of the deterioration of oxygen transport for pure and 3 mol% Zr-doped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ induced by thermal annealing*. J. Mater. Chem. A. 2017; 5(10), pp. 4982-4990.
29. Xiuxia Meng, Bo Meng, Xiaoyao Tan, Naitao Yang, Zi-Feng Ma. *Synthesis and properties of $Ba_{0.5}Sr_{0.5}(Co_{0.6}Zr_{0.2})Fe_{0.2}O_{3-\delta}$ perovskite cathode material for intermediate temperature solid-oxide fuel cells*. Mater. Res. Bull. 2009; 44(6), pp. 1293-1297.
30. Hui Lu, Zengqiang Deng, Jianhua Tong, Weishen Yang. *Oxygen permeability and structural stability of Zr-doped oxygen-permeable $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane*. Mater. Lett. 2005; 59(18), pp. 2285-2288.
31. S. M. Fang, C. Y. Yoo, H. J. M. Bouwmeester. *Performance and stability of niobium-substituted $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes*. Solid State Ionics. 2011; 195(1), pp. 1-6.
32. Fang Wang, Takashi Nakamura, Keiji Yashiro, Junichiro Mizusaki, Koji Amezawa. *Effect of Nb doping on the chemical stability of BSCF-based solid solutions*. Solid State Ionics. 2014; 262, pp. 719-723.
33. Lana-Simone Unger, Christian Niedrig, Stefan F. Wagner, Wolfgang Menesklou, Stefan Baumann, Wilhelm A. Meulenbergh, Ellen Ivers-Tiffée. *Yttrium doping of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ part I: Influence on oxygen permeation, electrical properties, reductive stability, and lattice parameters*. J. Eur. Ceram. Soc. 2018; 38(5), pp. 2378-2387.
34. M. W. den Otter, H. J. M. Bouwmeester, B. A. Boukamp, H. Verweij. *Reactor flush time correction in relaxation experiments*. J. Electrochem. Soc. 2001; 148(2), pp. J1-J6.
35. J. E. ten Elshof, M. H. R. Lankhorst, H. J. M. Bouwmeester. *Oxygen Exchange and Diffusion Coefficients of Strontium-Doped Lanthanum Ferrites by Electrical Conductivity Relaxation*. J. Electrochem. Soc. 1997; 144(3), pp. 1060-1067.
36. R. Shannon. *Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides*. Acta Cryst. A. 1976; 32(5), pp. 751-767.
37. Philipp Müller. *Electron Microscopical Investigations of Doped and Undoped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ for Oxygen Separation Membranes* [Ph.D. thesis]. Karlsruhe:

- Laboratorium für Elektronenmikroskopie (LEM), Karlsruher Institut für Technologie (KIT); 2013.
38. Matthias Simon Meffert. *Electron microscopy studies of Y-, Sc- and Zr-doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ceramics for oxygen separation membranes* [Ph.D. thesis]. Karlsruhe: Laboratorium für Elektronenmikroskopie (LEM), Karlsruher Institut für Technologie (KIT); 2017.
 39. Laura Almar, Heike Störmer, Matthias Meffert, Julian Szász, Florian Wankmüller, Dagmar Gerthsen, Ellen Ivers-Tiffée. *Improved Phase Stability and CO_2 Poisoning Robustness of Y-Doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ SOFC Cathodes at Intermediate Temperatures*. ACS Appl. Energy Mater. 2018; 1(3), pp. 1316-1327.

Appendix A3

Detailed methodology for Electrical Conductivity Relaxation experiments

Electrical Conductivity Relaxation (ECR) is a versatile characterization method for transport properties in MIEC oxides, as values for the chemical diffusion coefficient D_{chem} and chemical surface exchange coefficient k_{chem} are obtained in a single measurement. Furthermore, that measurement can be performed in a large range of conditions, for example the temperature, oxygen partial pressure, concentrations of CO_2 and SO_2 , and relative humidity can be varied. Various measurement modes are possible; typically, a series of experiments is performed to determine the values of D_{chem} and k_{chem} as a function of the above-mentioned parameters. Otherwise, a series of experiments can be performed to determine the values of D_{chem} and k_{chem} as a function of time to monitor the effect of structural changes in the ceramic.

For the experiments in this thesis, a bar-shaped sample and the four-probe method were used to measure the electrical conductivity. The four-probe method requires two electrodes to supply the current and two separate electrodes to measure the voltage in the sample over a certain distance. This allows for a higher precision as compared with the simpler two-probe method since the lead and contact resistances of the voltage probes do

Figure A3.1. ECR sample mounted in sample holder for electrical conductivity measurements using the four-probe method.

not contribute to the total resistance. An example of an ECR sample mounted on the sample holder is given in Figure A3.1. The relative dimensions of the sample are such that the surface area of the bar ends can be assumed not to contribute to any oxygen transport, allowing for the use of 2D model. Typically, the length, width and thickness of a sample are around 15 mm x 6 mm x 0.5 mm. The distance between the voltage and current probe on one side of the sample is about 2 mm. A sample of this size just fits into the sample chamber of the reactor, of which the dimensions are made small to reduce the flush time, a property that is part of the model used for fitting the obtained data.

In a typical ECR measurement, the sample is inserted in the reactor, the initial gas flow is set, and the reactor is heated slowly ($1 - 5\text{ }^{\circ}\text{C min}^{-1}$) to the desired annealing temperature (usually slightly above the maximum temperature planned to reach in a series of experiments). The experiment starts after the annealing is complete, the desired starting temperature is reached, and the conductivity of the sample is stable. The mixture of gases must have a known partial pressure of oxygen. By rapidly switching a valve in the gas inlet trajectory, gas from a second supply line with a different $p\text{O}_2$ as the gas from the first supply line, is led through the reactor. To induce an almost instantaneous change in the $p\text{O}_2$ of the reactor, switching between the two inlet gas lines needs to be as fast as possible (preferably in the order of 10 ms). The reactor is considered as a continuously ideally stirred tank reactor (CISTR), thereby assuming perfect mixing. As described previously, in reality the switch cannot be instantaneous, and the model can be made more accurate by incorporating a flush time variable ³⁴.

After the initial flushing, the conductivity of the sample, given by Equation A3.1, starts to respond to the changed conditions in the reactor.

$$\sigma = \frac{Id}{UA} \quad (\text{A3.1})$$

Here, I is the current applied through the sample by probes I1 and I2, U the voltage measured over probes U1 and U2, d is the distance between probes U1 and U2, and A the cross-sectional sample area. Figure A3.2 schematically shows the response of the

Figure A3.2. Change in conductivity after an (almost) instantaneous step change in pO_2 .

conductivity to the step in pO_2 . As the current is kept constant throughout the measurement, the change in conductivity appears by a change in the voltage. For most of the measurements, a simple approximation may be that a stable equilibrium is reached after the measurement was performed during a time $t = 15 \cdot \tau$, with τ representing the characteristic time of the exponential growth given by equation A3.2:

$$g(t) = \frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - e^{(-t/\tau)} \quad (\text{A3.2})$$

Where $g(t)$ is the normalized conductivity, σ_0 and σ_∞ are the conductivities $\sigma(t)$ at time $t = 0$ and $t = \infty$, respectively. At $t = 15 \cdot \tau$, the value of the normalized conductivity would reach a value of > 0.9999997 if Equation A3.2 would be valid, a value sufficiently close to the equilibrium value of 1. This approach worked well for automatically determining when a measurement could be stopped and a new step change in pO_2 could be induced. This approach is best combined with a minimum relaxation time of about 5 minutes, which ensures that experiments with materials with a slow reaction to a step change in pO_2 are not terminated too early due to the influence of noise. To obtain the values of

D_{chem} and k_{chem} from ECR data, more elaborate equations than Eq. A3.2 are required. In this thesis, the model used to fit data obtained in ECR measurements is based on the model proposed by Watterud ² and extended with the flush time correction proposed by den Otter ³⁴. Equations A3.3 – A3.5 are used to fit the normalized conductivity data:

$$g(t) = 1 - \prod_{i=x,y} \sum_{m=1}^{\infty} \frac{2L_i^2}{\beta_{m,i}^2 (\beta_{m,i}^2 + L_i^2 + L_i)} \frac{\tau_{m,i}}{\tau_{m,i} - \tau_f} \cdot \exp\left(-\frac{t}{\tau_{m,i}}\right) - \frac{\tau_f}{\tau_{m,i}} \exp\left(-\frac{t}{\tau_f}\right) \quad (\text{A3.3})$$

$$\tau_{m,i} = \frac{b_i^2}{D_{\text{chem}} \beta_{m,i}^2} \quad (\text{A3.4})$$

$$L_i = \frac{b_i k_{\text{chem}}}{D_{\text{chem}}} = \beta_{m,i} \tan \beta_{m,i} \quad (\text{A3.5})$$

In these equations, τ_f is the flush time constant of the reactor, and $2b_i$ the sample dimension along coordinate i , whilst $\beta_{m,i}$ are the non-zero roots of Equation A3.5 ³⁴. Furthermore, $L_c = D_{\text{chem}}/k_{\text{chem}}$ represents the critical length scale related to the influence of the chemical diffusion coefficient and chemical surface exchange coefficient on the re-equilibration behavior. This can also be expressed by the chemical Biot number, $Bi = \frac{b_i k_{\text{chem}}}{D_{\text{chem}}}$, which shows a value of 1 if both coefficients are of equal importance to the rate of re-equilibration, values below 1 if the rate is mainly by limited by surface exchange processes, and above 1 if it is mainly limited by solid state diffusion. If values below 0.03 or above 30 are obtained, the influence of one of the two processes on the re-equilibration rate is theoretically too small to be determined reliably ³⁴. In some cases however, it was observed that the upper boundary could be stretched to a value of around 50 before the value of k_{chem} became unreliable.

Three parameters are evaluated simultaneously: the transport related parameters D_{chem} and k_{chem} as well as the time at which the conductivity starts to change (t_0). Fitting a dataset with a nonlinear equation requires the input of initial values for the fitting parameters which are close to the expected final values. Any influence of initial values on

the final result due to the convergence of the fitting routine to a local minimum should be avoided. Rather than repeating the fitting routine with a large variety of input data – as performed in literature³ – we use approximate input values based on the measured data to save computation time. Equations A3.6 – A3.10 are used to calculate these input values. The value of $D_{\text{chem,init}}$ is approximated by Eq. 11 in³⁴, the value of τ_1 is calculated by solving $g(t) = 1 - e^{-t/\tau_1} = e^{-1}$. This is done under the assumption that the relaxation is fully governed by solid state diffusion.

$$D_{\text{chem,init}} = \frac{\tau_1 \pi^2}{4a^2} \quad (\text{A2.6})$$

in which a is half the sample thickness, assuming that the thickness is much smaller than the length and width of the sample (2D geometry). The value of $k_{\text{chem,init}}$ is calculated by integration of the linear first order rate expression which governs the surface exchange reaction, in line with literature⁴:

$$\frac{\partial C}{\partial t} = -\frac{Sk_{\text{chem,init}}}{V}[c(t) - c(\infty)] \quad (\text{A2.7})$$

$$\int_{c(0)}^{c(t)} \frac{1}{c(t) - c(\infty)} \partial C = \int_0^t -\frac{Sk_{\text{chem,init}}}{V} \partial t \quad (\text{A2.8})$$

$$\frac{c(t) - c(\infty)}{c(0) - c(\infty)} = \exp\left(-\frac{tSk_{\text{chem,init}}}{V_1}\right) \quad (\text{A2.9})$$

$$= \exp\left(-\frac{t}{\tau_1}\right) \quad (\text{A2.10})$$

With substitution of $\frac{V}{Sk_{\text{chem,init}}} = \frac{a}{k_{\text{chem,init}}}$ by τ_1 , and assuming that the relaxation is fully governed by surface exchange kinetics, the value of $k_{\text{chem,init}}$ can be determined based on the measured value of τ_1 . As oxygen diffusion pathways in ECR samples are from both the top and the bottom surface towards the middle of the sample, $c(\infty)$ represents the concentration of oxygen in the middle, and a represents half the sample thickness.

Furthermore, the input value for $t_{0,\text{init}}$ is the x value of the intersect of the tangent lines through the data points measured before and after the $p\text{O}_2$ switch takes effect. The

Figure A3.3. Determination of t_0 based on measurement data by taking the intersection of tangent lines based on points at $g(t) < 0.005$ and $0.005 < g(t) < 0.05$, respectively.

points obtained at the equilibrium before the switch are defined by $g(t) < 0.005$, while the first few points of the measurement are typically defined by $g(t) < 0.05$. The mentioned values may be changed if required due to a low signal-to-noise ratio or low sampling rate of the data. This procedure is schematically shown in A3.3.

The direct influence of t_0 on the value of χ^2 is limited, as a wrong value of t_0 affects only a few data points. The initial value does likely not affect the optimal value strongly, as the magnitude of physically reasonable variations in t_0 is small. As discussed in literature ⁵, in some cases it may be preferable not to treat t_0 as a fitting parameter, but instead to calculate it by treating the reactor as a CISTR. Based on experimental results, this is true if the process is mostly limited by D_{chem} , hence when the Biot number is close to the maximum value at which the mixed regime is valid ($\text{Bi} = 30$). In that case, a good alternative is to assume that $t_{0,\text{init}} = t_0$.

Fitting single data files and fitting multiple data files using a more constrained set of fitting parameters are both possible. For example, when comparing the effect of a surface coating on k_{chem} , data from two samples can be fitted with a value of D_{chem} which is forced to be equal for both samples. A matrix of fitting parameters can be made, an example is given in Table A3.1. Assuming that two samples of equal composition are exposed to an equal step in $p\text{O}_2$ at equal temperature T , one may expect to find the same value for D_{chem} in both samples and in all measurements. If large variations in the value of k_{chem} are observed, it could be considered to remove t_0 as fitting parameter, and to use the values determined by intersecting tangent lines instead.

Table A3.1. Example of fitting parameters matrix.

Sample 1 - without surface coating			Sample 2 - with surface coating		
$k_{\text{chem},1}$	$k_{\text{chem},2}$	$k_{\text{chem},3}$	$k_{\text{chem},4}$	$k_{\text{chem},5}$	$k_{\text{chem},6}$
D_{chem}					
$t_{0,1}$	$t_{0,2}$	$t_{0,3}$	$t_{0,4}$	$t_{0,5}$	$t_{0,6}$

To assess the quality of the fit, the goodness-of-fit parameter χ^2 is used:

$$\chi^2 = \sum_{k=0}^n \frac{g_k - g_{m,k}}{g_k} \quad (\text{A2.11})$$

in which g_k and $g_{m,k}$ represent the obtained value of normalized conductivity at data point k and the value predicted by the model. The difference between the measured and predicted values is inherently small when the new equilibrium has almost been reached and larger just after the sample starts to adapt to the changed atmosphere. The number of data points on which the goodness-of-fit is based thus affects the absolute value, hence no value could be quoted below which the model fits acceptably well to the data. To enable automation of the fitting procedure, data of a complete set of experiments are cut to an equal value of $x\tau$. Values of x are typically 8 – 10, an empirically determined range with values high enough to ensure that equilibrium is reached, but low enough to limit

the number of data points close to equilibrium. If most of the data points are found to be close to or scattering around the final normalized conductivity value of 1, the least-squares method may become less accurate, as it takes the noise around the final value into account to determine the optimal fit.

Figure 4 shows typical normalized conductivity data (orange dots) as obtained by ECR measurements, together with the obtained fit (blue line) and the residual deviation between the calculated and the measured data (grey dots). Next to that, Fig. A3.4B shows the error plot which is used to determine if the fitting procedure has found a local minimum or the absolute minimum in χ^2 . To obtain this figure, the values of χ^2 are calculated for a 50 x 50 grid of values for D_{chem} and k_{chem} , spaced x around the values estimated by the fitting procedure. Based on this plot, the influence of both fitting variables on the value of χ^2 can be judged: a curved figure and a large difference in χ^2 between the assessed points indicates that both parameters can be extracted with a high confidence.

The estimated errors in the fitting constants are standard errors determined based on the Jacobian matrix which is generated during the fitting procedure. A detailed description of the procedure to calculate these errors is given in literature ⁶.

Figure A3.4A) Normalized conductivity as a function of time, as measured in an ECR experiment. B) Corresponding error plot.

As a final note on automated ECR measurements and fitting, one should be aware that automation is never perfect. Raw data should be checked during the measurement, most notably to check whether the sample is allowed sufficient time to reach an equilibrium state. If not, the measurement time may be too short, or the sample may be unstable due to a phase transition or the formation of a secondary phase. Furthermore, to determine the repeatability of re-equilibration, it is a good habit to start plotting and fitting the data while the measurement is running.

References

40. G. Watterud. *Determination of Oxygen Transport Coefficients in Perovskites and Perovskite related Materials with mixed Conductivity* [Ph.D. thesis]. Trondheim, NTNU; 2005.
41. C.B. Gopal, S. M. Haile. *An electrical conductivity relaxation study of oxygen transport in samarium doped ceria*. J. Mater. Chem. A. 2014; 2(7), pp. 2405-2417.
42. N. H. Perry, J.J. Kim, H. L. Tuller. *Oxygen surface exchange kinetics measurement by simultaneous optical transmission relaxation and impedance spectroscopy: Sr(Ti₃Fe)O_{3-d} thin film case study*. Sci. Technol. Adv. Mater. 2018; 19(1), pp. 130-141.
43. Y. Li, K. Gerdes, H. Diamond, X. Liu. *An improved method to increase the predictive accuracy of the ECR technique*. Solid State Ionics. 2011; 204-205, pp. 104-110.
44. N.A.W. van Riel. *Template for parameter estimation with Matlab Optimization Toolbox; including dynamic systems*. Eindhoven University of Technology; 2011, <https://dx.doi.org/10.13140/2.1.3335.5846>

CHAPTER 4

Structure, electrical conductivity and oxygen transport properties of perovskite -type oxides $\text{CaMn}_{1-x-y}\text{Ti}_x\text{Fe}_y\text{O}_{3-\delta}$

Abstract

Calcium manganite-based perovskite-type oxides hold promise for application in chemical looping combustion processes and oxygen transport membranes. In this study, we have investigated the structure, electrical conductivity and oxygen transport properties of perovskite-type oxides $\text{CaMn}_{1-x-y}\text{Ti}_x\text{Fe}_y\text{O}_{3-\delta}$. Distinct from previous work, data of high temperature X-ray diffraction in the temperature range 600-975 °C demonstrates that $\text{CaMnO}_{3-\delta}$ (CM) transforms from orthorhombic to a mixture of orthorhombic and tetragonal phases at temperatures exceeding ~ 880 °C. Partial substitution of manganese by iron and/or titanium to yield $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ (CMT), $\text{CaMn}_{0.85}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CMF), and $\text{CaMn}_{0.725}\text{Ti}_{0.125}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CMTF) leads to a different phase behaviour. While CMT remains orthorhombic up to 975 °C, corresponding to the highest temperature of the experiments, CMF and CMTF undergo an orthorhombic → tetragonal → cubic sequence of phase transitions. Electrical conductivity relaxation measurements are conducted to determine the chemical diffusion coefficient (D_{chem}) and the surface exchange coefficient (k_{chem}) of the materials. The results demonstrate that oxygen transport is hindered in the tetragonal phase if occurring, which is attributed to a possible ordering of oxygen vacancies. The small polaron electrical conductivity of CM in the cited temperature range is lowered upon partial manganese substitution, by about 10% for CMF and up to half an order of magnitude for CMF and CMTF.

4.1. Introduction

Oxygen carrier materials (OCMs) for chemical looping combustion (CLC) share similar requirements with materials used for oxygen transport membranes (OTMs). Both applications require materials showing fast oxygen transport kinetics and reliable operation in atmospheres containing CO_2 , SO_2 , and/or water. Calcium manganite, in which 12.5 mol% of manganese is substituted by titanium, was shown to hold promise for CLC applications¹⁻³. More recently, it was demonstrated that an improved performance was found for $\text{CaMn}_{0.875-x}\text{Fe}_x\text{Ti}_{0.125}\text{O}_{3-\delta}$. The partial co-substitution of manganese by iron enhances the oxygen storage capacity and release kinetics, and lowers the degradation rate. Optimal performance was found for the composition with 15 mol% iron⁴. Asymmetric OTM membranes based on $\text{CaTi}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3-\delta}$ operated in CO_2 -containing atmospheres showed a stable oxygen flux over a period of 6 months, without significant degradation.⁵ In this work, we have determined the evolution of structure and oxygen transport properties of $\text{CaMnO}_{3-\delta}$ (CM), $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ (CMT), $\text{CaMn}_{0.85}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CMF), and $\text{CaMn}_{0.725}\text{Ti}_{0.125}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CMTF) with temperature, using high-temperature X-ray diffraction, thermal analysis, thermogravimetry and electrical conductivity relaxation measurements.

4.2. Experimental

4.2.1. Powder synthesis and sintering

CM, CMT, CMF and CMTF powders were synthesized as described previously⁴. The powders were milled in a planetary mill (Retsch PM 100) in ethanol for 30 min at 250 rpm in a 150 mm diameter zirconia bowl using 5 mm zirconia balls. The powder was dried and sieved, and the fraction below 45 μm was pressed into a pellet, which was further compacted in a cold isostatic press. The green pellet was placed onto a platinum foil inside a tubular furnace and heated (200 K h^{-1}) under a flow of 2% H_2 in nitrogen up to $\sim 800^\circ\text{C}$. Upon reaching that temperature, the atmosphere was changed to a flow of pure nitrogen, and the sample further heated with an unchanged rate until the sintering

temperature was reached (1450 °C for CM and CMT, 1400 °C for CMF and CMTF). After a 12 h dwell, the sample was cooled down to 1250 °C at a rate of 5 °C min⁻¹, and after reaching this temperature, the gas flow was changed to 10% oxygen in nitrogen. The sample was kept for 6 h at 1250 °C, and slowly cooled down (1 °C min⁻¹) to room temperature in order to avoid the formation of cracks. Dense ceramic pellets were obtained with relative densities in excess of 99%, as measured by Archimedes' method.

4.2.2. X ray diffraction

X-ray powder diffraction measurements (XRD) at room temperature were performed on a Bruker Da Vinci diffractometer with a LYNXEYE XE detector using CuK α radiation accelerated at 40 kV and 40 mA. Finely ground and sieved powder (<90 μ m) was placed into a back-loaded sample holder and data was collected from 15° to 75° with a step size of 0.013° and 1 s counting time. For high temperature X-ray diffraction measurements (HT-XRD) measurements, a Rigaku Ultima IV instrument with CuK α radiation accelerated at 40 kV and 40 mA was employed. The powder samples were heated to 975 °C under a 30 ml min⁻¹ flow of synthetic air. XRD patterns were recorded from 975 °C down to 600 °C with 25 °C intervals. At each temperature the sample was allowed to equilibrate for 10 min. Data were acquired in the 2 θ range 10–75° with a step size of 0.02° and scan speed of 1 °C min⁻¹. The GSAS-II software package was used for Rietveld refinements of the patterns ⁶.

4.2.3. Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) data were collected on a Netzsch STA 449 F3 Jupiter instrument. For DTA experiments, an Al₂O₃ crucible filled with about 50 mg of powder was placed onto the sample holder. The sample was heated to 1000 °C under a synthetic air flow. After a 30 min dwell, the sample was cooled to 100 °C, and a second thermal cycling procedure to 1000 °C and back to 100 °C was performed. Throughout the experiment, the flow rate was kept constant at 100 ml min⁻¹, and heating and cooling rates were 10 °C min⁻¹. Netzsch Proteus software

was used to record the voltage difference between the thermocouples touching the sample crucible and a similarly sized empty crucible.

For determination of changes in the oxygen stoichiometry of the samples, TGA experiments were performed using larger crucibles to increase the experimental accuracy of the instrument. About 175 mg of powder was placed into the crucible. Data were collected in the range 650 -1000°C, with intervals of 25 °C, at 4.5, 10, 21, 42 and 90% O_2 in N_2 , maintaining a flow rate of 200 ml min^{-1} (STP), while using heating and cooling rates of 10 °C min^{-1} . The chosen partial pressures of oxygen correspond with those used in the electrical conductivity relaxation (ECR) experiments. At each temperature and oxygen partial pressure, the sample was allowed to equilibrate. Dwell stages were at least 30 min in the range 1000 °C – 775 °C, 45 min at 750 and 725 °C, 60 min at 700 and 675°C, and 90 min at 650 °C. The data was corrected for the buoyancy effect by performing measurements with an empty alumina crucible under identical flow rates and gas atmospheres.

4.2.4. Electrical conductivity and conductivity relaxation measurements

Thin rectangular bars with approximate dimensions $12 \times 6 \times 0.5 \text{ mm}^3$ were cut out of the sintered sample pellets, and the two largest surfaces polished until a mirror-like finish was obtained. The final thicknesses of the samples were 0.64 mm, 0.57 mm, 0.47 mm and 0.46 mm for CM, CMT, CMF, and CMTF, respectively. A four-probe dc method was used to collect data of electrical conductivity of the samples. Two gold wires (Alfa Aesar, 99.999%, 0.25 mm diameter and approximately 4 cm in length) were wrapped around the sample close to the bar ends to serve as current leads. Two additional gold wires were wrapped around the sample, about 2 mm remote from the previously fixed electrodes, as voltage probes. Prior to mounting, four indents were manually cut using a diamond blade along each long side of the sample to keep the electrodes fixed in their position. Sulphur-free gold paste (MaTeck GmbH, Jülich, Germany) was applied to improve the electrical contact between the electrodes and sample. Finally, the sample

was thermally treated in air to sinter the gold paste, using a chamber furnace at a temperature of 950 °C, and heating and cooling rates of 1 °C min⁻¹.

The sample was suspended above an alumina rod that functions as sample holder by tightly wrapping the sample electrodes around the Au wires of the sample holder. Care was taken that gas could flow freely around the sample. The sample holder was slid into the Al₂O₃ reactor with a diameter of 12 mm, thereby confining the sample to a chamber of 2.6 cm³. Using a gas flow rate of 280 ml min⁻¹, and assuming a continuously ideally stirred tank reactor, the small reactor volume ensures a flush time between 0.13 s at 925 °C and 0.16 s at 650 °C. A K-type thermocouple was placed a few millimetres beneath the sample and used to continuously monitor the temperature. Two parallel gas streams, each with a total flow rate of 280 ml min⁻¹ and with a controlled oxygen partial pressure (between 0.01 and 1 atm) were created by mixing dried oxygen and nitrogen in the desired ratios using Brooks GF040 mass flow controllers. One of these streams was led through the reactor and subsequently through the oxygen sensor (Systech Zr893/4), which was used to monitor the $p\text{O}_2$. Once an oxidation or reduction process was completed, a pneumatically-operated four-way valve was used to rapidly switch to the other gas stream, thereby aiming to achieve an instantaneous step change in $p\text{O}_2$. A Keithley 2400 SourceMeter® was used to provide a current of 30-100 mA through the sample, depending on the sample conductivity. Another instrument of the same type was used to measure the voltage over the sample with a sampling rate of about 10 Hz.

The sample was heated to 925 °C with a heating rate of 1 °C min⁻¹ under a 280 ml min⁻¹ flow of synthetic air. Electrical conductivity relaxation (ECR) measurements were performed after step changes in $p\text{O}_2$ between 0.147 to 0.215 atm. It was assumed that equilibrium was reached after a time of 15 τ_c , where τ_c is the characteristic time when the transient conductivity is fitted to a regular exponential function of the elapsed time. A series of five oxidative and five reductive steps was performed for each temperature in the range 925 - 650 °C. The temperature was changed step wise, with intervals of 25 °C, using cooling rates of 1 °C min⁻¹. To check the

reproducibility, the same series of oxidative and reductive steps was repeated upon increasing the temperature back to 925 °C and measuring at each 25 °C interval. The series of measurements was set up with a custom-made LabVIEW program, which was also used for data acquisition. Data of the electrical conductivity of the samples in synthetic air ($p\text{O}_2 = 0.21 \text{ atm}$) of the samples was collected at each temperature.

The transient conductivity after each $p\text{O}_2$ step change was normalized according to Eq. 4.1. Normalized data were cut off at $10\tau_c$ and fitted to Eqs. 4.2-4.4 to obtain the chemical diffusion coefficient D_{chem} and the surface exchange coefficient k_{chem} .

$$g(t) = \frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0} \quad (4.1)$$

$$g(t) = 1 - \prod_{i=y,z} \sum_{m=1}^{\infty} \frac{2L_i^2}{\beta_{m,i}^2 (\beta_{m,i}^2 + L_i^2 + L_i)} \frac{\tau_{m,i}}{\tau_{m,i} - \tau_f} \left(e^{-\frac{t}{\tau_{m,i}}} - \frac{\tau_f}{\tau_{m,i}} \left(e^{-\frac{t}{\tau_f}} \right) \right) \quad (4.2)$$

$$\tau_{m,i} = \frac{b_i^2}{D_{\text{chem}} \beta_{m,i}^2} \quad (4.3)$$

$$L_i = \frac{b_i}{L_c} = \beta_{m,i} \tan \beta_{m,i} \quad (4.4)$$

In these equations, $g(t)$ is the normalized conductivity, σ_0 and σ_∞ are the conductivities $\sigma(t)$ at time $t = 0$ and $t = \infty$, respectively, τ_f the flush time constant of the reactor, and $2b_i$ the sample dimension along coordinate i , whilst $\beta_{m,i}$ are the non-zero roots of Eq. 4.4. The critical thickness $L_c = D_{\text{chem}}/k_{\text{chem}}$ is the critical thickness below which oxygen surface exchange prevails over bulk oxygen diffusion in determining the rate of re-equilibration rate after a $p\text{O}_2$ step change. The flush time τ_f was calculated from

$$\tau_f = \frac{V_r}{\theta_v} \frac{T_{\text{STP}}}{T_r} \quad (4.5)$$

in which V_r is the volume (2.58 cm³) of the chamber in which the sample is located, θ_v the gas flow rate through the reactor, T_r the temperature in the reactor, and T_{STP} the temperature at standard conditions. D_{chem} and k_{chem} , together with t_0 , were fitted using a non-linear least-squares program based on the Levenberg-Marquardt algorithm. To

prevent finding local minima in the fitting routine, initial estimates for the fitting parameters were calculated, using

$$D_{\text{init}} \approx \frac{b_z}{\tau_c} \quad (4.6)$$

$$k_{\text{init}} \approx \frac{b_z}{\tau_c} \quad (4.7)$$

where D_{init} and k_{init} are the initial values for the fitting parameters D_{chem} and k_{chem} , respectively, and b_z is half the sample thickness, noting that $b_z \ll b_x, b_y$. Equation 4.6 assumes that diffusion governs the relaxation process, while Eq. 4.7 assumes that surface exchange governs the relaxation. The intersection between the tangent line of the conductivity before the $p\text{O}_2$ step and that of the conductivities between $g = 0.005$ and $g = 0.05$ served as the initial value for the parameter t_0 . Values of D_{chem} and k_{chem} obtained from fitting data of at least three subsequent reduction steps were averaged. More detailed descriptions of the ECR technique and the model used for data fitting are given elsewhere^{7,8}.

4.3. Results and discussion

4.3.1. Structure and phase stability

Room temperature XRD powder diffractograms of all compositions studied in this work are shown in Fig. 4.1. Corresponding cell parameters from Rietveld profile refinements in the orthorhombic space group $Pnma$ are listed in Table 4.1. Single phase perovskites were obtained for CM, CMT, and CMTF. A few extra peaks observed at $2\theta = 32^\circ - 34^\circ$ observed in the pattern for CMF are attributed to the presence of an impurity phase.

The room temperature cell parameters obtained for CM as listed in Table 4.1 are found to be in good agreement with $a = 5.281(1) \text{ \AA}$, $b = 7.453(1) \text{ \AA}$ and $c = 5.266(1) \text{ \AA}$ reported by Leonidova *et al.*⁹, $a = 5.274(3) \text{ \AA}$, $b = 7.467(5) \text{ \AA}$ and $c = 5.277(2) \text{ \AA}$ by Rørmark *et al.*¹⁰, and $a = 5.282 \text{ \AA}$, $b = 7.452 \text{ \AA}$ and $c = 5.265 \text{ \AA}$ by Taguchi *et al.*¹¹. The

small differences between the obtained data in each of these studies and the current study might be related to a different oxygen stoichiometry of the samples, depending on the atmosphere and cooling rate.

Table 4.1. Cell parameters obtained from Rietveld refinements of room temperature XRD patterns.

	a [Å]	b [Å]	c [Å]
CM	5.2810(8)	7.4567(4)	5.2671(7)
CMT	5.2985(2)	7.4783(8)	5.2820(8)
CMF	5.2978(7)	7.4829(4)	5.2881(5)
CMTF	5.3148(2)	7.5076(1)	5.3056(1)

Fig. 4.2 shows the HT-XRD patterns of CM recorded in air on cooling from 975 °C to 600 °C with 25 °C intervals. Inspection of the diffraction data reveals that above 800 °C some additional reflections appear in the 2θ region 38.5–42.0° with relative intensities less than 1 %. A magnification of this part of the diffraction pattern is given Fig. A4.1. The additional reflections are ascribed to partial demixing of CM, which would suggest that the composition at high temperature lies in a miscibility gap, or the exsolution of an impurity phase takes place.

On the basis of a combined DTA and HT-XRD (at room temperature, 900 and 920 °C) study, Taguchi *et al.*¹¹ proposed a phase transition sequence for CM from orthorhombic ($Pnma$) to tetragonal ($I4/mcm$) at 896 °C, and from tetragonal to cubic ($Pm\bar{3}m$) at 913 °C. In subsequent thermal analysis studies^{10, 12}, the two sequential peaks have also been assigned to these phase transitions. Pseudo-cubic lattice parameters obtained from Rietveld refinements of the HT-XRD patterns recorded for CM in this study are given in Fig. 4.3a. Our results reveal that CM remains orthorhombic up to 875°C, while at higher temperatures the refinements yield a mixture of orthorhombic and tetragonal phases, i.e., from 10% tetragonal at 900 °C to 71% at 975°C. No evidence is

Figure 4.1. Measured (red symbols) and calculated (black line) XRD patterns for CM, CMT, CMF and CMTF at room temperature. Bragg positions and the residual plot are indicated. Extra peaks, attributed to copper $K\beta$ and tungsten $L\alpha$ are labeled with v and *, respectively.

Figure 4.2. HT-XRD patterns of CM recorded in air on cooling from 975 °C to 600 °C. Stars denote regions in which aberrations of the instrument are known to be present. A magnification of the 2θ region 38.5–42.0° is given in the appendix of this chapter (Fig. A4.1), showing the appearance of a new phase at temperatures above approximately 800 °C.

There are only small discrepancies between the onset temperatures found in this study (903 °C and 921 °C) and those reported by Taguchi *et al.*¹¹ (896 °C and 913 °C) and Rørmark *et al.*¹⁰ (904 °C and 923 °C).

Lattice parameters from Rietveld refinements of the HT-XRD patterns for CMT are given in Figs. 4.3b. The DTA curve recorded for this material is shown in Fig. 4.4b, from which it becomes clear that the endothermic phase transitions observed on heating of CM are shifted to slightly higher temperatures (927 °C and 942 °C) in CMT. The Rietveld refinements for CMT, however, do not give evidence for a phase transition in this material. The HT-XRD patterns (Fig. 4.3b) can be indexed orthorhombically up to

Figure 4.3. Pseudo cubic lattice parameters as a function of temperature for (a) CM, (b) CMT, (c) CMF, and (d) CMFT. Lattice parameters were calculated, using: $a_c = a_{\text{ortho}}/\sqrt{2}$, $b_c = b_{\text{ortho}}/\sqrt{2}$, and $a_c = c_{\text{ortho}}/2$ for the orthorhombic ($Pnma$) structure, and $a_c = b_c = a_{\text{tetra}}/\sqrt{2}$ and $c_c = c_{\text{tetra}}/2$ for the tetragonal ($I4/mcm$) structure. For the cubic ($Pm\bar{3}m$) structure $a_c = b_c = c_c = a_{\text{cubic}}$.

the maximum temperature of 975 °C covered by the experiments. The refinements of HT-XRD patterns for CMF and CMFT (Figs. 4.3c and d, respectively) clearly show an orthorhombic $\rightarrow$ tetragonal $\rightarrow$ cubic sequence of transitions occurring in both materials upon heating. The corresponding XRD patterns are compatible with space groups $Pnma$, $I4/mcm$, and $Pm\bar{3}m$, respectively, consistent with the sequence of transitions in CM reported by Taguchi *et al.*¹¹. The same sequence of phase transitions has been reported

for $\text{CaFe}_x\text{Ti}_{1-x}\text{O}_{3-\delta}$.^{13,14} The DTA curves recorded for CMF and CMTF are shown in Fig. 4.4c and d, respectively. No peaks can be discerned, indicating that the structural transformations in both materials are continuous.

Figure 4.4. DTA curves for (a) CM, (b) CMT, (c) CMF, and (d) CMTF recorded under heating and cooling in synthetic air. The insets in (a) and (b) show magnified regions around the endothermic phase transitions occurring upon heating in CM and CMT, respectively.

4.3.2. Oxygen nonstoichiometry

The temperature-induced phase transitions as observed in CM, CMF and CMTF may result from cooperative tilting of BO_6 octahedra, which is the most commonly observed distortion in perovskite structures^{15,16}. The orthorhombic $Pnma$ structure, in

Glazer's notation ^{17,18} denoted by $a^-a^-c^+$, is one of the most common perovskite variants with a three-tilt system ^{15,16}. With increasing temperature, materials with this structure lose their tilts via a series of transitions, ending up with the ideal cubic $Pm\bar{3}m$ structure, in which there are no tilts ($a^0a^0a^0$) ¹⁹. Several authors have discussed that the sequence of structural phase transitions in parent CM is influenced by the degree of oxygen nonstoichiometry exhibited by the material ^{9,10}. From the pO_2 - T - δ phase diagram of CM published by Leonidova *et al.* ⁹ it may be inferred that the intermediate tetragonal $I4/mcm$ structure with tilt configuration $a^0a^0c^-$ is absent at ideal oxygen stoichiometry. Results of density functional theory (DFT) calculations indicate that the phase may appear as a result of ordering of oxygen vacancies ¹⁹.

The temperature and oxygen partial pressure dependence of the oxygen nonstoichiometry of CM, CMT, CMF and CMTF in this work was studied by TGA.

Figure 4.5. TGA of CM, CMT, CMF and CMTF during heating and cooling in synthetic air at 10 °C min⁻¹. The inset shows a magnification of the temperature region where phase transitions occur in CM and CMT.

Fig. 4.5 shows the corresponding weight changes as a function of temperature during heating in synthetic air ($p_{\text{O}_2} = 0.21$ atm). The weight changes are reversible on heating and cooling (not shown). The temperature at which oxygen loss starts in CMF and CMTF is 350-400 °C, while for CM and CMT it is not released below about 650 °C.

Figure 4.6. Oxygen stoichiometry ($3-\delta$) at different temperatures for (a) CM, (b) CMT, (c) CMF) and (d) CMTF calculated from data of TGA. Lines help to guide the eye.

The degree of oxygen nonstoichiometry is notably more pronounced for the former two materials, which is ascribed to the presence of the more reducible iron cations.

The inset in Fig. 4.5 shows that the slope of the temperature dependence of the weight change in both CM and CMT changes slightly after the apparent phase transitions occurring in both materials. For CM, this observation is consistent with the phase diagram published for this material by Leonidova *et al.*⁹. The observed onset temperatures, 902°C and 927°C for CM and 921°C and 950°C for CMT, are in fair agreement with the corresponding results from DTA (see Fig. 4.4).

As shown by Leonidova *et al.*⁹ and Rørmark *et al.*¹⁰, the phase transition temperatures in CM decrease with increasing oxygen deficiency. It is therefore postulated here that the lower transition temperatures observed for CMF and CMTF (cf. Figs. 4.3c and d) compared to those reported for CM by, e.g., Taguchi *et al.*¹¹ might be related to the comparatively high oxygen deficiencies exhibited by the former two materials. This further suggests that the transition temperatures can be tuned by the degree of manganese substitution. Additional research is required to demonstrate our hypothesis.

The oxygen stoichiometry ($3-\delta$) as a function of $\log(p\text{O}_2)$ for the different materials is presented in Fig. 4.6. The corresponding TGA measurements were performed to support analysis of data obtained from ECR measurements as will be discussed below. For the evaluation it was assumed that $\delta = 0$ at room temperature.

4.3.3. Electrical conductivity

Fig. 4.7 shows the temperature dependences of the electrical conductivity of the investigated materials in this study as a function of temperature at $p\text{O}_2 = 0.21$ atm. The conductivity of CM, CMF and CMTF show Arrhenius behaviour with activation energies in the range 80 – 92 kJ mole⁻¹. For CMT, a change in activation energy is apparent at ~800°C.

Figure 4.7. Total electrical conductivity as a function of temperature measured at $p\text{O}_2 = 0.21$ atm.

Electrical conductivity in undoped CM is due to the formation of small polarons, which migrate via thermally activated hopping^{14,15}. Charge disproportionation, involving the transfer of an electron between adjacent Mn^{4+} ions,

leads to the formation of localized electrons Mn^{3+} (Mn_{Mn}') and electron holes Mn^{5+} ($\text{Mn}_{\text{Mn}}^{\cdot}$) that are trapped by local lattice distortions due to electron-phonon coupling: these are the *n*- and *p*-type small polarons, respectively. The negative sign of the Seebeck coefficient confirms that the *n*-type polarons are the dominant charge carriers in CM^{9,15}. The *p*-type polaronic charge carriers in CM appear to be effectively immobile⁹. The electrical conductivity in CM is thus expected to obey: $\sigma \propto [\text{Mn}_{\text{Mn}}'] [\text{Mn}_{\text{Mn}}^{\times}]$. Since variations in $[\text{Mn}_{\text{Mn}}^{\times}]$ are very small¹⁴, the conductivity is essentially governed by the concentration of Mn^{3+} cations ($[\text{Mn}_{\text{Mn}}']$). In addition to reaction (4.9), their concentration is affected by the exchange of oxygen between the gas phase and the oxide,

and by aliovalent doping. Charge neutrality requirements predict that acceptor doping, *e.g.* Fe^{3+} substituted for Mn^{4+} (Fe'_{Mn}) will lower the electrical conductivity, which is in line with the observation that the electrical conductivity decreases on going from CM to CMF (Fig. 4.7).

Such an explanation is also consistent with the increase in electrical conductivity observed upon donor doping of CM with Nb^{5+16} . It is further seen from Fig. 4.7 that the electrical conductivity of CM drops almost half an order of magnitude after the isovalent substitution of Mn^{4+} with Ti^{4+} ions, suggesting that it is the mobility of the *n*-type small polarons that is highly affected by the titanium substitution. A detailed study, however, is required to substantiate this conclusion and to provide further insights in the mechanism of electrical conduction in these solids.

4.3.4. Electrical conductivity relaxation

The oxygen transport properties of CM, CMT, CMF and CMTF were evaluated by ECR experiments. Normalized conductivity curves acquired from 925 to 650 °C after

Figure 4.8. Normalized conductivity curves for CMT. Data are acquired from 650 to 925 °C with 25 °C intervals, after a $p\text{O}_2$ step change from 0.215 to 0.146 atm. Data for other compositions are given in the appendix of this chapter.

a $p\text{O}_2$ step change from 0.215 to 0.146 atm for CMT are shown in Fig. 4.8. Excellent reproducibility was found during heating and cooling experiments. Similar results were obtained for the other compositions. In general, faster re-equilibration times after a $p\text{O}_2$ step change are observed with increase of temperature, although it should be noted that in the specific case of CMT (as can be inferred from Fig. 4.8) and that of CM (not shown) the re-equilibration times at the highest temperatures are observed to increase again with further increase of temperature.

A typical fit and error colour map obtained from fitting of data of a single relaxation experiment are given in Fig. 4.9. Analysis of experimental data allows simultaneous determination of D_{chem} and k_{chem} provided that both processes contribute in a quantifiable manner to the overall relaxation process. The latter is constrained by the accuracy of measurements, e.g., the noise of data, but also by the extent to which the re-equilibration after a $p\text{O}_2$ step change is determined by diffusion and surface exchange. A useful quantity in this respect is $b_z/L_c = b_z k_{\text{chem}}/D_{\text{chem}}$ (cf. Eq. 4.4, noting that $b_z \ll b_x, b_y$), which can be identified with the Biot number (Bi) commonly used in analysis of mass transport, and which parameter represents the ratio between two characteristic times: b_z^2/D_{chem} for diffusion and b_z/k_{chem} for surface exchange. A Biot plot for the data obtained in this study is given in Fig. 4.10, showing that for given thicknesses and conditions (see the experimental section) oxygen transport in CMT, CMF and CMTF over the entire range

Figure 4.9. (a) Normalized conductivity curve for CMF, obtained at 775 °C after a $p\text{O}_2$ step change from 0.146 to 0.215 atm. The solid blue line represents the non-linear least squares fit to Eqs. 4.2-4.4, and the residual is shown by the grey dots. (b) Corresponding error plot, in which the most probable values for D_{chem} and k_{chem} correspond with the highest value of $1/\chi^2$.

Figure 4.10. Biot number (Bi) as a function of temperature. Error bars indicate the standard error calculated based on averaging at least three experiments per temperature. Following Den Otter *et al.*⁷ the mixed-controlled region is found for $0.03 \leq Bi \leq 30$.

in temperature is in the mixed controlled region ($0.03 \leq Bi \leq 30$)⁷, whereas that of CM is in the diffusion-controlled region. Over a large range in temperature it was not possible to extract values of k_{chem} for CM from the data of experiments. Though a few data points of Bi for CM are shown in Fig. 4.10, the corresponding values of k_{chem} are not considered very accurate.

Arrhenius plots of D_{chem} and k_{chem} derived from the data of ECR measurements on CM, CMT, CMF and CMTF are shown in Fig. 4.11. A reasonable to good agreement of the values extracted from data of oxidation and reduction runs is obtained, suggesting that at given experimental conditions the constancy of D_{chem} and k_{chem} over the applied the $p\text{O}_2$ step change as assumed in the fitting procedure is satisfied accordingly⁷. Fig. 4.11 shows that the Arrhenius plots of D_{chem} and k_{chem} for all four compositions studied are subject to significant curvature. The curvature of the plots appears to be highly similar for both parameters, which holds for CMT, CMF and CMTF, suggesting that for each of these materials D_{chem} and k_{chem} are strongly correlated. Other authors have arrived at

Figure 4.11. Inverse temperature dependence of the chemical diffusion coefficient (D_{chem}) and the surface exchange coefficient (k_{chem}) for (a) CM, (b) CMT, (c) CMF, and (d) CMTF. Dashed lines serve as a guide to the eye. The filled and open symbols represent the data of oxidation and reduction step changes, respectively. The structures occurring in the different temperature regions are designated by their space groups. The vertical dashed lines denote by approximation the temperatures at which the phase transitions occur.

similar conclusions on the basis of studies on different materials. For example, see Refs. 24–27. A similar statement cannot be made for CM as, as was mentioned above, accurate values for k_{chem} for CM could not be obtained from the fitting procedure.

To further analyse the data, the oxygen self-diffusion coefficients, D_s , and the oxygen vacancy diffusion coefficients, D_v , for CM, CMT, CMF and CMTF were evaluated from the measured values of D_{chem} , using the relationships

$$D_{\text{chem}} = \gamma_0 D_s \quad (4.10)$$

$$D_{\text{chem}} = \gamma_v D_v \quad (4.11)$$

where γ_0 and γ_v are the thermodynamic factors²³,

$$\gamma_0 = \frac{1}{2} \frac{\partial \ln(pO_2)}{\partial \ln(3 - \delta)} = \frac{(3 - \delta)}{2} \frac{\partial \ln(pO_2)}{\partial(3 - \delta)} \quad (4.12)$$

$$\gamma_v = \frac{1}{2} \frac{\partial \ln(pO_2)}{\partial \ln(\delta)} = \frac{\delta}{2} \frac{\partial \ln(pO_2)}{\partial(\delta)} = -\frac{\delta}{2} \frac{\partial \ln(pO_2)}{\partial(3 - \delta)} \quad (4.13)$$

which can be derived from corresponding data of the oxygen nonstoichiometry for each of the compositions (Fig. 4.6). Strictly speaking, Eqs. (4.10) and (4.11) hold for materials with predominant electronic conductivity²³. Corresponding results for D_s and D_v for all four compositions are given in Figs. 4.12 and 4.13, respectively. The results reveal that for CMT (Figs. 4.12b and 4.13b) both parameters show Arrhenius behaviour over the entire range in temperature covered by the experiments. For CM (Figs. 4.12a and 4.13a), the linear behaviour extends up to ~880 °C, at which temperature the material transforms partially from orthorhombic (*Pnma*) to a mixture of orthorhombic (*Pnma*) and tetragonal (*I4/mcm*) phases. The high values observed for the average activation energies of D_s , $236 \pm 8 \text{ kJ mol}^{-1}$ and $260 \pm 4 \text{ kJ mol}^{-1}$ for CM and CMT, respectively, confirms that there are very few oxygen vacancies in both materials. The latter is reflected in the much lower activation energies found for D_v of both compositions, $123 \pm 10 \text{ kJ mol}^{-1}$ and $102 \pm 5 \text{ kJ mol}^{-1}$ for CM and CMT, respectively.

Contrary to the corresponding results for CM and CMT, the temperature dependences of D_s (Figs. 4.12c and 4.12d) and D_v (Figs. 4.13c and 4.13d) for CMF and

Figure 4.12. Inverse temperature dependence of the oxygen self-diffusion coefficient (D_S) for (a) CM, (b) CMT, (c) CMF, and (d) CMTF. Dashed lines serve as a guide to the eye. The filled and open symbols represent the data of oxidation and reduction step changes, respectively. The structures occurring in the different temperature regions are designated by their space groups. The vertical dashed lines denote by approximation the temperatures at which the phase transitions occur.

CMTF show significant departures from linear Arrhenius behaviour. For both compositions, the $\log(D_S)$ vs $1/T$ and $\log(D_V)$ vs $1/T$ plots show a reverse S-shape, *i.e.*, the $\log(D_S)$ and $\log(D_V)$ values levelling off in the intermediate temperature region, while increasing again at higher temperatures. The different temperature regions can be clearly

Figure 4.13. Inverse temperature dependence of the oxygen vacancy coefficient (D_V) for (a) CM, (b) CMT, (c) CMF, and (d) CMTF. Dashed lines serve as a guide to the eye. The filled and open symbols represent the data of oxidation and reduction step changes, respectively. The structures occurring in the different temperature regions are designated by their space groups. The vertical dashed lines denote by approximation the temperatures at which the phase transitions occur.

linked to the orthorhombic $\rightarrow$ tetragonal $\rightarrow$ cubic transformations occurring in both materials.

Overall, the results in this study suggest that oxygen transport in the tetragonal $I4/mcm$ phase, which occurs in CM, CMF and CMTF, and possibly also in CMT at higher temperatures than those covered by the present investigations, is reduced, e.g., by (partial)

ordering of oxygen vacancies. The latter would be consistent with the results of recent DFT calculations on the parent phase CM by Klarbring and Simak,¹⁹ in which the authors show that it is unlikely that the tetragonal phase appears as a result of a purely displacive mechanism, but rather may appear as a result of an ordering of oxygen vacancies. Further structural investigations using high-temperature neutron diffraction would be required to confirm these findings.

4.4. Conclusions

The present study reveals that $\text{CaMnO}_{3-\delta}$ (CM) transforms from orthorhombic to a mixture of orthorhombic and tetragonal phases at temperatures exceeding $\sim 880^\circ\text{C}$. It is further found that in the temperature range $600\text{--}975^\circ\text{C}$ covered by the HT-XRD experiments $\text{CaMn}_{0.85}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CMF) and $\text{CaMn}_{0.725}\text{Ti}_{0.125}\text{Fe}_{0.15}\text{O}_{3-\delta}$ (CMTF) undergo a sequence of phase transitions from orthorhombic to tetragonal to cubic. $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ (CMT) is found to remain orthorhombic up to highest temperatures covered by the HT-XRD experiments. The small polaron hopping conductivity of CM is reduced by partial manganese substitution with iron and/or titanium. Distinct departures of the temperature dependences of the oxygen self-diffusion and oxygen vacancy diffusion coefficients for CM, CMF and CMFT from Arrhenius-type of behaviour are interpreted to reflect reduced oxygen transport in the tetragonal phases occurring in these materials. The latter is consistent with recent results of DFT calculations on the parent phase CM showing that the tetragonal phase may appear as a result of an ordering of oxygen vacancies¹⁹.

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References

1. Hallberg, P.; Jing, D.; Rydén, M.; Mattisson, T.; Lyngfelt, A., *Chemical Looping Combustion and Chemical Looping with Oxygen Uncoupling Experiments in a Batch Reactor Using Spray-Dried $\text{CaMn}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($M = \text{Ti, Fe, Mg}$) Particles as Oxygen Carriers*. Energy & Fuels. 2013; 27(3), pp. 1473-1481.
2. Leion, H.; Larring, Y.; Bakken, E.; Bredesen, R.; Mattisson, T.; Lyngfelt, A., *Use of $\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_3$ as Oxygen Carrier in Chemical-Looping with Oxygen Uncoupling*. Energy & Fuels. 2009; 23(10), pp. 5276-5283.
3. Sundqvist, S.; Leion, H.; Rydén, M.; Lyngfelt, A.; Mattisson, T., *$\text{CaMn}_{0.875}\text{Ti}_{0.125}\text{O}_{3-\delta}$ as an Oxygen Carrier for Chemical-Looping with Oxygen Uncoupling (CLOU)—Solid-Fuel Testing and Sulfur Interaction*. Energy Technol. 2013; 1(5-6), pp. 338-344.
4. Thoréton, V.; Pishahang, M.; Mokkelbost, T.; Wiik, K.; Larring, Y., *Microstructural Stability of Tailored $\text{CaMn}_{0.875-x}\text{Fe}_x\text{Ti}_{0.125}\text{O}_{3-\delta}$ Perovskite Oxygen Carrier Materials for Chemical Looping Combustion*. Energy Technol. 2017; 5(9), pp. 1579-1587.
5. Xing, W.; Fontaine, M.-L.; Li, Z.; Polfus, J.M.; Larring, Y.; Denonville, C.; Henriksen, P.P.; Bredesen, R.; Nonnet, E.; Stevenson, A., *Asymmetric tubular $\text{CaTi}_{0.6}\text{Fe}_{0.15}\text{Mn}_{0.25}\text{O}_{3\delta}$ membranes: Membrane architecture and long-term stability*. J. Membr. Sci. 2018; 548, pp. 372-379.
6. Toby, B. H.; Von Dreele, R. B. *GSAS-II: the genesis of a modern open-source all purpose crystallography software package*. J. Appl. Crystallogr. 2013, 46, pp. 544-549.
7. den Otter, M.W.; Bouwmeester, H.J.M.; Boukamp, B.A.; Verweij, H., *Reactor flush time correction in relaxation experiments*. J. Electrochem. Soc. 2001, 148(2), pp. J1-J6.
8. Watterud, G.; *Determination of Oxygen Transport Coefficients in Perovskites and Perovskite related Materials with mixed Conductivity*. [PhD Thesis], 2005. ISBN 8247172747.
9. Ekaterina I. Leonidova, Ilya A. Leonidov, Mikhail V. Patrakeev, Victor L. Kozhevnikov. *Oxygen non-stoichiometry, high-temperature properties, and phase diagram of $\text{CaMnO}_{3-\delta}$* . J. Solid State Electrochem. 2011; 15(5), pp. 1071-1075.
10. Rormark, L.; Wiik, K.; Stolen, S.; Grande, T. *Oxygen stoichiometry and structural properties of $\text{La}_{1-x}\text{A}_x\text{MnO}_{3+\delta}$ ($A = \text{Ca or Sr}$ and $0 \leq x \leq 1$)*. J. Mat. Chem. 2002; 12(4), pp. 1058-1067.
11. H. Taguchi, M. Nagao, T. Sato, M. Shimada. *High-temperature phase transition of $\text{CaMnO}_{3-\delta}$* . J. Solid State Chem. 1989; 78(2), pp. 312-315.
12. Thiel, P.; Populoh, S.; Yoon, S.; Saucke, G.; Rubenis, K.; Weidenkaff, A. *Charge-carrier hopping in highly conductive $\text{CaMn}_{1-x}\text{M}_x\text{O}_{3-\delta}$ thermoelectrics*. J. Phys. Chem. C. 2015; 119 (38), pp. 21860-21867.

13. Becerro, I.; Redfern, S.A.T.; Carpenter, M.A.; Knight, K.S., Seifert, F. *Displacive Phase Transitions in and Strain Analysis of Fe-Doped CaTiO_3 Perovskites at High Temperatures by Neutron Diffraction*. J. Solid State Chem. 2002; 167, pp. 459–471.
14. Redfern, S.A.T. *High temperature structural phase transitions in CaTiO_3* . J. Phys. Condens. Matter. 1996; 8(43), pp. 8267–8275.
15. Howard, C.J. and Stokes, H.T. *Group-Theoretical Analysis of Octahedral Tilting in Perovskites*. Acta Cryst. 1998; B54, pp. 782–789.
16. Howard, C.J. and Stokes, H.T. *Structures and phase transitions in perovskites – a group-theoretical approach*. Acta Cryst. 2005; A61, pp. 93–111.
17. Glazer, A.M. The classification of tilted octahedra in perovskites. Acta Cryst. 1972; B28, pp. 3384–3392.
18. Glazer, A.M. *Simple ways of determining perovskite structures*. Acta Cryst. 1975; A31, pp. 756–762.
19. Klarbring, J.; Simak, S.I., *Nature of the octahedral tilting phase transitions in perovskites: A case study of CaMnO_3* . Phys. Rev. B. 2018; 97(2), id. 024120
20. Schrade, M.; Kabir, R.; Li, S.; Norby, T.; Finstad, T.G., *High temperature transport properties of thermoelectric $\text{CaMnO}_{3-\delta}$ – Indication of strongly interacting small polarons*. J. Appl. Phys., 2014; 115, id. 103705.
21. Goldyreva, E.I.; Leonidov, I.A.; Patrakeev, M.V., Kozhevnikov, V.L., *Oxygen non-stoichiometry and defect equilibria in $\text{CaMnO}_{3-\delta}$* . J Solid State Electrochem. 2012; 16(3), pp. 1187–1191.
22. Bocher, L.; Aguirre, M.H.; Robert, R.; Logvinovich, D.; Bakardjieva, S.; Hejtmanek, J.; Weidenkaff, A. *High-temperature stability, structure and thermoelectric properties of $\text{CaMn}_{1-x}\text{Nb}_x\text{O}_3$ phases*. Acta Mater. 2009; 57(19), pp. 5667–5680.
23. Bouwmeester, H.J.M and Burggraaf, A.J. *The CRC Handbook of Solid State Electrochemistry*, Eds. P.J. Gellings, H.J.M. Bouwmeester, CRC press, 1997; p.481.
24. Kilner, J.A.; de Souza, R.A.; Fullarton, I.C. *Surface exchange of oxygen in mixed conducting perovskite oxides*. Solid State Ionics 1996; 86–88, pp. 703–709.
25. de Souza, R.A. and Kilner, J.A. *Oxygen transport in $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Co}_y\text{O}_{3\pm\delta}$ perovskites: Part II. Oxygen surface exchange*. Solid State Ionics 1999; 126, pp. 153–161.
26. van der Haar, L.M.; den Otter, M.W.; Morskate, M.; Bouwmeester, H.J.M; Verweij, H. *Chemical Diffusion and Oxygen Surface Transfer of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ Studied with Electrical Conductivity Relaxation*. J. Electrochem. Soc. 2002; 149, pp. J41–J46.

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27. Saher, S.; Meffert, M.; Störmer, H.; Gerthsen, D.; Bouwmeester, H.J.M. Grain-size dependence of the deterioration of oxygen transport for pure and 3 mol% Zr-doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ induced by thermal annealing. *J. Mater. Chem. A*. 2017; 5, pp. 4982–4990.

Appendix A4

Figure A4.1. Magnification of the HT-XRD pattern of CM in the 2θ region 38.5° – 42.0° . Figure A4.2. Normalized conductivity curves for CMT. Data are acquired from 650 to 925 °C with 25 °C intervals, after a $p\text{O}_2$ step change from 0.215 to 0.146 atm.

CHAPTER 5

Enhancing oxygen flux through dual-phase oxygen transport membranes using Pr_6O_{11} nanoparticles

Abstract

$\text{Fe}_2\text{NiO}_4\text{-Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$ (NFO-CTO) composite membranes are of interest to separate oxygen from air. This chapter describes a method to improve the oxygen permeation rate through NFO-CTO membranes. Specifically, the effect of activating porous NFO-CTO layers – sandwiched on both sides of the dense NFO-CTO membrane – with Pr_6O_{11} nanoparticles is studied. Measurements in the temperature range 850 – 700 °C revealed a 2-4 fold increase in the oxygen flux after coating a 30- μm -thick porous NFO-CTO layer on both membrane sides, and a 6-12 fold increase relative to the bare membrane after activating the porous layers with Pr_6O_{11} nanoparticles into both coated layers. No degradation of the oxygen fluxes was found in CO_2 -containing atmospheres. Pulse isotopic exchange measurements confirmed an increase in the oxygen surface exchange rate of more than one order of magnitude after dispersion of Pr_6O_{11} nanoparticles on the surface of NFO-CTO composite powders. Electrochemical impedance spectroscopy measurements on symmetrical cells, using Gd-doped ceria (CGO) as the electrolyte and Pr_6O_{11} -activated NFO-CTO electrodes, showed a 10-fold decrease in the polarization resistance compared to non-infiltrated electrodes in air. Modification of porous layers by activation with Pr_6O_{11} nanoparticles is considered a viable route to enhance the oxygen fluxes across composite membranes.

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5.1 Introduction

The production of oxygen is a key step in several industrial processes. Approximately 150 million tons of oxygen are produced each year ¹, setting oxygen as the third largest chemical commodity worldwide ². Main applications are industrial manufacture (in particularly in the steel industry), power generation and medical uses. In addition, process efficiencies can in some industrial applications be enhanced by using pure oxygen instead of air. This is especially the case for power generation applications, in which the use of pure oxygen improves overall process efficiency and avoids emission of greenhouse gases. Combustion in oxygen-rich atmospheres leads to an increase of the flame temperature, either reducing the fuel consumption or enabling the use of alternative fuels with lower heat capacity (and lower cost). Moreover, mass and volume of flue gases are considerably reduced (up to 75%), and therefore smaller installations and equipment are needed, reducing capital and O&M costs. As a result of using oxygen-rich streams, flue gases mainly consist of CO₂ and H₂O. CO₂ can be easily separated from H₂O by condensing the water, yielding a pure stream of CO₂. Once purified, CO₂ can be utilized in several industrial processes, such as supercritical applications, carbonation of beverages, polymer foam blowing, urea production and medical gases ³. Cryogenic distillation of air is presently the standard technology for the production of pure oxygen. Nevertheless, high energy costs and the need of huge installations make the application of this technology economically unfeasible for most of the target applications ⁴. Therefore, oxygen transport membrane (OTM) technology is presented as an appealing alternative for the supply of oxygen in small and medium-scale installations ⁵⁻⁷.

Since the pioneering works on OTMs in the 70s ⁸⁻¹⁰, and after a large number of studies during the last decades, several materials with high oxygen permeation rates have been developed ^{11,12}. Despite the high oxygen fluxes reached with perovskite-type oxides like Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-δ} (BSCF), issues such as a lack of mechanical and chemical stability ¹³ and a complete loss in performance when exposed to CO₂-containing environments ¹⁴⁻¹⁶, limit their industrial applicability. To overcome these, several groups are developing CO₂-stable dual-phase materials ¹⁷⁻¹⁹. Amongst all studied materials, one of the most promising is the dual phase composite 60-40 vol% Fe₂NiO₄ - Ce_{0.8}Tb_{0.2}O_{2-δ} (NFO-CTO) ²⁰⁻²². This spinel-fluorite dual-phase material has been studied under

oxyfuel-like environments with excellent results in terms of stability²⁰⁻²² and performance, i.e. thin NFO-CTO membranes deposited on LSCF freeze-casted supports reached oxygen fluxes above $1\text{--}2\text{ ml min}^{-1}\text{ cm}^{-2}$ under CO_2 -containing environments at $850\text{ }^\circ\text{C}$ ²¹. However, the fluxes are still below $5\text{--}10\text{ ml min}^{-1}\text{ cm}^{-2}$, which are required to ensure techno-economic feasibility of OTMs²³. Strategies to optimize the performance of OTMs include reduction of membrane thickness and surface modification, especially via catalytic activation. The latter represents an effective method for improving the oxygen fluxes when the oxygen fluxes are limited by the surface exchange kinetics, i.e. for relatively thin membranes and/or at intermediate temperatures (below $800\text{ }^\circ\text{C}$). The addition of a porous layer can enhance the membrane performance by increasing the specific surface area and thereby increasing the number of active sites for oxygen exchange^{24,25}. For composite materials, these are the triple phase boundaries (TPB) where the gas phase meets the ionic and electronic conducting phases and where oxygen incorporation and release reactions occur. As sketched in Fig. 5.1, the fine-grained porous layer provides a much larger number of TPB sites than the bare membrane surface. The porous layers are of a similar composition as the dense layer to warrant thermo-mechanical compatibility.

In recent years, infiltration of active components into porous scaffolds has been gaining increased attention to enhance the performance of SOFC electrodes²⁶, as previously practiced to improve the performance of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}\text{--Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ cathodes²⁷. Following previous studies of modification of SOFC cathodes by infiltration with praseodymium oxide (Pr_6O_{11}) nanoparticles²⁷⁻²⁹, the present work focuses on enhancing the oxygen permeation rate of $\text{Fe}_2\text{NiO}_4\text{--Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$ (NFO-CTO) dual-phase composite membranes, with a 60:40 ratio between the spinel (NFO) and fluorite (CTO) phases. This is achieved by activating the porous NFO-CTO layers with Pr_6O_{11} coated on both membrane sides. Electrochemical impedance spectroscopy (EIS) and pulse isotopic exchange (PIE) are used to investigate the influence of Pr_6O_{11} activation on surface exchange kinetics.

Figure 5.1. Schematics showing the ionic and electronic percolative paths and the distribution of TPB sites for an NFO-CTO composite membrane with and without a porous activation layer (of similar composition). Transport of oxygen ions and electrons in the activation layer is enabled via percolative pathways for both charge carriers.

5.2 Experimental

5.2.1 Preparation of samples

NFO and NFO-CTO composite powders were prepared via a one-pot Pechini process. To this end, corresponding metal nitrates were dissolved in distilled water ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were provided by Sigma Aldrich, $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by ABCR GmbH). Subsequently, citric acid (Sigma Aldrich) and ethylene glycol were added as chelating and gelating agents in a molar ratio of metal: citric acid: ethylene glycol 1:2:4. After drying (up to 270 °C), the obtained gel was fired at 600 °C to obtain finely dispersed powders with the correct structural phases, as confirmed by X-ray diffraction (XRD). Dense NFO and NFO-CTO

ceramics were obtained by uniaxial pressing of the corresponding powders at 125 MPa, followed by sintering of the obtained disks in air at 1400 °C for 10 h (2 °C min⁻¹ heating rate, 5 °C min⁻¹ cooling rate). For oxygen permeation measurements, membranes with a diameter of 15 mm and thicknesses of 0.6–0.7 mm were obtained from the sintered NFO-CTO disks after grinding and polishing with sandpaper.

Powders of CTO and Ce_{0.8}Gd_{0.2}O_{1.9} (CGO) were synthesized by the co-precipitation method³⁰. CGO was co-doped with cobalt to improve the sinterability of the powder. This was done by impregnating Co(NO₃)₂·6H₂O dissolved in deionized water to reach a final 2 mol % content. The obtained powders were calcined in air at 800 °C for 5 h. Dense ceramics were obtained after uniaxial pressing of the powders, followed by sintering the obtained disks in air at 1480 °C for 4 h (2 °C min⁻¹ heating rate and 5 °C min⁻¹ cooling rate). The densities of all the samples were checked by the Archimedes method, resulting in relative densities above 98%.

For EIS and oxygen permeation measurements, 30-μm-thick porous layers of NFO-CTO were screen-printed on both sides of either CGO electrolyte disks or NFO-CTO membranes. Ink for screen-printing was made by mixing a 1:2 weight ratio of NFO-CTO powder previously ball-milled for 8 h and an ethyl cellulose (6 wt%) solution in terpineol in a three roll mill. After deposition, the obtained composite ceramic structures were sintered in air at 1100 °C for 2 h. Catalytic activation of the porous NFO-CTO scaffold layers was accomplished by infiltration, ensuring proper dispersion of catalyst particles³¹. To this end, a 2 M solution of Pr(NO₃)₃·6H₂O (Sigma-Aldrich) in ethanol-water (in a volume ratio 1:1) was dripped onto the porous composite scaffold layers, being infiltrated by capillary forces. After infiltration, the samples were dried at 80 °C for 1 h, and calcined in air at 850 °C for 2 h.

NFO, CTO and NFO-CTO composite powders for PIE measurements were obtained by crushing dense sintered ceramics, and subsequent sieving of the obtained powder through a 100 μm mesh. Composite powders for PIE measurements were activated with Pr₆O₁₁ nanoparticles by incipient wetness impregnation using a 2 M solution of Pr(NO₃)₃·6H₂O (Sigma Aldrich) in ethanol-water (in a volume ratio 1:1) and subsequent calcination for 2 h at 850 °C in air.

5.2.2 Samples characterization

Microstructural study

Identification of the crystalline phases of the samples was done by means of X-ray diffraction (XRD). The measurements were carried out using a PANalytical CubiX fast diffractometer, using CuK α 1 radiation ($\lambda = 1.5406 \text{ \AA}$) and a X'Celerator detector in Bragg-Brentano geometry. XRD patterns recorded in the 2θ range from 10° to 90° were analyzed using X'Pert Highscore Plus software. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) analyses were performed using a ZEISS Ultra55 field emission scanning electron microscope. In these experiments, cross sections of the membranes before and after the permeation tests were analyzed. A backscattered electron detector (BSD) was used for investigating the distribution of the phases in the dual-phase composite.

Pulse Isotopic Exchange measurements

PIE measurements were conducted using a home-made set-up³². The powder sample was loaded in the centre of a quartz tubular micro-reactor with an inner diameter of 2 mm. Quartz wool plugs were used to secure the packed powder bed. The length and mass of the packed bed were typically 10 mm and 0.08 g, respectively. $^{16}\text{O}_2$ mixed with Ar was used as carrier gas, and fed through the reactor with a total flow rate of 30 ml min^{-1} (NTP). Gases were dried using Agilent gas clean moisture filters before entering the reactor. Oxygen isotope gas was purchased from Cambridge Isotope Laboratories, Inc. ($> 97 \text{ atom\% } ^{18}\text{O}_2$). A six-port valve with a 500 μl sample loop was used for injection of the $^{18}\text{O}_2/\text{N}_2$ pulse into the $^{16}\text{O}_2/\text{Ar}$ carrier gas, the pulse having the same $p\text{O}_2$ as the carrier gas. The diluent nitrogen in the pulse was used for internal calibration of the mass spectrometer (Omni Star TM GSD 301 Pfeiffer-Vacuum). The mean residence time of the reactor varied between 10 and 30 ms, depending on temperature. Prior to measurements, the sample was pre-treated at 850°C for 2 h (heating rate 5°C min^{-1}) to remove possibly adsorbed water and CO_2 , and subsequently cooled to 50°C at rate of 5°C min^{-1} . Measurements were performed at a $p\text{O}_2$ of 0.21 atm. Averaged values of the $^{18}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ effluent fractions in three pulse experiments, at a given temperature, were used for calculation of the exchange rate. The reactor was equilibrated prior to each

measurement before data acquisition. The overall surface exchange rate, $\mathfrak{R}_0$ [mol (O) m⁻² s⁻¹], was calculated from ^{32,33}

$$\mathfrak{R}_0 = \frac{2F_m}{S} \ln \left(\frac{f_i^{18}}{f_e^{18}} \right) \quad (4.1)$$

where f_i^{18} and f_e^{18} are the ¹⁸O isotope fractions in the pulse at the inlet and exit of the reactor, respectively, F_m is the molar flow rate of oxygen through the packed bed, S the total surface area of the sample. The fraction f^{18} is calculated from $f^{18} = 0.5f^{34} + f^{36}$.

Electrochemical impedance spectroscopy

NFO-CTO/CGO/NFO-CTO symmetrical cells for two-electrode impedance measurements were prepared by coating 30 µm-thick NFO-CTO layers onto both sides of a 0.8 mm-thick CGO electrolyte disks. Measurements were performed at zero bias and an excitation voltage of 20 mV in the frequency range 0.01 – 3·10⁵ Hz, using a Solartron 1470E multichannel potentiostat and a 1455A frequency response analyzer. Measurements were performed at 850 °C, under different atmospheres (N₂, CO₂) and at different $p\text{O}_2$ (0.05-0.21 bar). In all cases, the total flow remained constant (100 ml min⁻¹). The impedance spectra were analysed using ZView®2 software. The impedance spectra were fitted using the equivalent circuit $LR_e(R_1Q_1)(R_2Q_2)(R_3Q_3)$ (see Fig. S2c), where L is an inductance, R_e the apparent electrolyte resistance, R_i ($i = 1,2,3$) a resistance, and Q_i ($i = 1,2,3$) a constant phase element.

Oxygen permeation measurements

Oxygen permeation studies were carried out in a lab-scale quartz reactor. Synthetic air (100 ml min⁻¹) was used as feed gas, while pure argon or a gas mixture containing 30 vol% CO₂, balance argon, were used as sweep gases (150 ml min⁻¹). Both gas streams were at atmospheric pressure. The temperature was measured by a thermocouple attached to the membrane. A PID controller maintained the temperature within 2 °C of the set point. Sealing was achieved using Au and Ag O-rings applying different sealing temperatures, i.e. 1000 °C and 850 °C, respectively. The bare membrane was sealed with Au O-rings whereas Ag O-rings were used for sealing activated membranes. This was

done in order to avoid coarsening phenomena of catalyst particles at higher temperatures. The permeate gas stream was analyzed by online gas chromatography, using a Varian CP-4900 micro-GC equipped with Molsieve5A, Pora-Plot-Q glass capillary, and CP-Sil modules. The leakage of oxygen was subtracted in the calculation of the oxygen flux. The contribution of leakage to the apparent oxygen flux was below 3% in all cases. The data reported here were all obtained after steady state was achieved. Each measurement was repeated three times to minimize the experimental error, which was typically below 0.5%.

5.3 Results and discussion

5.3.1 Microstructural study

Microscopy was conducted on membranes with pristine (non-infiltrated) and infiltrated activation layers. Figure 5.2a shows a cross-sectional Scanning Electron Microscope (SEM) image of the interface between the dense membrane and the NFO-CTO activation layer. The activation layer is highly porous and shows a good attachment to the membrane surface. An enlarged view of the activation layer is given in Fig 5.2b. Grain sizes of NFO and CTO phases range between 50-100 nm, and both phases appear to be well intermixed. In Fig. 5.2c, an activation layer is shown after infiltration and subsequent calcination at 850 °C. Nanoparticles are deposited all over the surface of the porous NFO-CTO scaffold as needle-like structures of about 500 nm length. No significant pore blocking is observed when activating with Pr_6O_{11} (see appendix, Fig. A5.1), therefore catalyst infiltration is not expected to imply a hindrance in the gas flow through the porous layer.

X-ray diffraction (XRD) analysis revealed that the infiltrated catalyst after sintering in air at 850 °C is present as Pr_6O_{11} particles³⁴. Fig. 5.2d shows the XRD pattern of the Pr_6O_{11} -activated layer, confirming the presence of NFO, CTO and Pr_6O_{11} . No evidence of impurity phases is found.

Figure 5.2. BSD-SEM images of activated NFO-CTO membranes: a) cross-sectional view of the porous scaffold/dense membrane interface of a non-infiltrated sample; bright grains represent the CTO phase and dark grains the NFO phase, magnification views of b) non-infiltrated composite scaffold, c) composite scaffold infiltrated with Pr₆O₁₁ nanoparticles, d) XRD pattern of the Pr₆O₁₁-infiltrated activation layer.

5.3.2 Oxygen permeation

Oxygen permeation measurements were performed on NFO-CTO membranes with thicknesses in the range of 0.6–0.7 mm. Three types of membranes were measured: (i) a bare membrane, (ii) a membrane on both sides coated with 30 μm-thick porous NFO-CTO layers, and (iii) a membrane having Pr₆O₁₁ nanoparticles activating the porous NFO-CTO layers. In Figure 5.3a, the oxygen permeation fluxes for the three membranes measured under air/Ar gradient are plotted as a function of temperature. The

addition of a porous NFO-CTO layer improves the oxygen flux from a value of 0.025 to 0.064 ml min⁻¹ cm⁻², at 850 °C, corresponding to a 2.5-fold improvement, while at 750 °C a fourfold improvement is observed. The enhancement in oxygen flux induced by the deposition of porous layers on both membrane surfaces can be ascribed to the concomitant increase in specific surface area (Fig. 5.1) and, thus, in the number of TPB sites available for oxygen exchange. Similar improvements in the oxygen flux obtained via surface activation of single-phase membranes through deposition of porous layers have been reported previously^{35,36}. For the dual-phase NFO-CTO membrane, the porous fine-grained NFO-CTO layers provide much larger numbers of TPB sites compared to the bare membrane surface, facilitating the oxygen reduction and evolution kinetics (see also Fig. 5.1)^{37,38}. The improvement in the oxygen permeation flux becomes more significant for the membrane presenting Pr₆O₁₁ nanoparticles in the porous NFO-CTO layers. A sixfold improvement is obtained at 850 °C reaching an oxygen flux of 0.14 ml min⁻¹ cm⁻². At lower temperatures the positive effect of membrane activation is even more evident: a twelvefold increase is found at 750 °C with respect to the bare membrane, thus confirming the promoting effect on the surface exchange reactions, typically limiting permeation at these temperatures. This is also confirmed by observing the activation energies (E_a) estimated for the different samples, which are included in Fig. 5.3a. For the case of the non-activated membrane, the E_a is estimated at 152 and 171 kJ mol⁻¹ in the temperature ranges of 1000 – 850 °C and 850 – 750 °C, respectively. When activating a membrane with NFO-CTO porous layers, a significant decrease in E_a from 152 to 97 kJ mol⁻¹ is observed in the range 850–775 °C, ascribed to the improvement in surface kinetics by the increase of TPB sites. Nevertheless, the fact that below 775 °C the E_a becomes equal for the bare and for the NFO-CTO membrane denotes a strong thermal limitation of surface reactions at these low temperatures. The latter does not occur with the Pr₆O₁₁-activated membrane, presenting E_a values of 86 kJ mol⁻¹ in the full temperature range of the measurement. In conclusion, impregnation of the porous layer with Pr₆O₁₁ nanoparticles leads to an improvement in the processes related to permeation over the full temperature range.

Figure 5.3A) Temperature dependence of the oxygen flux for (i) a bare NFO-CTO membrane, (ii) a membrane with porous layers at both surfaces, and (iii) a membrane after activation of the porous layers with Pr₆O₁₁ nanoparticles. B) Stability of oxygen flux through samples with and without Pr₆O₁₁ nanoparticles at 850 °C, with indicated sweep gases. Activation energies are specified for each of the materials and temperature regions.

Additionally, oxygen permeation was studied over a prolonged time to investigate the stability of the activated membrane at work (Figure 5.3b). First, the NFO-CTO+Pr coated membrane was subjected to an air/argon gradient at 850 °C for 30 hours. After this, no significant change in the permeation rate was found. The value of J_{O_2} stabilized at 0.13 ml min⁻¹ cm⁻². Subsequently, the sweep gas was changed to a 30% CO₂ in Ar mixture (mimicking oxyfuel conditions with respect to p_{CO_2}) while the feed gas was not changed. The gas switching does not induce a significant change in J_{O_2} although previous studies revealed a slight drop under similar operating conditions for ceria-based membranes²¹. The small loss in oxygen flux can be related to a stronger CO₂ adsorption on the active sites generated by Pr₆O₁₁ activation, hindering the oxygen reduction reactions involved in the oxygen permeation. During the following 24 hours on stream, the Pr₆O₁₁-activated membrane exhibited stable behavior. Regarding the membrane coated with porous layers (labeled as NFO-CTO), similar test conditions were applied

with a continuous 30% CO₂ in Ar sweeping during 24 h. In contrast to the Pr₆O₁₁-activated layer, the oxygen flux exhibits a very minor increase upon switching to CO₂ sweep gas. This beneficial effect of CO₂ as sweep gas has been previously observed for NFO-CTO membranes at temperatures above 850 °C^{20,22}. This is ascribed to the better sweeping properties and higher thermal emissivity of CO₂ with respect to Ar. The actual net effect of CO₂ depends on how surface exchange limits the overall membrane permeation with respect to ionic bulk and gas-phase transport.

5.3.3 Pulse isotopic exchange

Pulse Isotopic Exchange (PIE) measurements clearly demonstrate that the Pr₆O₁₁-activated NFO-CTO composite powder is much more active than the bare (i.e., non-activated) NFO-CTO powder for oxygen exchange. Figure 5.4 shows the oxygen isotope fractions as a function of temperature for both materials. At a temperature of around 800 °C, about half of the original fraction of ¹⁸O₂ in the pulse volume is converted into ¹⁶O₂ and ¹⁶O¹⁸O for the bare composite powder, whereas this temperature is lowered to about 570 °C after activation with Pr₆O₁₁.

Figure 5.4. Oxygen isotope fractions as a function of temperature from PIE measurements, at $p_{\text{O}_2} = 0.21$ atm, on powders of a) NFO-CTO and b) NFO-CTO activated with Pr₆O₁₁. Note that the x-axis scales are different. Dashed lines serve as guides to the eye.

Figure 5.5 shows the calculated surface exchange rates ($\mathfrak{R}_0$) of the bare and Pr_6O_{11} -activated NFO-CTO powders as well as corresponding values derived from measurements on powders of the individual NFO and CTO phases. The results show that NFO exhibits poor oxygen exchange kinetics, which is attributed to a low oxygen vacancy concentration of this material³⁹. The values of $\mathfrak{R}_0$ for bare NFO-CTO and CTO are close to each other above $\sim 725^\circ\text{C}$, suggesting that the faster surface exchange of the CTO phase determines the exchange rate found for the composite. The observation that the bare composite exhibits a higher value of $\mathfrak{R}_0$ below $\sim 725^\circ\text{C}$ than both constituents is interpreted to reflect a synergy between both phases. The enhanced exchange rate at these low temperatures might be due to the availability of electrons provided by the NFO phase, while at higher temperatures p-type conductivity in CTO may start to play a role in the electrical conductivity of the composite. The enhanced exchange rate is further observed for composites with different NFO to CTO ratios (See Fig. A5.2). However, more research is needed to explain this observation. Furthermore, the exchange rate of NFO-CTO is increased by more than one order of magnitude after activation with Pr_6O_{11} nanoparticles (Fig. 5.5), in line with permeation results (Fig. 5.3) and previous reports on SOFC cathodes^{27-29, 44}. The impregnation does not affect the activation energy of the composite.

With regard to the activation energies, NFO results present a significantly low E_a value, with only 11 kJ mol^{-1} , mainly due to its predominant electronic conductivity and the minor effect of temperature on improving oxygen exchange for such a material. In contrast, CTO performance is highly influenced by temperature with higher E_a (105 kJ mol^{-1}), as previously described for ionic conductors based on different doped cerias⁴⁰⁻⁴². For the case of NFO-CTO, two different E_a regions can be identified: $T > 725^\circ\text{C}$ with a value close to that of CTO, and $T < 725^\circ\text{C}$, much closer to NFO behavior. This E_a change reflects a change in the prevailing gas exchange mechanism, being related to the CTO exchange mechanism⁴⁰ at high temperature and to NFO below 725°C , where the surface concentration of oxygen vacancies is much lower than that for CTO, thus diminishing the concentration of active sites available for O_2 adsorption and incorporation. The latter behavior may be linked to the change in the E_a slope observed for the permeation measurement through the NFO-CTO activated membrane (Fig. 5.3a). When activating with Pr_6O_{11} , and assuming the same tendency for the values

Figure 5.5. Temperature dependence of the surface exchange rate of NFO, CTO, non-activated and Pr_6O_{11} -activated NFO-CTO composite powders. Activation energies are specified for each of the materials; for NFO-CTO two different energies are calculated for the regions above and below 700 °C.

above 700 °C, a significant difference for the Pr_6O_{11} -activated NFO-CTO sample can be observed with respect to the non-activated sample, with a diminution in the E_a from 136 to 109 kJ mol^{-1} .

5.3.4 Electrochemical characterization

To further investigate the catalytic effect of Pr_6O_{11} addition into the NFO-CTO activation layers, EIS measurements were performed on NFO-CTO/CGO/NFO-CTO symmetrical cells. Figures 5.6a and 5.6b show impedance spectra of cells with non-activated and Pr_6O_{11} -activated NFO-CTO electrodes recorded in air, 5% of O_2 in N_2 , and 5% of O_2 in CO_2 after subtraction of the apparent electrolyte resistance. The

Figure 5.6. (a) Nyquist plot of NFO-CTO, (b) Nyquist plot of NFO-CTO impregnated with Pr_6O_{11} , (c and d) Bode plots corresponding to the Nyquist plots, (e) total polarization resistance, (f) fitting results of the bare and Pr_6O_{11} -impregnated NFO-CTO electrodes in different atmospheres at 850 °C at high frequency and (g) low and medium frequencies.

polarization resistance (R_p) increases for both electrodes when switching from air to gases with 5% of O_2 as well as after the replacement of N_2 by CO_2 , but to a minor extent. This phenomenon should be ascribed to the reduction of the available oxygen on the electrode surface for the oxygen reduction reaction. In the case where the atmosphere is changed from air to 5% of O_2 , the increase in R_p is only related to the lower $p\text{O}_2$ in the electrode, worsening the surface processes and increasing the resistance of the low frequency processes. On the other hand, CO_2 competes with O_2 for the oxygen reduction reaction active sites. This effect mainly affects the resistance at low frequencies (surface processes) and shifts the relaxation frequency to lower values. After Pr_6O_{11} activation of the NFO-CTO electrodes, R_p is one order of magnitude lower regardless of the atmosphere composition. Figures 5.6c and d show the Bode plots corresponding to the Nyquist plots in 5.6a and b, and reveal that Pr_6O_{11} ameliorates processes appearing at frequencies ranging from 0.1 to ~10 Hz.

EIS spectra fitting using the proposed equivalent circuit provides further evidence about the magnitude and origin of this improvement (See Figs. 5.6e-g). In the case of the pristine NFO-CTO electrode, three arcs were distinguished: two at low frequencies (LF1, 1-2 Hz and LF2, 3-4 Hz), and another at high frequencies (HF, 15-16 kHz). Upon activation with Pr_6O_{11} , the LF arcs are reduced by two orders of magnitude, and become negligible in air (for LF1). The low frequency arcs have been associated with surface processes like oxygen adsorption, dissociation, or reduction⁴³⁻⁴⁵. However, in the Pr_6O_{11} -activated electrode, two arcs are present in the Nyquist spectrum, one at low frequencies (LF2, 1-2 Hz) and another one at medium frequencies (MF, 200-500 Hz). Both arcs are one or even two orders of magnitude smaller than the LF1 resistance of the pristine sample. This effect is attributed to the above-observed enhancement of the surface exchange reaction. In addition, the contribution of HF processes decreases, and this can be assigned to transport properties of Pr_6O_{11} oxide covering the NFO-CTO electrode surface, which may favor the surface transport of both oxygen species and electron holes^{27,28}. Furthermore, Pr_6O_{11} possesses relatively high electronic conductivity and improves the oxygen surface processes^{27,28,46} and the surface exchange rate at the tested temperatures (Fig. 5.5).

The influence of different atmospheres on the electrochemical performance was further studied. The dependency of the resistance on $p\text{O}_2$ ($R \propto p_{\text{O}_2}^{-m_i}$) can shed further light on the nature of the limiting steps in the oxygen reduction process⁴⁷⁻⁴⁹. The untreated electrode shows a $p\text{O}_2$ -independent contribution at HF, which can be assigned to solid-state oxide ion transport through the composite. Nevertheless, the infiltrated NFO-CTO electrode presents a small dependence on $p\text{O}_2$ ($m_{\text{HF}} \approx 0.19$ in $R_{\text{HF}} \propto p_{\text{O}_2}^{-m_i}$), which can be ascribed to the p-type electronic conductivity ($\sigma \approx p_{\text{O}_2}^{1/6}$) conferred by the infiltrated Pr_6O_{11} . As shown in Fig. 5.6f, the LF1 resistance of the non-infiltrated electrode is $p\text{O}_2$ dependent ($m_{\text{LF1}} \approx 0.32$ in $R_{\text{LF}} \propto p_{\text{O}_2}^{-m_i}$) and can be related to the diffusion of atomic oxygen species as well as charge transfer ($\text{O}_{\text{ads}} + \text{e}^- \rightarrow \text{O}^-_{\text{ads}}$)^{44,47}. In the case of the treated electrode, the resistance at medium frequency (MF, $m_{\text{LF1}} \approx 0.38$) can be assigned to the same limiting process, but in this case the resistance is reduced by more than one order of magnitude. The activation of the porous

layer with Pr_6O_{11} enhances the reduction of the adsorbed oxygen and shifts the frequency to higher values⁵⁰.

The coupled effect of low $p\text{O}_2$ and presence of CO_2 was studied with the Pr_6O_{11} -activated NFO-CTO electrodes to mimic membrane sweeping conditions. CO_2 induces a rise in MF and LF resistances and this stems from the competitive adsorption of O_2 and CO_2 at the active sites, having a stronger effect for the Pr_6O_{11} -activated sample with a higher increase in LF2 resistance (Fig. 6c and 6d). This increase in MF and LF frequencies when the electrodes were contacted with CO_2 is in agreement with results from oxygen permeation experiments (Figure 5.3b) in which J_{O_2} of the Pr_6O_{11} -activated membrane slightly decreased when switching to a CO_2 -containing atmosphere. Furthermore, the bulk transport properties of the electrode are not influenced by the CO_2 presence, since the resistance at HF remains constant⁵¹.

5.4 Conclusions

NFO-CTO dual-phase composite membranes were coated on both sides with 30 μm -thick porous scaffolds of the fine-grained NFO-CTO that were further activated with Pr_6O_{11} nanoparticles to enhance surface exchange kinetics. Measurements in the temperature range 850 – 700 °C revealed a 2-4 fold increase of the oxygen flux after coating porous NFO-CTO layers on both sides of the dense membrane, and a 6-12 fold increase relative to the bare membrane after activation with Pr_6O_{11} nanoparticles into both coated layers. No degradation of the oxygen fluxes was found in CO_2 -containing atmospheres, illustrating the potential use of the developed NFO-CTO membranes in oxyfuel applications.

PIE measurements confirmed an increased exchange rate of composite NFO-CTO powders by more than one order of magnitude after activation with Pr_6O_{11} nanoparticles. Furthermore, EIS measurements on NFO-CTO/CGO/NFO-CTO symmetrical cells showed a strong decrease in the polarization resistance after Pr_6O_{11} activation of the porous NFO-CTO electrodes. The present results demonstrate that addition of Pr_6O_{11} nanoparticles into porous activation layers is a promising route to enhance oxygen permeation fluxes across dual-phase membranes.

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References

1. J. Emsley. *Nature's Building Blocks: An A-Z guide to the elements*. 2001.
2. A.C. Bose, G.J. Stiegel, P.A. Armstrong, B.J. Halper, E.P. Foster. *Progress in Ion Transport Membranes for Gas Separation Applications*. In: Bose Arun C., ed. *Inorganic Membranes for Energy and Environmental Applications*: Springer New York; 2009:3-25.
3. *Usos del CO₂: un camino hacia la sostenibilidad*. Plataforma Tecnológica Española del CO₂; 2013.
4. M.J. den Exter, W.G. Haije, J.F. Vente. *Viability of ITM Technology for Oxygen Production and Oxidation Processes: Material, System, and Process Aspects*. In: Bose Arun C., ed. *Inorganic Membranes for Energy and Environmental Applications*: Springer New York; 2009:27-51.
5. M.A. Habib, H.M. Badr, S.F. Ahmed, *et al.* *A review of recent developments in carbon capture utilizing oxy-fuel combustion in conventional and ion transport membrane systems*. Int. J. Energ Res. 2011; 35(9), pp. 741-764.
6. S.S. Hashim, A.R. Mohamed, S. Bhatia. *Oxygen separation from air using ceramic-based membrane technology for sustainable fuel production and power generation*. Renew. Sust. Energ. Rev. 2011; 15(2), pp. 1284-1293.
7. P. Markewitz, J. Marx, A. Schreiber, P. Zapp. *Ecological evaluation of coal-fired oxyfuel power plants - cryogenic versus membrane-based air separation*. Energy Procedia. 2013; 37, pp. 2864-2876.
8. T. Takahashi, T. Esaka, H. Iwahara. *Electrical conduction in the sintered oxides of the system Bi₂O₃ - BaO*. J. Solid State Chem. 1976; 16(3), pp. 317-323.
9. B. Cales, J.F. Baumard. *Oxygen semipermeability and electronic conductivity in calcia-stabilized zirconia*. J. Mater. Sci. 1982; 17(11), pp. 3243-3248.
10. B. Cales, J.F. Baumard. *Mixed conduction and defect structure of ZrO₂-CeO₂-Y₂O₃ solid solutions*. J. Electrochem. Soc. 1984; 131(10), pp. 2407-2413.

11. C. Gaudillere, J. Garcia-Fayos, J. Serra. *Enhancing oxygen permeation through hierarchically-structured perovskite membranes elaborated by freeze-casting*. J. Mater. Chem. A. 2013, pp. 3828-3833.
12. S. Baumann, J.M. Serra, M.P. Lobera, S. Escolástico, F. Schulze-Küppers, W.A. Meulenbergh. *Ultrahigh oxygen permeation flux through supported $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes*. J. Membr. Sci. 2011; 377(1-2), pp. 198-205.
13. C. Niedrig, S. Taufall, M. Burriel, W. Menesklou, S.F. Wagner, S. Baumann, E. Ivers-Tiffée. *Thermal stability of the cubic phase in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)*. Solid State Ionics. 2011; 197(1), pp. 25-31.
14. M. Arnold, H. Wang, A. Feldhoff. *Influence of CO_2 on the oxygen permeation performance and the microstructure of perovskite-type $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ membranes*. J. Membr. Sci. 2007; 293(1-2), pp. 44-52.
15. J. Yi, M. Schroeder, T. Weirich, J. Mayer. *Behavior of $Ba(Co, Fe, Nb)O_{3-\delta}$ Perovskite in CO_2 -Containing Atmospheres: Degradation Mechanism and Materials Design*. Chem. Mater. 2010; 22(23), pp. 6246-6253.
16. J. Yi, M. Schroeder. *High temperature degradation of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes in atmospheres containing concentrated carbon dioxide*. J. Membr. Sci. 2011; 378(1-2), pp. 163-170.
17. H. Luo, T. Klande, Z. Cao, F. Liang, H. Wang, J. Caro. *A CO_2 -stable reduction-tolerant Nd-containing dual phase membrane for oxyfuel CO_2 capture*. J. Mater. Chem. A. 2014; 2(21), pp. 7780-7787.
18. K.S. Yun, C.-Y. Yoo, S.-G. Yoon, J.H. Yu, J.H. Joo. *Chemically and thermo-mechanically stable LSM-YSZ segmented oxygen permeable ceramic membrane*. J. Membr. Sci. 2015; 486, pp. 222-228.
19. J.H. Joo, K.S. Yun, J.-H. Kim, Y. Lee, C.-Y. Yoo, J.H. Yu. *Substantial Oxygen Flux in Dual-Phase Membrane of Ceria and Pure Electronic Conductor by Tailoring the Surface*. ACS Applied Materials & Interfaces. 2015; 7(27), pp. 14699-14707.
20. M. Balaguer, J. Garcia-Fayos, C. Solis, J.M. Serra. *Fast Oxygen Separation Through SO_2 - and CO_2 -Stable Dual-Phase Membrane Based on $NiFe_2O_4$ - $Ce_{0.8}Tb_{0.2}O_{2-\delta}$* . Chem. Mater. 2013; 25(24), pp. 4986-4993.
21. C. Gaudillere, J. Garcia-Fayos, M. Balaguer, J.M. Serra. *Enhanced Oxygen Separation through Robust Freeze-Cast Bilayered Dual-Phase Membranes*. ChemSusChem. 2014; 7(9), pp. 2554-2561.

22. J. Garcia-Fayos, M. Balaguer, J.M. Serra. *Dual-Phase Oxygen Transport Membranes for Stable Operation in Environments Containing Carbon Dioxide and Sulfur Dioxide*. ChemSusChem. 2015; 8(24), pp. 4242-4249.
23. H.J.M. Bouwmeester. *Dense ceramic membranes for methane conversion*. Catal. Today. 2003; 82(1-4), pp. 141-150.
24. H. Pan, L. Li, X. Deng, B. Meng, X. Tan, K. Li. *Improvement of oxygen permeation in perovskite hollow fibre membranes by the enhanced surface exchange kinetics*. J. Membr. Sci. 2013; 428, pp. 198-204.
25. M.P. Lobera, M. Balaguer, J. Garcia-Fayos, J.M. Serra. *Rare Earth-doped Ceria Catalysts for ODHE Reaction in a Catalytic Modified MIEC Membrane Reactor*. ChemCatChem. 2012; 4(12), pp. 2102-2111.
26. D. Ding, X.X. Li, S.Y. Lai, K. Gerdes, M.L. Liu. *Enhancing SOFC cathode performance by surface modification through infiltration*. Energy & Environmental Science. 2014; 7(2), pp. 552-575.
27. L. Navarrete, C. Solís, J.M. Serra. *Boosting the oxygen reduction reaction mechanisms in IT-SOFC cathodes by catalytic functionalization*. J. Mater. Chem. A. 2015; 3(32), pp. 16440-16444.
28. C. Nicollet, A. Flura, V. Vibhu, A. Rougier, J.-M. Bassat, J.-C. Grenier. *An innovative efficient oxygen electrode for SOFC: Pr₆O₁₁ infiltrated into Gd-doped ceria backbone*. Int. J. Hydrogen Energy. pp. 15538-15544.
29. R. Chiba, H. Aono, K. Kato. *An SOFC Cathode Infiltrated with Pr₆O₁₁*. ECS Transactions. 2013; 57(1), pp. 1831-1840.
30. M. Balaguer, C. Solís, J.M. Serra. *Structural-Transport Properties Relationships on Ce_{1-x}Ln_xO_{2-δ} System (Ln = Gd, La, Tb, Pr, Eu, Er, Yb, Nd) and Effect of Cobalt Addition*. The Journal of Physical Chemistry C. 2012; 116(14), pp. 7975-7982.
31. C. Solís, M. Balaguer, F. Bozza, N. Bonanos, J.M. Serra. *Catalytic surface promotion of highly active La_{0.85}Sr_{0.15}Cr_{0.8}Ni_{0.2}O_{3-δ} anodes for La_{5.6}WO_{11.4-δ} based proton conducting fuel cells*. Appl. Catal., B. 2014; 147, pp. 203-207.
32. H.J.M. Bouwmeester, C. Song, J. Zhu, J. Yi, M.v.S. Annaland, B.A. Boukamp. *A novel pulse isotopic exchange technique for rapid determination of the oxygen surface exchange rate of oxide ion conductors*. PCCP. 2009; 11(42), pp. 9640-9643.
33. C.-Y. Yoo, B.A. Boukamp, H.J.M. Bouwmeester. *Oxygen surface exchange kinetics of erbia-stabilized bismuth oxide*. J Solid State Electrochem. 2011; 15(2), pp. 231-236.

34. A. Jain, S.P. Ong, G. Hautier, *et al.* *Commentary: The Materials Project: A materials genome approach to accelerating materials innovation.* APL Materials. 2013; 1(1), pp. 011002.
35. C. Gaudillere, J. Garcia-Fayos, J.M. Serra. *Oxygen Permeation Improvement under CO₂-Rich Environments through Catalytic Activation of Hierarchically Structured Perovskite Membranes.* ChemPlusChem. 2014; 79(12), pp. 1720-1725.
36. J.M. Serra, J. Garcia-Fayos, S. Baumann, F. Schulze-Kueppers, W.A. Meulenberg. *Oxygen permeation through tape-cast asymmetric all-La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} membranes.* J. Membr. Sci. 2013; 447, pp. 297-305.
37. J.H. Joo, K.S. Yun, Y. Lee, J. Jung, C.Y. Yoo, J.H. Yu. *Dramatically Enhanced Oxygen Fluxes in Fluorite-Rich Dual-Phase Membrane by Surface Modification.* Chem. Mater. 2014; 26(15), pp. 4387-4394.
38. M. Ramasamy, S. Baumann, J. Palisaitis, *et al.* *Influence of Microstructure and Surface Activation of Dual-Phase Membrane Ce_{0.8}Gd_{0.2}O₂-FeCo₂O₄ on Oxygen Permeation.* J. Am. Ceram. Soc. 2016; 99(1), pp. 349-355.
39. X. Shi, Y.-F. Li, S.L. Bernasek, A. Selloni. *Structure of the NiFe₂O₄(001) surface in contact with gaseous O₂ and water vapor.* Surface Science. 2015; 640, pp. 73-79.
40. M. Balaguer, C.-Y. Yoo, H.J.M. Bouwmeester, J.M. Serra. *Bulk transport and oxygen surface exchange of the mixed ionic-electronic conductor Ce_{1-x}Tb_xO_{2-δ} (x = 0.1, 0.2, 0.5).* J. Mater. Chem. A. 2013; 1(35), pp. 10234-10242.
41. A.M. D'Angelo, A.C.Y. Liu, A.L. Chaffee. *Oxygen Uptake of Tb-CeO₂: Analysis of Ce³⁺ and Oxygen Vacancies.* The Journal of Physical Chemistry C. 2016; 120(26), pp. 14382-14389.
42. J.A. Lane, J.A. Kilner. *Measuring oxygen diffusion and oxygen surface exchange by conductivity relaxation.* Solid State Ionics. 2000; 136-137, pp. 997-1001.
43. S.B. Adler. *Factors governing oxygen reduction in solid oxide fuel cell cathodes.* Chem. Rev. 2004; 104(10), pp. 4791-4843.
44. J.D. Kim, G.D. Kim, J.W. Moon, Y.I. Park, W.H. Lee, K. Kobayashi, M. Nagai, C.E. Kim. *Characterization of LSM-YSZ composite electrode by ac impedance spectroscopy.* Solid State Ionics. 2001; 143(3-4), pp. 379-389.
45. M.J. Jorgensen, M. Mogensen. *Impedance of solid oxide fuel cell LSM/YSZ composite cathodes.* J. Electrochem. Soc. 2001; 148(5), pp. A433-A442.
46. V. Thangadurai, R.A. Huggins, W. Weppner. *Mixed ionic-electronic conductivity in phases in the praseodymium oxide system.* J Solid State Electrochem. 2001; 5(7-8), pp. 531-537.
47. R. Peng, T. Wu, W. Liu, X. Liu, G. Meng. *Cathode processes and materials for solid oxide fuel cells with proton conductors as electrolytes.* J. Mater. Chem. 2010; 20(30), pp. 6218-6225.

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48. F.H. van Heuveln, H.J.M. Bouwmeester. *Electrode properties of Sr-doped LaMnO₃ on yttria-stabilized zirconia. 2. Electrode kinetics*. J. Electrochem. Soc. 1997; 144(1), pp. 134-140.
 49. Y. Takeda, R. Kanno, M. Noda, Y. Tomida, O. Yamamoto. *Cathodic Polarization Phenomena of Perovskite Oxide Electrodes with Stabilized Zirconia*. J. Electrochem. Soc. 1987; 134(11), pp. 2656-2661.
 50. F. Mauvy, C. Lalanne, J.M. Bassat, J.C. Grenier, H. Zhao, L.H. Huo, P. Stevens. *Electrode properties of Ln₂NiO_{4+δ} (Ln = La, Nd, Pr) - AC impedance and DC polarization studies*. J. Electrochem. Soc. 2006; 153(8), pp. A1547-A1553.
 51. V.B. Vert, J.M. Serra. *Study of CO₂ stability and electrochemical oxygen activation of mixed conductors with low thermal expansion coefficient based on the TbBaCo₃ZnO_{7+δ} system*. J. Power Sources. 2011; 196(9), pp. 4270-4276.

Appendix A5

Figure A5.1. Micrographs made with the Scanning Electron Microscope using backscattered electrons, with a) NFO-CTO backbone, and b) backbone after impregnation with Pr_6O_{11} nanoparticles.

Figure A5.1 shows two examples of pore structures, as observed when looking at cross sections of the porous backbone. The presence of Pr_6O_{11} particles does not lead to significant pore blockage, as the amount and size of open space are roughly equal before and after impregnation.

Figure A5.2 shows the dependence of the activation energy of the overall surface exchange coefficient on temperature. This dependence is reported in the main paper for CTO-NFO containing 60 mol% NFO and 40 mol% CTO, and it is visible for different ratios of the composite constituents as well as shown in this appendix. Note further that increasing the amount of fluorite in the composite leads to an increased overall surface exchange rate at temperatures above roughly 725 °C, while it is disadvantageous for the exchange rate at lower temperatures. This may partly be due to the effect which also causes the nonconstant activation energy, i.e. the occurrence of p-type conductivity in CTO becoming relevant for the total electrical conductivity at temperatures above around

Figure A5.2. Temperature dependence of overall surface exchange rate of NFO-CTO composites with three different molar ratios of constituents (with the spinel phase indicated first).

725 – 750 °C. At temperatures where CTO is a mixed conductor, the influence of NFO on the overall surface exchange rate will be lower than at temperatures where its electronic conductivity is required for the surface exchange. Composites with higher concentrations of the fluorite therefore show faster surface exchange at higher temperatures.

Figure A5.3. Capacity (a) and frequency (b) obtained from fitting the electrochemical impedance spectra. Data were measured at 850 °C and in the indicated gas mixtures.

CHAPTER 6

Carbonation and decarbonation characteristics of strontium-containing perovskite-type ferrites

Abstract

The isothermal carbonation of perovskite-type oxides $\text{SrFe}_{0.9}\text{Al}_{0.1}\text{O}_{3-\delta}$ and $\text{SrFe}_{1-x}\text{Ti}_x\text{O}_{3-\delta}$ ($x = 0.1, 0.2, 0.5$) upon exposure to 25% CO_2 in Ar has been investigated at temperatures in the range 600–850 °C by combined thermogravimetric analysis (TGA) and temperature-programmed desorption/decomposition (TPD). Both methods yield consistent results, showing that $\text{SrFe}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ is more resistant to carbonation than $\text{SrFe}_{0.9}\text{Al}_{0.1}\text{O}_{3-\delta}$. The latter is explained by the higher acidity of Ti^{4+} compared to Al^{3+} . Both solids exhibit a maximum CO_2 uptake around 700–750 °C, which is accounted for by a balance between thermodynamics and kinetics of the carbonation reaction. Most notably, TPD experiments reveal for the partially carbonated perovskite phases a correlation between the onset temperature of decarbonation, T_o , and the temperature maintained during the carbonation pre-treatment. This behavior is attributed to the SrO activity in the carbonated perovskite phase, i.e., T_o decreases with decreasing SrO activity. To verify this hypothesis, T_o for SrCO_3 decomposition was measured by TGA in powder mixtures with $\text{Sr}_4\text{Fe}_6\text{O}_{13}$, $\text{SrFe}_{12}\text{O}_{19}$ and Fe_2O_3 , as a function of CO_2 partial pressure ($p\text{CO}_2$). The results graphically represented in an Ellingham diagram confirm that T_o for SrCO_3 decomposition in the said mixtures decreases with decreasing SrO activity in the ferrites and decreasing $p\text{CO}_2$. Of the perovskite oxides investigated in this study only $\text{SrFe}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ is found to be resistant to carbonation under 0.25 bar of CO_2 at 700 °C.

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6.1 Introduction

Many perovskite oxides are targeted for applications that bring the oxide in contact with acidic gases. Examples of such applications include, amongst others, their use as catalyst for methane reforming ¹ and reduction of CO₂ ² or NO_x ³, as sorbent material, e.g., for absorption of CO₂ from flue gases ⁴, as electrode material ⁵ or as oxygen transport membrane (OTM) ^{6,12}. Mixed ionic-electronic conducting (MIEC) perovskite oxides, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) ⁷⁻⁹, La_{0.5}Ba_{0.5}CoO_{3-δ} (LBC) ¹⁰, or SrCo_{1-x}Fe_xO_{3-δ} (SCF) and derivatives ^{11,12}, show excellent performance as a SOFC cathode. However, the alkaline-earth containing perovskite oxide are susceptible to carbonate formation already upon exposure to the low but significant level of CO₂ (380 ppm) in air, leading to performance deterioration with time ¹³. Numerous reports have also been made of studies in which the oxygen flux through the MIEC perovskite oxides used as OTM is found to degrade with time, or is blocked instantaneously, when CO₂ is used as the sweep gas ¹⁴⁻¹⁶. Not only the formed carbonate may limit the oxygen permeation flux ^{14, 17-19}, carbonation (and decarbonation) processes may also alter the microstructure and/or composition of the original perovskite oxide, which ultimately may cause membrane failure ^{14,20}. In the reported studies on BSCF ²⁰, SCF ²¹, Ba(Co, Fe, Zr)O_{3-δ} ¹⁴, Ba(Co, Fe, Nb)O_{3-δ} ¹⁶, scanning electron microscopy revealed formation of a surface carbonate layer followed by an alkaline-earth depleted layer on top of the original perovskite membrane layer. The original microstructure and oxygen permeation fluxes are (partially) recovered if the perovskite oxide is treated in a CO₂-free atmosphere. Clearly, an improved understanding of the impact of CO₂ on the stability of alkaline-earth containing perovskites is required from the perspective of using these materials as OTMs in oxygen fuel combustion or catalytic membrane reactors.

Up to the present, our understanding about the thermodynamics and kinetics of carbonate formation on alkaline-earth perovskite oxides remains rather poor. Relative stabilities of the perovskite oxides with emphasis on the role of the SrO activity have been discussed by Yokokawa *et al.* ^{22,23}. Guidelines for improving their CO₂ resistance have

been presented by Brandão *et al.* ²⁴. For a recent review on stability and CO₂-resistance of MIEC perovskite and perovskite-related structured membranes, see Zhang *et al.* ²⁵. Doping of the perovskite oxides with high-valent, redox-stable acidic cations such as Al³⁺, Ti⁴⁺, Nb⁵⁺, Sb⁵⁺, Mo⁵⁺ and Ta⁵⁺ has been recognized as an option to enhance stability and CO₂ resistance of the perovskite oxide against carbonation (or sulfonation) ²⁵. As the first part of this study, we have examined carbonation of SrFe_{0.9}Al_{0.1}O_{3-δ} (SFA10) and SrFe_{1-x}Ti_xO_{3-δ} (x = 0.1, 0.2, 0.5, abbreviated as SFT10, SFT20 and SFT50, respectively) by combined thermogravimetric analysis (TGA) and temperature programmed desorption/decomposition (TPD). Compositions in the SFT series have been reported as promising SOFC cathode ^{26,27} and OTM ²⁸ materials. As the second part of this study, we have measured the onset temperatures of thermal decomposition of SrCO₃ in the pure carbonate and in powder mixtures with either Sr₄Fe₆O₁₃, SrFe₁₂O₁₉ or Fe₂O₃ at different values of CO₂ partial pressure (*p*CO₂). These measurements were conducted to verify the hypothesis whether the onset temperature of decarbonation of partially carbonated perovskite phases is linked with the SrO activity in the latter.

6.2 Experimental

6.2.1. Synthesis and sample preparation

Powders of SrFe_{0.9}Al_{0.1}O_{3-δ} (SFA) and SrFe_{1-x}Ti_xO_{3-δ} (SFT; x = 0.1, 0.2, 0.5) were prepared by a modified Pechini method. Precursor materials, Sr(NO₃)₂ and Fe(NO₃)₃·9H₂O, with purities of > 99%, and Ti(OC₃H₇)₄ (titanium (IV) propoxide), with a purity of >98%, were purchased from Sigma-Aldrich, while Al(NO₃)₃·9H₂O with a purity of >99% was purchased from Acros Organics. C₆H₈O₇ (citric acid, >99.5%) and C₁₀H₁₆N₂O₈ (EDTA, >99%) were used as chelating agents. Both were purchased from Sigma-Aldrich as well. EDTA was dissolved in Milli-Q water. The pH of this solution was raised to 4 by dropwise addition of NH₄OH (30 vol%). Stoichiometric amounts of the metal nitrates were dissolved in Milli-Q water to which the EDTA solution was added and after which the pH was adjusted to 7 using NH₄OH (30 vol%). For the

synthesis of $\text{SrFe}_{1-x}\text{Ti}_x\text{O}_{3-\delta}$ (SFT), titanium (IV) isopropoxide was dissolved in dry ethanol in a glovebox under a dry N_2 atmosphere. A stoichiometric portion of the EDTA solution was heated to 60 °C and the $\text{Ti}(\text{OC}_3\text{H}_7)_4$ solution added under vigorous stirring. Precipitation of TiO_2 was not observed. The pH of the obtained solution was raised to 7 by dropwise addition of NH_4OH (30 vol%) and subsequently mixed with the solution of the other chelated metal ions. The metal-EDTA complexes were fixed into a polymeric network by addition of citric acid powder. The molar ratio of citric acid : EDTA : metal ions was 1.5 : 1 : 1 in all cases.

For the preparation of powders from the obtained precursor solutions, an appropriate amount of NH_4NO_3 was added to serve as oxidant in the auto-combustion reaction. The viscous solution was transferred into a stainless-steel pot and heated on a hot plate, set to 350 °C. Evaporation of the water caused formation of a vigorously boiling gel that eventually self-ignited. The obtained fluffy powders were crushed in a bowl using a single agate ball with a diameter of 5 cm. The powders were calcined at 950 – 1000 °C for 10 – 12 h to obtain single-phase perovskites, as confirmed by X-ray diffraction (XRD) measurements using a Bruker D2 Phaser instrument with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184$ Å). After calcination, the powders were ball-milled in ethanol for 24 h and dried. The resultant powders were manually ground in an agate mortar until they passed through a 120 mesh sieve ($d < 125$ µm). The sieved powders were annealed in air at 1000 °C for 1 h and then cooled to room temperature.

SrCO_3 and Fe_2O_3 (both > 99%) were purchased from Sigma-Aldrich, and $\text{SrFe}_{12}\text{O}_{19}$ (99.5%) from Alfa Aesar. $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ was prepared by solid state reaction. To this end, stoichiometric amounts of SrCO_3 and Fe_2O_3 were mixed in an agate mortar. The powder mixture was calcined in air at 1000 °C for 10 h using heating and cooling rates of 5 °C min^{-1} . XRD confirmed formation of $\text{Sr}_4\text{Fe}_6\text{O}_{13}$. No evidence of impurities or formation of second phases was found. For measurements of the onset temperature of thermal decomposition of SrCO_3 in mixtures with different ferrite oxides, powders of

$\text{Sr}_4\text{Fe}_6\text{O}_{13}$, $\text{SrFe}_{12}\text{O}_{19}$ or Fe_2O_3 were manually mixed with powder of SrCO_3 in a ratio 2:1, 11:1, 2:1, respectively, using an agate mortar and pestle set.

6.2.2. Characterization

Thermogravimetric analysis (TGA) data were collected using a Netzsch TG 449 F3 Jupiter. About 225 mg of powder was put into an Al_2O_3 crucible and placed in the TGA. Measured weight data were corrected for buoyancy effects. For the isothermal carbonation experiments, the powder was heated up to the desired set-point temperature at a rate of $5\text{ }^\circ\text{C min}^{-1}$ in Ar (75 ml min^{-1} ; purity $\geq 99.996\%$) and allowed to equilibrate at this specific temperature for at least 2 h prior to measurements. After mixing CO_2 ($\geq 99.996\%$) into the Ar stream up to a total flow rate of 100 ml min^{-1} , the weight change due to carbonation was measured as a function of time up to 15 h.

For measurements of the onset temperature of thermal SrCO_3 decomposition, T_o , in pure SrCO_3 powder and in powder mixtures with either $\text{Sr}_4\text{Fe}_6\text{O}_{13}$, $\text{SrFe}_{12}\text{O}_{19}$ or Fe_2O_3 , a CO_2 - Ar gas mixture with known $p\text{CO}_2$ was fed into the TGA reactor, with a total flow rate of 100 ml min^{-1} . The powder or powder mixture was heated to $600\text{ }^\circ\text{C}$ with a rate of $20\text{ }^\circ\text{C min}^{-1}$, and subsequently to temperatures $1100\text{--}1300\text{ }^\circ\text{C}$ with $2\text{ }^\circ\text{C min}^{-1}$. The onset temperature was determined at $p\text{CO}_2$ values of 0.02, 0.05, 0.10, 0.25 and 1 atm. The temperature at which the mass loss was 0.1% of the initial mass (at $600\text{ }^\circ\text{C}$) was taken as the value for T_o . The initial and final sample masses were used for normalization of the observed mass.

For temperature-programmed desorption/decomposition (TPD) measurements, the powders were uniaxially pressed into pellets at 25 MPa. These were manually crushed and sieved, while the sieved fraction in the range $125 < d < 300\text{ }\mu\text{m}$ was used as a packed bed, typically with a mass and length of 200 mg and 20 mm, respectively. The powder-packed bed was fixed in the centre of a tubular quartz reactor with an inner diameter of 3 mm using quartz wool plugs. Prior to measurement, the powder was carbonated *in situ*. To this end, the reactor was heated at a rate of $20\text{ }^\circ\text{C min}^{-1}$ under

Ar (37.5 ml min^{-1}) up to the temperature ($600 - 850 \text{ }^{\circ}\text{C}$) at which carbonation was carried out, held isothermally at this temperature for 15 min, and then CO_2 was mixed in with the Ar stream up to a total flow rate of 50 ml min^{-1} . Maintaining these conditions, the powder was carbonated for 15 h. Hereafter, the powder was quenched to room temperature by taking the reactor out of the oven. TPD data were collected by heating the reactor from room temperature to $900 \text{ }^{\circ}\text{C}$ at a rate $5 \text{ }^{\circ}\text{C min}^{-1}$, using Ar as carrier gas. The $m/z = 44$ signal intensity was monitored at a sampling rate of 12 Hz using an on-line mass spectrometer (MS, Pfeiffer Vacuum OmniStar GSD 301) at the exit of the reactor. The temperature at which the MS signal reached 0.1% of the maximum value of the CO_2 desorption peak was taken as the onset temperature for decarbonation.

6.3 Results and discussion

6.3.1. Carbonation of $\text{SrFe}_{0.9}\text{Al}_{0.1}\text{O}_{3-\delta}$ and $\text{SrFe}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ ($x = 0.1, 0.2, 0.5$)

Exposure of $\text{SrFe}_{0.9}\text{Al}_{0.1}\text{O}_{3-\delta}$ (SFA10) and $\text{SrFe}_{0.9}\text{Ti}_{0.1}\text{O}_{3-\delta}$ (SFT10) to 25% CO_2 in Ar in the range of temperatures $600 - 850 \text{ }^{\circ}\text{C}$ leads to carbonation of both perovskite oxides. Figure 6.1 shows the mass increase for both solids measured by TGA as a function

Figure 6.1. CO_2 uptake as a function of time for (a) SFA10 and (b) SFT10 in 25% CO_2 in Ar at different temperatures as measured by TGA.

of time at various carbonation temperatures. The shape of the obtained curves suggests that the reaction after 15 h of exposure is not complete (the samples subsequently being referred to as partially carbonated). At all temperatures, the CO_2 uptake observed for SFA10 exceeds that of SFT10, which clearly indicates that the more acidic Ti^{4+} cation is the more effective substituent in reducing carbonation. At 700 °C, the CO_2 uptake for SFA10 after 15h of exposure is 8.4 wt.% to be compared with 0.6 wt.% observed for SFT10.

Figure 6.2 shows the CO_2 -TPD profiles for both compositions after pre-treatment of the powders in 25% CO_2 in Ar for 15 h at different temperatures. The duration and carbonation conditions are chosen similar to those maintained in the TGA experiments. Several interesting features can be noted from the figure. First, consistent with the results from the TGA experiments (Fig. 6.1), the CO_2 desorption peak area – which reflects the degree of carbonation – is found to be a function of the temperature of carbonation temperature. Second, the onset temperature of decomposition of the formed carbonate, T_o , on the partially carbonated perovskite phase gradually shifts to lower temperature if the CO_2 pre-treatment (carbonation) is carried out at a lower temperature.

Figure 6.2. CO_2 -TPD profiles for (a) SFA10 and (b) SFT10 after isothermal carbonation in 25% CO_2 in Ar at the indicated temperatures. Note the different scales of the y-axes in both figures.

Figure 6.3 shows that the trend in the CO₂ desorption peak area (normalized to the value at 700 °C) with carbonation temperature is similar to that derived for the overall mass change observed during the TGA experiments. Both methods thus reveal that the maximum carbonation degree after the CO₂ treatment occurs for SFA10 at a temperature of 700 °C, while for SFT10 it is evaluated to occur between 700 and 750 °C. We attribute the observations to a balance between thermodynamics and kinetics of the carbonation reaction. With lowering the temperature, the affinity (defined as the negative of the molar reaction Gibbs energy, $\Delta_r G$) of the carbonation reaction increases²², and hence the rate of reaction. However, at too low temperatures the kinetics of the reaction becomes sluggish, which ultimately leads to a maximum carbonation rate at a specific temperature. It is to be noted that other parameters such as composition, particle size, oxygen nonstoichiometry, gas flow rates etc. in addition may impact the rate of the carbonation reaction.

Figure 6.3. Comparison of TGA and TPD data for (a) SFT10 and (b) SFA10 after isothermal carbonation in 25% CO₂ in Ar at different temperatures (T_c). Shown are the normalized data for both compositions from Figs. 1 and 2, respectively. The full lines serve as a guide to the eye.

With the decrease of the CO₂ pre-treatment temperature from 750, 700, 650 to 600 °C, T_o of partially carbonated SFA10 shifted to 611, 563, 519 to 480 °C, respectively. The corresponding T_o values for partially carbonated SFT10 are 712, 558, 528 and 445 °C,

respectively. Similar observations were made for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) after a pre-treatment in 1% CO_2 in He for 2 h at various temperatures, and was explained by the authors in terms of a decreasing bond strength of CO_2 with decreasing temperature ²⁹. We attribute the observed lowering of T_0 with the temperature of carbonation to the decreasing thermodynamic activity of SrO (a_{SrO}) in the partially carbonated, i.e., decomposed, perovskite phases. Although such a trend can be inferred from stability diagrams of related alkali-earth perovskites ³⁰, we have chosen to validate this hypothesis by the measurement of onset temperatures of SrCO_3 decomposition mixed with powder of either $\text{Sr}_4\text{Fe}_6\text{O}_{13}$, $\text{SrFe}_{12}\text{O}_{19}$ or Fe_2O_3 . These investigations are presented in the next section.

As mentioned above, an effective way to enhance the CO_2 resistance is by partial substitution of the B-site cations with more acidic ions. Figure 6.4 shows the CO_2 uptake at 700°C as a function of the duration of exposure (25% CO_2 in Ar) for $\text{SrFe}_{1-x}\text{Ti}_x\text{O}_{3-\delta}$, confirming that enhanced stability towards CO_2 is obtained by increasing the partial substitution of Fe with Ti.

Figure 6.2. CO_2 uptake as a function of time for $\text{SrFe}_{1-x}\text{Ti}_x\text{O}_{3-\delta}$ ($x=0.1, 0.2$, and 0.5) in 25% CO_2 in Ar at 700°C as measured by TGA.

6.3.2. Thermal decomposition of SrCO_3 in mixtures with different strontium-oxide ferrites

TGA experiments were performed on powder mixtures of strontium carbonate and different ferrites in the binary oxide system $\text{SrO-Fe}_2\text{O}_3$ to investigate the influence of a_{SrO} in the ferrite oxide on the onset temperature of decomposition of SrCO_3 . Several intermediate phases with different structures are known to occur in the $\text{SrO-Fe}_2\text{O}_3$ system, which can be represented as $(1-x) \text{SrO} + \text{FeO}_{1.5} = \text{Sr}_{1-x}\text{FeO}_{2.5-x}$. In the range $0 \leq x \leq 1$, these are $\text{Sr}_2\text{Fe}_2\text{O}_5$ ($x = 0$; space group $Ibm2$ ³¹), $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ ($x = 1/3$; space group $Icc2_1$ ³¹), SrFe_2O_4 ($x = 1/2$; space group $Pnam$ ³²), $\text{SrFe}_{12}\text{O}_{19}$ ($x = 11/12$; space group $P6_3/mmc$ ³¹), and Fe_2O_3 ($x = 0$; space group $R3c$ ³¹), which includes the end members. To avoid oxidation of the oxidation state +3 for iron to +4, the TGA experiments were conducted in an inert ('oxygen-free') atmosphere so that iron remains in its 3+ oxidation state over the entire range in temperature. For example, when the Sr/Fe ratio is unity, oxidation of orthorhombic brownmillerite $\text{Sr}_2\text{Fe}_2\text{O}_5$ may lead to formation of the oxygen-deficient cubic perovskite phase $\text{SrFeO}_{3-\delta}$ ³¹.

Thermodynamics

The thermal decomposition of SrCO_3 is represented by

The free Gibbs energy change for the reaction can be written as

$$\Delta G_r(T, p\text{CO}_2) = \Delta G_r^0(T) + RT \ln(p\text{CO}_2) \quad (6.2)$$

Decomposition occurs when $\Delta G_r(T, p\text{CO}_2) < 0 \text{ kJ mol}^{-1}$, while the onset temperature, T_o , at given $p\text{CO}_2$, can be calculated from

$$\Delta G_r^0(T_o) = -RT_o \ln(p\text{CO}_2) \quad (6.3)$$

noting that the activity for pure solids such as SrO is unity: $a_{\text{SrO}} = 1$.

For a mixture consisting of SrCO_3 and $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$, the overall reaction can be written as

where $(x - x')$ represents the change in SrO stoichiometry in $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$ per mole of SrCO_3 . Here, we have ignored the change in the oxygen stoichiometry of $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$ by possible exchange of oxygen between the oxide and the gas phase. As mentioned above, this is why we have chosen to conduct the TGA experiments in an ‘oxygen-free’ atmosphere. Reaction (4) can be resolved into

The free Gibbs energy change for the overall reaction reads

$$\Delta G_r(T, p\text{CO}_2) = \Delta G_r^0(T) + RT \ln(p\text{CO}_2) + RT \ln(a_{\text{SrO}}) \quad (6.7)$$

where the term $RT \ln(a_{\text{SrO}})$ refers to the thermodynamic work required to dissolve 1 formula unit of SrO into the host structure $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$ at constant pressure and temperature. By analogy to the above, the onset temperature of thermal decomposition of SrCO_3 in the mixture, at given $p\text{CO}_2$, is calculated from

$$\Delta G_r^{0'}(T_o) = -RT_o \ln(p\text{CO}_2) \quad (6.8)$$

where we have defined $\Delta G_r^{0'}(T) = \Delta G_r^0(T) + RT \ln(a_{\text{SrO}})$. Hence, when $a_{\text{SrO}} < 1$, T_o in the powder mixture is lowered relative to that observed for the pure carbonate. The SrO activity in the double oxide $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$ follows from the apparent change in the standard free Gibbs energy of thermal decomposition of SrCO_3 in the presence of the double oxide: $RT \ln(a_{\text{SrO}}) = \Delta G_r^{0'}(T) - \Delta G_r^0(T)$.

Although not of interest in this study, the host structure may undergo one or more structural transformations upon dissolving SrO in $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$, depending on the

extent of reaction. It is further noted that evolution of CO_2 from the sample by decomposition of SrCO_3 at $T > T_0$ and concomitant increase of the SrO activity in the oxide (which tends to increase the value of T_0) may obscure experimental determination of T_0 . Furthermore, at $T < T_0$, carbonation of the sample at given $p\text{CO}_2$ may occur, lowering the SrO activity in the oxide. Carbonation eventually stops when a_{SrO} reaches a value at which the decomposition pressure equals the ambient partial pressure of CO_2 .

Ellingham diagrams

Figure 6.5 shows normalized mass changes for pure SrCO_3 measured by TGA, and the Ellingham diagram constructed from the observed onset temperatures of thermal decomposition at different values of $p\text{CO}_2$. Also shown in Fig. 6.5b are the standard free Gibbs energies of reaction calculated from data of other studies using TGA³³⁻³⁶, equilibrium pressures measured using manometry^{34,37}, and from thermodynamic databases^{38,39}.

It is to some surprise to see that in Fig. 6.5b significant differences are observed among the results of different studies. In particular, the results from calculations based on the compilation of thermochemical compilation by Barin³⁹ highly underestimate the observed onset temperatures. For comparison, T_0 at $p\text{CO}_2 = 1$ bar ($\Delta G_r^0(T) = 0$ kJ mole⁻¹) on the basis of the data provided by Barin³⁹ is calculated to be 1435 K, which is much lower than 1493 K observed by Shirhat *et al.*³³, 1505 K by Tsuji *et al.*³⁶, 1532 K by Baker³⁵, and the 1548 K by Scholten *et al.*³⁴, where we have limited comparison to values of T_0 extracted from data of TGA experiments. The extrapolated value of T_0 at $p\text{CO}_2 = 1$ bar from this work, 1524 K, is comparatively close to the value observed by 1532 K by Baker *et al.*³⁵. At least, in part, the scatter in the results can be assigned to different heating/cooling in the reported studies, which varied from 2 °C min⁻¹ in the present study and that of Baker *et al.*³⁵ to 20 °C min⁻¹ used in the study of Scholten *et al.*³⁴, and in part, to different definitions of the onset temperature, either the extrapolated onset temperature (recommended by ASTM[®] 40) or the true onset temperature (where the measured values begin to deviate from the base line). The heating rate is preferably as low

Figure 6.5. (a) Normalized mass change by TGA of SrCO_3 in different concentrations of CO_2 (balance Ar) during heating at $2\text{ }^{\circ}\text{C min}^{-1}$, and (b) Ellingham diagram for the thermal decomposition of SrCO_3 in comparison with data from different sources.

as possible. In this study the heating rate was set to $2\text{ }^{\circ}\text{C min}^{-1}$ to avoid that the measurements would become prohibitively time-consuming. As mentioned in the experimental section, the temperature at which the observed mass loss upon heating was 0.1% of the initial mass was taken as the value for T_0 . In the study of Baker *et al.*³⁵, an average was taken between the onset temperatures observed upon heating (decarbonation) and cooling (carbonation), which explains that the observed values for T_0 in this study are slightly higher than those found by Baker *et al.*³⁵. We conclude that the above comparison provides a justification of our experimental approach, but also that the results urge for a re-evaluation of thermodynamic data published for SrCO_3 as noted before by others^{33,34}.

Figure 6.6a shows TGA curves for pure SrCO_3 and mixtures of it with different strontium oxide ferrites recorded in 10% CO_2 (balance Ar), confirming that the onset temperature of SrCO_3 decomposition in the powder mixtures is lowered in the sequence $\text{SrCO}_3 > \{\text{SrCO}_3 + \text{Sr}_4\text{Fe}_6\text{O}_{13}\} > \{\text{SrCO}_3 + \text{SrFe}_{12}\text{O}_{19}\} > \{\text{SrCO}_3 + \text{Fe}_2\text{O}_3\}$. Similar results are obtained at other CO_2 concentrations (see Figs. A6.1–A6.3). Figure 6.6b shows the Ellingham diagrams constructed from the estimated onset temperatures for each of these curves. For the mixture $\{\text{SrCO}_3 + \text{Sr}_4\text{Fe}_6\text{O}_{13}\}$ measured in 90% CO_2 evaluation of T_0 was not possible with high enough accuracy due to carbonation of $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ under the given conditions prior to reaching the onset temperature of thermal decomposition of SrCO_3 in the mixture (Fig. A6.3). Equations for the apparent standard Gibbs free energies of the reactions can be expressed as: $\Delta G_r^0(T) = A + BT$. Values for A (the standard enthalpy of reaction, ΔH_r^0) and B (negative of the standard entropy change of the reaction, ΔS_r^0) are listed in Table 6.1. Estimates for the SrO activities in $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ and $\text{SrFe}_{12}\text{O}_{19}$ obtained from these relationships are listed in Table 6.2, assuming validity of extrapolation of the $\Delta G_r^0(T)$ relationship for pure SrCO_3 to ranges of temperature of the corresponding relationships obtained for the powder mixtures. It is quite clear from this table that the SrO activity in both double oxides is quite low, a feature which reflects their chemical stability.

Figure 6.6 (a) Normalized mass change by TGA of pure SrCO_3 and powder mixtures of SrCO_3 with the indicated oxides in 10% CO_2 (balance Ar) during heating at 2°C min^{-1} , and (b) corresponding Ellingham diagrams for the thermal decomposition of SrCO_3 constructed from these data.

Table 6.1 Standard Gibbs free energy change of SrCO_3 decomposition in pure SrCO_3 and in mixtures of SrCO_3 and different strontium oxide ferrites: $\Delta G_r^0(T) = A + BT$.

	A	B	Range
	[kJ mol ⁻¹]	[kJ mol ⁻¹ K ⁻¹]	[K]
SrCO_3	236.2	-0.1542	1216-1584
$\{\text{SrCO}_3 + \text{Sr}_4\text{Fe}_6\text{O}_{13}\}$	277.4	-0.2265	1023-1260
$\{\text{SrCO}_3 + \text{SrFe}_{12}\text{O}_{19}\}$	244.6	-0.2134	943-1184
$\{\text{SrCO}_3 + \text{Fe}_2\text{O}_3\}$	224.6	-0.2012	907-1160

Table 6.2 Activities of SrO in $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ and $\text{SrFe}_{12}\text{O}_{19}$.

T	a_{SrO} in $\text{Sr}_4\text{Fe}_6\text{O}_{13}$	a_{SrO} in $\text{SrFe}_{12}\text{O}_{19}$
[K]	[-]	[-]
1000	2.36×10^{-2}	2.22×10^{-3}
1050	4.51×10^{-2}	5.12×10^{-3}
1100	8.12×10^{-2}	1.09×10^{-2}
1150	1.59×10^{-1}	2.19×10^{-2}
1200	2.27×10^{-1}	4.12×10^{-2}

The value of a_{SrO} is determined by the stabilization energy of the double oxide (enthalpy of formation from the constituent oxides) and temperature. Following Yokokawa *et al.*²², the stabilization energy of $\text{Sr}_{1-x}\text{FeO}_{2.5-x}$ may be defined as

$$\delta(\text{Sr}_{1-x}\text{FeO}_{2.5-x}) = \Delta G_f(\text{Sr}_{1-x}\text{FeO}_{2.5-x}) - \{(1-x)\Delta G_f(\text{SrO}) + x\Delta G_f(\text{FeO}_{1.5})\} \quad (6.9)$$

where the ΔG_f 's are the Gibbs free enthalpies of formation of the corresponding oxides. The value of a_{SrO} will be smaller with higher stabilization energy. Even within the co-existence region of the double oxide phase, the value of a_{SrO} may vary in a range depending on the co-existing phases. It is further noted that also the oxygen potential will affect the apparent SrO activity. As discussed by Yokokawa *et al.*²² for perovskite oxides

$(\text{La,Sr})\text{MnO}_3$, $(\text{La,Sr})\text{CoO}_3$ and $(\text{La,Sr})\text{FeO}_3$, in these cases the valence stability of the transition metal ion will influence the apparent value of a_{SrO} .

The Ellingham diagram shown in Fig. 6.6b suggests that, at any given $p\text{CO}_2$, thermal decomposition of SrCO_3 (decarbonation) occurs when $T > T_0$, but that carbonation occurs when $T < T_0$. As mentioned above, only for the mixture $\{\text{SrCO}_3 + \text{Sr}_4\text{Fe}_6\text{O}_{13}\}$ exposed to 90% CO_2 in Ar carbonation of the double oxide was traced prior to reaching the onset temperature of decomposition of SrCO_3 in the powder mixture (Fig. A6.3). This observation suggests that, contrary to the rate of decarbonation, the kinetics of carbonation are in general poor, especially at low SrO activity in the ferrite oxide and at low values of $p\text{CO}_2$. Rather than the long-term exposure to a CO_2 -containing atmosphere at a given temperature, the present method, i.e. measurement of the onset temperature of SrCO_3 decomposition in a powder mixture with the SrO-containing double oxide, represents a fast and reliable route to establish the stability limits of the double oxide under investigation. It is anticipated that the method can be extended to other earth alkaline-containing double oxides and related oxides, such as the perovskite-type oxides proposed for use as OTM membrane. At the time of writing this thesis, such measurements are in progress.

6.4 Concluding remarks

In this study, we have investigated the carbonation characteristics of SFA10 and SFT10 by combined TGA and TPD measurements. At the specific conditions of partial pressures of CO_2 , temperature and duration of the CO_2 treatment (25% CO_2 in Ar, 600–850 °C, 15 h) carbonation of both oxides is found to occur, albeit that that SF10 is found way more resistant to carbonation (as reflected by the much higher weight increase) than SFA10. The latter is explained by the higher acidity of Ti^{4+} compared to Al^{3+} . While STF10 and STF20 are subject to carbonation, STF50 appears to be resistant to carbonation on ageing in 25% CO_2 at 700 °C.

SFA10 and SFT10 both exhibit a maximum CO₂ uptake around 700–750 °C, which is accounted for by a balance between thermodynamics and kinetics of the carbonation reaction. The TPD experiments further reveal a correlation between the onset temperature of decarbonation and the temperature maintained during the carbonation pre-treatment. Thermal analyses of powder mixtures of SrCO₃ and double oxides in the SrO-Fe₂O₃ system, *i.e.*, measurement of the onset temperature of thermal decomposition ('decarbonation') of SrCO₃ in these mixtures, substantiate the conclusion that the different onset temperatures observed for decarbonation of the partially carbonated phases are related to the SrO activity in the latter. Analysis permits evaluation of the strontium oxide activity in the double oxides. It is anticipated that this approach can be extended to establish the stability limits of other Sr- and earth-alkaline containing materials.

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References

1. Bhavani, A. G.; Kim, W. Y.; Lee, J. S., *Barium Substituted Lanthanum Manganite Perovskite for CO₂ Reforming of Methane*. ACS Catal., 2013, 3 (7), pp. 1537–1544.
2. Shi, R.; Waterhouse, G. I. N.; Zhang, T., *Recent Progress in Photocatalytic CO₂ Reduction Over Perovskite Oxides*. Solar RRL, 2017, 1 (11), pp. 1700126.
3. Zhu, J.; Li, H.; Zhong, L.; Xiao, P.; Xu, X.; Yang, X.; Zhao, Z.; Li, J., *Perovskite Oxides: Preparation, Characterizations, and Applications in Heterogeneous Catalysis*. ACS Catal., 2014, 4 (9), pp. 2917–2940.
4. Dunstan, M. T.; Liu, W.; Pavan, A. F.; Kimpton, J. A.; Ling, C. D.; Scott, S. A.; Dennis, J. S.; Grey, C. P., *Reversible CO₂ absorption by the 6H Perovskite Ba₄Sb₂O₉*. Chem. Mater., 2013, 25 (24), pp. 4881–4891.
5. Medvedev, D.; Lyagaeva, J.; Plaksin, S.; Demin, A.; Tsiakaras, P.; *Sulfur and carbon tolerance of BaCeO₃–BaZrO₃ proton-conducting materials*. J. Power Sources, 2015, 273, pp. 716–723.

6. Luo, H.; Efimov, K.; Jiang, H.; Feldhoff, A.; Wang, H.; Caro, J.; *CO₂-stable and cobalt-free dual-phase membrane for oxygen separation*. Angew. Chem. Int. Ed. 2011, 50(3), pp. 759-763.
7. Yan, A.; Cheng, M.; Dong, Y.; Yang, W.; Maragou, V.; Song, S.; Tsiakaras, P., *Investigation of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} based cathode IT-SOFC: I. The effect of CO₂ on the cell performance*. Appl. Catal. B, 2006, 66 (1), 64-71.
8. Arnold, M.; Wang, H.; Feldhoff, A., *Influence of CO₂ on the oxygen permeation performance and the microstructure of perovskite-type (Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-δ} membranes*. J. Memb. Sci., 2007, 293 (1-2), pp. 44-52.
9. Athayde, D. D.; Souza, D. F.; Silva, A. M. A.; Vasconcelos, D.; Nunes, E. H. M.; Motuzas, J.; Diniz da Costa, J. C.; Vasconcelos, W. L., *Carbonation passivation layer of scandium loaded BSCF perovskite*. Ceram. Int., 2017, 43 (17), pp. 15179-15184.
10. Arulmozhi, N.; Kan, W. H.; Thangadurai, V.; Karan, K., *Kinetics and thermodynamics of carbonation of a promising SOFC cathode material La_{0.5}Ba_{0.5}CoO_{3-δ} (LBC)*. J. Mater. Chem. A, 2013, 1 (47), pp. 15117-15127.
11. Zeng, Q.; Zuo, Y.-b.; Fan, C.-g.; Chen, C.-s., *CO₂-tolerant oxygen separation membranes targeting CO₂ capture application*. J. Memb. Sci., 2009, 335 (1), pp. 140-144.
12. Chen, W.; Chen, C. S.; Winnubst, L., *Ta-doped SrCo_{0.8}Fe_{0.2}O_{3-δ} membranes: Phase stability and oxygen permeation in CO₂ atmosphere*. Solid State Ionics, 2011, 196 (1), pp. 30-33.
13. Park, J.H.; Kim, J.P.; Son, S.H.; *Oxygen permeation and stability of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membrane according to trace elements and oxygen partial pressure in synthetic air*. Energy Proc., 2009, 1, pp. 369-374.
14. Czuprat, O.; Arnold, M.; Schirrmeister, S.; Schiestel, T.; Caro, J., *Influence of CO₂ on the oxygen permeation performance of perovskite-type BaCo_xFe_yZr_zO_{3-δ} hollow fiber membranes*. J. Memb. Sci., 2010, 364 (1), pp. 132-137.
15. Yi, J.; Schroeder, M., *High temperature degradation of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membranes in atmospheres containing concentrated carbon dioxide*. J. Memb. Sci., 2011, 378 (1-2), pp. 163-170.
16. Yi, J.; Weirich, T. E.; Schroeder, M., *CO₂ corrosion and recovery of perovskite-type BaCo_{1-x-y}Fe_xNb_yO_{3-δ} membranes*. J. Memb. Sci., 2013, 437, pp. 49-56.
17. Partovi, K.; Bittner, M.; Caro, J., *Novel CO₂-tolerant Al-containing membranes for high-temperature oxygen separation*. J. Mater. Chem. A, 2015, 3 (47), pp. 24008-24015.
18. Zhou, J.; Tang, X.; Wu, C.; Wang, H.; Zhang, Y.; Ding, W.; Jin, Y.; Sun, C., *A study on the degradation and recovery mechanisms of perovskite Ba_{1.0}Co_{0.7}Fe_{0.2}Nb_{0.1}O_{3-δ} membrane under CO₂-containing atmosphere*. J. Phys. Chem. C, 2015, 119 (43), pp. 24229-24237.

19. Klande, T.; Ravkina, O.; Feldhoff, A., *Effect of A-site lanthanum doping on the CO₂ tolerance of SrCo_{0.8}Fe_{0.2}O_{3-δ} oxygen-transporting membranes*. J. Memb. Sci., 2013, 437, pp. 122-130.
20. Liang, F.; Jiang, H.; Luo, H.; Caro, J.; Feldhoff, A., *Phase stability and permeation behavior of a dead-end Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} tube membrane in high-purity oxygen production*. Chem. Mater., 2011, 23(21), pp. 4765-4772.
21. Yi, J.; Feng, S.; Zuo, Y.; Liu, W.; Chen, C.S., *Oxygen permeability of Sr_{0.95}Co_{0.8}Fe_{0.2}O_{3-δ} in CO₂- and H₂O-containing atmosphere*. Chem. Mater., 2005, 17(23), pp. 5856-5861.
22. Yokokawa, H.; Sakai, N.; Kawada, T.; Dokiya, M., *Thermodynamic stabilities of perovskite oxides for electrodes and other electrochemical materials*. Solid State Ionics, 1992, 52 (1), pp. 43-56.
23. Yokokawa, H.; Sakai, N.; Horita, T.; Yamaji, K.; Brito, M. E.; Kishimoto, H., *Thermodynamic and kinetic considerations on degradations in solid oxide fuel cell cathodes*. J. Alloys Compd. 2008, 452 (1), pp. 41-47.
24. Brandão, A.; Monteiro, J. F.; Kovalevsky, A. V.; Fagg, D. P.; Kharton, V. V.; Frade, J. R., *Guidelines for improving resistance to CO₂ of materials for solid state electrochemical systems*. Solid State Ionics, 2011, 192 (1), pp. 16-20.
25. Zhang, C.; Sunarso, J.; Liu, S., *Designing CO₂-resistant oxygen-selective mixed ionic-electronic conducting membranes: guidelines, recent advances, and forward directions*. Chem. Soc. Rev., 2017, 46(10), pp. 2941-3005.
26. Cowin, P. I.; Lan, R.; Petit, C. T. G.; Tao, S., *Conductivity and redox stability of perovskite oxide SrFe_{1-x}Ti_xO_{3-δ} (x ≤ 0.3)*. Solid State Sciences, 2015, 46, pp. 62-70.
27. Yang, G.; Su, C.; Chen, Y.; Dong, F.; Tade, M. O.; Shao, Z., *Cobalt-free SrFe_{0.9}Ti_{0.1}O_{3-δ} as a high-performance electrode material for oxygen reduction reaction on doped ceria electrolyte with favorable CO₂ tolerance*. J. Eur. Ceram. Soc., 2015, 35 (9), pp. 2531-2539.
28. Schulze-Küppers, F.; ten Donkelaar, S.F.P.; Baumann, S.; Prigorodov, P.; Sohn, Y.J.; Bouwmeester, H.J.M.; Meulenbergh, W.A.; Guillon, O., *Structural and functional properties of SrTi_{1-x}Fe_xO_{3-δ} (0 ≤ x ≤ 1) for the use as oxygen transport membrane*. Sep. Purif. Tech., 2015, 147, pp. 414-421.
29. Yan, A.; Liu, B.; Dong, Y.; Tian, Z.; Wang, D.; Cheng, M., *A temperature programmed desorption investigation on the interaction of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} perovskite oxides with CO₂ in the absence and presence of H₂O and O₂*. Appl. Catal., 2008, 80, pp. 24-31.
30. Klande, T.; Efimov, K.; Cusenza, S.; Becker, K.-D.; Feldhoff, A., *Effect of doping, microstructure, and CO₂ on La₂NiO_{4+δ}-based oxygen-transporting materials*. J. Solid State Chem., 2011, 184(12), pp. 3310-3318.

31. Gallagher P.K.; Sander, P.; Woodward, P.M.; Lokuheva I.N., *Reactions within the system, 2SrCO₃-Fe₂O₃*. J. Therm. Anal. Calor., 2005, 80, pp. 217–223.
32. Beretka, J.; Brown, T. *Studies on the reaction between strontium carbonate and iron(III) oxide*. Aust. J. Chem. 1971, 24 (2), pp. 237–242.
33. Shirsat, A.N.; Kaimal, K.N.G.; Bharadwaj, S.R.; Das, D., *Thermodynamic stability of SrCeO₃*. J. Sol. State Chem., 2004, 177, pp. 2007–2013.
34. Scholten, M.J.; Schoonman, J.; van Miltenburg, J.C., Oonk, H.A.J.; *Synthesis of strontium and barium cerate and their reaction with carbon dioxide*. Solid State Ionics, 1993, 61, pp. 83–91.
35. Baker, E.H., *The strontium oxide-carbon dioxide system in the pressure range 0.3–400 atmospheres*. J. Chem. Soc., 1963, pp. 339–3
36. Tsuji, T.; Kurono, H.; Yamamura, Y., *Formation reaction and thermodynamic properties of SrCe_{1-y}Eu_yO_{3-x}*. Solid State Ionics, 2000, 136–137, pp. 313–317.
37. Lander, J.J., *Experimental heat contents of SrO, BaO, CaO, BaCO₃ and SrCO₃ at high temperatures. Dissociation pressures of BaCO₃ and SrCO₃*. J. Am. Chem. Soc., 1951, 73 (12), pp. 5794–5797.
38. L'vov, B.; Ugolkov, V.L.; *Peculiarities of CaCO₃, SrCO₃ and BaCO₃ decomposition in CO₂ as a proof of their primary dissociative evaporation*. Thermochim. Acta, 2004, 410, pp. 47–55.
39. Barin, I.; *Thermochemical data of pure substances*. John Wiley and Sons Ltd, Third Ed., 2008. ISBN 9783527287451.
40. Zhao, J.-C., *Methods for phase diagram determination*. First edition, Elsevier Science, 2011, ISBN 9780080549965, p. 168.

Appendix A6

Figure A6.1. Normalized mass change by TGA of pure SrCO_3 and powder mixtures of SrCO_3 with the indicated oxides in 2% CO_2 (balance Ar) during heating at $2^{\circ}\text{C min}^{-1}$.

Figure A6.2. Normalized mass change by TGA of pure SrCO_3 and powder mixtures of SrCO_3 with the indicated oxides in 25% CO_2 (balance Ar) during heating at 2°C min^{-1} .

Figure A6.3. Normalized mass change by TGA of pure SrCO_3 and powder mixtures of SrCO_3 with the indicated oxides in 90% CO_2 (balance Ar) during heating at $2^{\circ}\text{C min}^{-1}$. Note that for the mixture $\{\text{SrCO}_3 + \text{Sr}_4\text{Fe}_6\text{O}_{13}\}$ carbonation of $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ occurs, prior to decomposition of SrCO_3 .

CHAPTER 7

Evaluation of power plant process designs with integrated Oxygen Transport Membranes

Abstract

In this chapter, we aim to find the most efficient and economically attractive way to use oxygen transport membranes (OTMs) for the supply of oxygen to combined cycle power plants. Using Aspen Plus, process simulations of integrated gasification combined cycle (IGCC) plants with pre-combustion or oxyfuel carbon capture technology, pre-combustion integrated reforming combined cycle (IRCC), and oxyfuel combustion natural gas combined cycle (NGCC) power plants are assessed. The oxyfuel NGCC power plant with OTM-based oxygen production shows the highest net efficiency (38.8%_{HHV}) among the simulated processes. At a CO₂ avoidance rate of 83.4%, the lowest LCOE of \$177 per MWh is calculated for the pre-combustion IRCC process. This is 26% lower than the LCOE of the oxyfuel IGCC, which is the most expensive process at \$239 per MWh. The specific pure oxygen demand (sPOD, the pure oxygen mass required to produce a unit of energy) differs by more than a factor 3 between the pre-combustion IRCC and oxyfuel IGCC process. The sPOD is a good predictor for the LCOE, hence minimization of the sPOD should be an important part of the design of power plants with integrated OTMs.

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7.1 Introduction

Carbon capture in fossil-fueled power plants and subsequent storage or utilization cover a range of processes that prevent CO₂ emission into the atmosphere. In these processes, CO₂ is produced by combustion of a fossil fuel feedstock, separated before emission, and used as a resource in other chemical processes (CCU, Carbon Capture and Utilization), stored underground (CCS, Carbon Capture and Storage), or both (CCUS, Carbon Capture, Utilization, and Storage). Although the idea of carbon capture in power generation units already exists for more than 25 years ¹, currently only three commercial scale power generation facilities perform carbon capture ².

Several reasons for the slow development of carbon capture can be indicated. First, implementing a carbon capture process into a power plant will lead to a higher energy price, because part of the thermal energy is required to power the carbon capture process. This causes electricity from fossil fuel based power plants with carbon capture to come with relatively high operational costs when compared to nuclear or wind power ³. When compared to power from coal-fired power plants that pay for a CO₂ emission allowance, costs of power generation with carbon capture can be considerably higher. This is true if the allowance price (mean value in the period 2013–2017 equals €6.98 ton⁻¹_{CO₂}) is lower than the CO₂ avoidance cost (typically €20 – €80 ton⁻¹_{CO₂} ^{4,5}, depending on assumptions and reference values) plus costs associated with transport of produced CO₂. As noted in literature, this is indeed the case for mature technologies, and likely as well for technologies under development ⁶. Second, carbon capture technology has not been proven in industrial-scale power plants before 2014. As the technology is not fully matured, the risk for cost overrun is still high. This is demonstrated in the Kemper County Energy Facility carbon capture project in the USA ^{7,8}. In this project, the final costs rose to more than twice the estimated costs, before finally deciding to change the fuel from coal to natural gas and to abandon carbon capture. Last, although various small-scale projects have shown and still continue to show that CO₂ can be stored underground reliably ^{9,10}, the long-term liability for stored CO₂ could be an unwanted risk for both

companies and governments. Moreover, before such a CO₂ storage project could start, a number of regulatory issues have to be dealt with and permits have to be obtained ¹¹. The CCS demonstration project in Barendrecht, Netherlands, has shown that the largely negative public opinion on underground CO₂ storage could limit the issuing of permits and contribute to canceling the project ¹².

Power plants that perform CCS or CCU on a commercial scale currently use post-combustion technology ¹³⁻¹⁵. Plans to build oxyfuel, pre-combustion, and post-combustion based CCS or CCU facilities exist ¹⁵, indicating that all three techniques are considered as viable options for scaling up. Factors such as fuel source and price, electricity price, plant location, plant size, plant manufacturer, and CO₂ capture or CO₂ avoidance target may all influence which technology is selected.

Oxyfuel combustion processes always require the supply of (almost pure) oxygen, as the name suggests, and most pre-combustion processes require oxygen as well. The most common process to produce oxygen for large-scale coal-fired power plants is cryogenic distillation ¹⁶. Since large quantities of gases have to be liquefied at temperatures well below the environmental temperature, the process is energy-intensive (160 – 240 kWh per ton of oxygen with 75 – 99% purity ¹⁷) and therefore expensive. As an alternative, Oxygen Transport Membranes (OTMs) could be used: a technology that is generally considered to be less energy-intensive than cryogenic distillation ¹⁶⁻¹⁹. To the best of the authors' knowledge, no commercial-scale electrical power generation process with carbon capture based on OTMs has started to operate yet. Praxair filed several patents on this topic in the last few years ²⁰⁻²², one of the few signs that companies consider the commercial operation of OTM-based oxygen production.

In this paper, we focus on Integrated Gasification Combined Cycle (IGCC), Integrated Reforming Combined Cycle (IRCC), and Natural Gas Combined Cycle (NGCC) power plants, because of their high net efficiencies as compared to supercritical or ultrasupercritical pulverized coal power plants ²³⁻²⁵. We first optimize process schemes to evaluate the plant efficiency, defined as the net amount of produced electricity divided

by the energy content of the fuel. Then, levelized cost of electricity (LCOE) and cost of CO₂ captured and avoided among these power plants fitted with OTMs. The unabated coal-fired IGCC plant in Puertollano, Spain, with an installed gross power output of 335 MW²⁶, is taken as the reference case. We discuss an oxyfuel IGCC process, pre-combustion IGCC processes with cryogenic distillation (abbreviated to ASU (Air Separation Unit) in tables and figures) and OTMs as oxygen supply technologies, as well as a pre-combustion IRCC and oxyfuel NGCC design. Assumptions for process conditions, energetic losses, and costs are generalized as much as possible for all assessed combinations of technologies to enable a comparison between layouts. This paper aims to assess whether or not it would be advantageous to implement OTM technology into various types of power plants in terms of efficiency and costs.

7.2 General process design

7.2.1. Goals and restrictions

All processes are individually tuned to maximize efficiency and minimize the electricity price, both in terms of used pieces of equipment and in terms of temperatures, pressures, and mass flows of streams. As the raw material prices are fixed at equal values, the main factors that distinguish the LCOE of the different processes are the Capital Expenditures (CapEx) and the energy efficiency. The influence of the Operating Expenditures (OpEx) is less strong, as many factors are equal for all process designs, and factors that differ are typically calculated as a percentage of the CapEx.

Furthermore, a few design restrictions were applied. The 335 MW coal-fired IGCC power plant in Puertollano, Spain²⁶, serves as the reference plant for designing processes. Since this plant started to operate in 1997 and combined cycle technology has strongly advanced since, some pieces of equipment are not the state-of-the-art. This is especially true for the gas turbine, of which the operating temperature is limited to

Figure 1. Simplified process scheme of the IGCC power plant in Puertollano. Line colors indicate the main constituents of the streams: O₂ in purple, N₂ in green, steam in blue, syngas in red, CO₂ in orange, and the rest in black. Electrical power is produced in the yellow-marked gas turbine and steam turbines.

1125 °C. Furthermore, the stringent impurity levels for CCS processes are taken into account for the produced CO₂²⁷, equipment is based exclusively on mature technology (apart from the OTM and the oxyfuel combustion technology), and the goal for the amount of CO₂ avoided per unit of produced energy is set to > 70% as compared to the reference plant. Design choices and differences therein among the processes are discussed in detail.

7.2.2. Reference plant design

ELCOGAS is the former operator of the Puertollano IGCC power plant and was a partner in the EU-funded GREEN-CC project. In this role, the company provided data on the plant layout, fuel composition and price, flue gas composition, and CapEx of plant sections, which serve as a basis for this study. Some of these data can be found in the literature²⁶, others have been obtained through personal correspondence. In literature, simulations of similar processes have been described²⁸⁻³⁰, sometimes also covering the Puertollano IGCC power plant^{29,30}.

Figure 7.1 shows a simplified process scheme of the Puertollano IGCC power plant. It resembles the standard scheme of an oxyfuel combustion IGCC power plant. In the gasifier, pulverized coal is converted into syngas using oxygen with a purity of $85\% \pm 5\%$. Oxygen is produced by a cryogenic distillation process, which is often referred to as an Air Separation Unit (ASU). Heat produced by the exothermic gasification reactions is used to produce steam in high and medium pressure boilers (HP and MP). The syngas is purified and combusted in the gas turbine. Heat produced by this combustion is converted into steam in the heat recovery steam generator (HRSG). Together with the steam from the HP and the MP boiler, it is used to drive a steam turbine. Nitrogen produced by cryogenic distillation is used both to transport coal into the gasifier, and to control the temperature in the gas turbine. A detailed process flow diagram of the plant as simulated in this study is presented in the supporting information (Fig. A7.2), together with tables indicating the temperature, pressure, mass flow rate, mass vapor fraction, and composition of each of the streams. Similar information is also given for the other process designs.

7.2.3. Composition of coal and natural gas

The simulated power plants are fed with 29 kg s^{-1} of a low-grade coal and petroleum coke (pet-coke) mixture with a mass ratio varying around 1:1. The results of the proximate and ultimate analyses of the Puertollano fuel mixture are shown in Table 7.1 for a given point in time. The results are close to those of the mixture used in the Puertollano plant as specified in literature²⁶. Slight differences observed between the literature data and the data used here are ascribed to differences in the coal and pet-coke compositions and differences in the mass ratio between the two types of fuel. Calculations of the LHV and HHV are shown in the supplementary information (A7.1).

Table 7.1. As-received fuel composition and heating values of the pet-coke/coal mixture and of methane.

Component	Unit	Coal/pet-coke mixture	Methane
Moisture	[wt%]	9.40	
Ash	[wt%]	22.85	
Carbon	[wt%]	65.35	74.87
Hydrogen	[wt%]	3.09	25.13
Nitrogen	[wt%]	1.50	
Oxygen	[wt%]	3.66	
Sulfur	[wt%]	3.54	
LHV	[MJ kg ⁻¹]	25.07	50.12
HHV	[MJ kg ⁻¹]	26.94	55.52

With the given fuel flow rate and a Lower Heating Value (LHV) of the mixture of 25.07 MJ kg⁻¹, the plant has a total energy input of 700 MW_{LHV} or 727 MW_{HHV} under full load conditions. Natural gas, used as primary fuel in the IRCC and NGCC plants and as secondary fuel to pre-heat the OTM feed in the oxyfuel and pre-combustion IGCC plants, is assumed to consist of pure methane. The HHV of methane is 890.6 kJ mol⁻¹³¹, or 55.52 MJ kg⁻¹ when recalculated into a mass-base value.

7.2.4. CO₂ purity requirements

The minimum purity of the CO₂ product stream used in this study is based on the requirements of CO₂ transport through pipelines, as described in detail by de Visser *et al.*²⁷. An overview of the specifications is also given in Table 7.2.

Table 7.2. Maximum impurity concentrations in CO₂ based on DYNAMIS quality recommendation. Reprinted from Ref. 27, with permission from Elsevier.

Component	Range	Unit
Temperature	≤30	°C
Pressure	110 – 150	bara
Phase	liquid	
CO ₂	>95	vol.%
H ₂ O	<500	ppm
H ₂ S	<200	ppmv
N ₂	<4	vol.%
Ar	<4	vol.%
H ₂	<4	vol.%
O ₂	<100	ppmv
CH ₄	<4	vol.%
SO ₂	<100	ppmv
CO	<0.2	vol.%
NO _x	<100	ppmv

7.2.5. Oxygen supply

Typically, industrial processes that have a large oxygen demand rely on cryogenic distillation³². According to an estimation of Air Products made in 1989, and to results obtained until 1997 from a lab-scale demonstration unit of the same company, OTM technology could enable 30 percent cost saving over conventional air separation technology such as cryogenic distillation or pressure swing adsorption (PSA). In more recent literature, authors often mention that OTMs are more energy-efficient than cryogenic distillation when integrated into coal-fired power plants^{23,28,33-35}; typically an increase of the total plant efficiency of 1-3 percent points (pp) is reported. To compare oxygen supply by cryogenic distillation with supply by OTM technology, the pre-combustion IGCC process is simulated with either of the two options in this study. Designs of the other processes have been limited to OTM-based oxygen supply only.

OTMs in this study have a rectangular flat sheet geometry with variable width and length, identical to the geometry under study within the EC-FP7 GREEN-CC (Graded Membranes for Energy Efficient New Generation Carbon Capture Process) project. Diffusion of oxygen through a 100 μm thick dense separation layer is assumed to be the only resistance for oxygen permeation. The membranes are sealed into a module, which is designed such that counter-current flow conditions are obtained. Previous calculations in literature have shown that the OTMs can be operated more efficiently using a sweep gas (four-end mode) than using vacuum (three-end mode) ^{35,36}. In this study, we therefore use various sweep gases to transport the permeated oxygen from the membrane into the coal gasifier. Multiple trains of modules, here referred to as the assembly, are used in a parallel arrangement to obtain a membrane island sufficiently large to supply all pure oxygen to the simulated power plants.

The membrane material of choice in this study is $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF). LSCF was selected because of its relatively high oxygen flux compared to many other perovskite oxides ³⁷, and higher stability than perovskite oxides with even higher fluxes such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) ³⁸, as well as for the large amount of experimental data on oxygen permeation that is available. The standard OTM operating temperature is in this study fixed at 850 °C: a temperature which was expected to give a good balance in the membrane performance on the one hand, and in the amount of energy required for feed pre-heating on the other hand. Furthermore, the temperature influences the membrane lifetime. More severe chemical instability may be encountered at lower temperatures, as demonstrated in literature for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ ³⁹, while at high temperatures the chance of membrane failure due to creep rupture is higher ⁴⁰. As the conditions vary among processes studied here, a single optimal temperature in terms of membrane failure may not exist.

7.3 Design of processes

The scope of this paper is limited to four process designs, which were defined within the GREEN-CC project as promising candidates for detailed analysis. All cases consider

combined cycle power plants, the differences lay in primary fuel type (coal and pet-coke, or natural gas) and plant design. The following cases are discussed:

- Coal-fired oxyfuel IGCC with oxygen supply by OTMs;
- Coal-fired pre-combustion IGCC with oxygen supply through OTMs or cryogenic distillation;
- Natural gas-fired pre-combustion Integrated Reforming Combined Cycle (IRCC) with oxygen supply by OTMs;
- Oxyfuel combustion Natural Gas Combined Cycle (NGCC) with oxygen supply by OTMs.

In the sections hereafter, the process schemes and design choices are shortly discussed for each of the cases. More details, such as stream data and detailed process flow diagrams are presented in Appendix A7. In contrast to the Puertollano IGCC reference plant, the processes described hereafter perform carbon capture, producing liquid CO₂ at a pressure of 120 bar and complying with the specifications for pipeline transport shown in Table 7.2.

7.3.1. IGCC with pre-combustion carbon capture

Figure 7.2 shows a simplified scheme of the simulated IGCC plant with pre-combustion layout. Like in the reference plant, coal and pet-coke are gasified with oxygen. Exhaust gas leaving the gasifier is quenched with another recycle stream, aiming to solidify sticky or molten particles that may otherwise cause blockages. Oxygen is provided by an OTM operated in the four-end mode, in which the sweep gas could be CO₂, steam, or air. CO₂ is not favorable as membrane sweep gas in a pre-combustion process, since it would push the equilibrium of the water gas shift reaction away from hydrogen.

Air can be used as sweep gas in a pre-combustion process, as the purity of obtained CO₂ and the efficiency of the Selexol-based H₂/CO₂ separation process do not significantly depend on the presence of nitrogen in the syngas. Furthermore, since air contains about 21% of oxygen, the oxygen flux through the OTMs can be lower to obtain

a stream with an equal oxygen mass flow rate as compared to a steam sweep. Therefore, the required membrane area is smaller when using air as sweep gas than when using steam. Due to the rapid increase in pO_2 over the length of a membrane when a steam sweep flow is enriched with permeating oxygen, the counteracting effect of the smaller pO_2 gradient over air-swept membranes on the required membrane area is limited. Sweeping with air thus turned out to be the best option. To compare between cryogenic distillation and OTMs, the same plant is simulated with air-swept OTMs as well as with cryogenic distillation. For the air-swept OTM, the driving force for oxygen permeation is created by using air at an absolute pressure of 10 bar in the feed and 1 bar in the sweep stream.

The $CO:H_2$ ratio of the syngas is shifted in a dual-stage water gas shift reactor to which liquid water is added at 216 °C at an intermediate point in the reactor. Feeding this extra water cools the temperature down to the initial 250 °C. By using a non-conventional $CoMoO_x$ -based catalyst doped with about 10 wt% K_2O , the steam demand for the shift is lowered compared to conventional sour water gas shift processes ⁴¹. This leaves more steam to be used in the steam turbine, thereby increasing the plant efficiency.

Figure 7.2. Simplified process scheme of OTM integration into a pre-combustion IGCC power plant. When supplying oxygen by cryogenic distillation, the OTM is replaced by the ASU. Rather than O_2 -depleted air, nitrogen is produced besides oxygen. In an ASU, no sweep gas would be required.

Complete removal of NO, NO₂, NH₃, HCN, S, SO₂, SO₃, H₂S and COS impurities is done within a section treated as a black box, since studying this separation process was out of the scope of this paper. This section is not taken into account for efficiency or cost calculations. Separation of CO₂ from the clean syngas, which further contains hydrogen and nitrogen, is performed in a subsequent section. A single-step Selexol process, which uses dimethyl ethers made from poly(ethylene glycol) with chain lengths ranging between 3 and 11 repeating units as the absorbing solvent mixture⁴², was selected. In this process, water vapor and CO₂ are selectively absorbed by the solvent and subsequently separated in a flash vessel. In the three-stage CO₂ compression, intercooling and flashing are performed to increase the compression efficiency and to remove remaining water. Carbon monoxide which is not converted to CO₂ in the WGS and hydrogen are led to the gas turbine, in a stream which also contains all nitrogen and about 7% of the CO₂ of the syngas. These gases are burnt with air in the gas turbine; the temperature of the turbine inlet is regulated by using oxygen-depleted air from the OTM and additional compressed air. With cryogenic distillation as oxygen supply, the turbine inlet temperature is regulated with nitrogen and additional air. The heat of the turbine exhaust gas is used to produce steam, and the combined steam flows are expanded in steam turbines.

7.3.2. IGCC with oxyfuel combustion carbon capture

Figure 7.3 shows a simplified scheme of the simulated IGCC plant with oxyfuel carbon capture. In this plant, coal and pet-coke are gasified with oxygen. Oxygen is provided by an OTM operated in the four-end mode, in which the sweep gas could be either CO₂ or steam. Air sweeping is not an option since the presence of large quantities of nitrogen in the flue gas obliges to add a CO₂/N₂ separation to the process. Steam turns out to be the most efficient sweep gas for the oxyfuel combustion IGCC design, mainly due to its availability in the process at the desired pressure. Part of the gas turbine exhaust gas is recycled to control the turbine inlet temperature. Exhaust gas leaving the gasifier is quenched with another recycle stream, aiming to solidify sticky or molten particles that may otherwise cause blockages. The gas is further cooled in two subsequent steam boilers

(HP, MP) to reach a suitable temperature for further purification, which is assumed to be equal as in the pre-combustion process. Clean syngas is burnt with oxygen and the resulting gases are used to drive a turbine. The heat of the turbine outlet gases is used to produce steam in a heat-recovery steam generator (HRSG).

The steam flow at the highest pressure is expanded to medium pressure in a steam turbine, after which it is combined with the rest of the medium pressure steam available from other plant sections. The medium pressure steam is again expanded in a steam turbine, combined with low pressure steam flows, and finally turned into liquid water by a condensing turbine.

The design of the oxyfuel combustion IGCC plant resembles that of Mletzko *et al.*⁴³, the main difference being that the cryogenic distillation based oxygen separation has been replaced by OTM technology in this study.

Figure 7.3. Simplified process scheme of OTM integration into oxyfuel combustion IGCC power plant.

7.3.3. IRCC with pre-combustion carbon capture

Figure 7.4 shows a simplified process scheme of the natural gas-fired pre-combustion IRCC power plant. Autothermal reforming (ATR) was selected as the best option among three processes that can be used to convert natural gas in syngas (with partial oxidation and hydrogen-fired steam-methane reforming as the alternatives), mainly because of its low oxygen consumption. In a pre-treatment step, which is beyond the scope of this paper, sulphur-containing compounds are converted into H_2S and alkanes. Hydrogen sulfide is subsequently taken away from the methane, for example by absorption, and higher alkanes converted into methane by pre-reforming⁴⁴. The desulphurization process is not included in the simulation, and therefore not taken into account when calculating the plant efficiency and LCOE. After desulphurization, the gas is mixed with steam, pre-heated using an external furnace (which is included in the simulation, and taken into account in calculations), and fed into the ATR. Oxygen from the OTM is fed to the ATR as well. Heat from the resulting CO/H_2 stream is exchanged with water to produce steam. In the current design, no additional steam is added in the WGS section to maximize the CO conversion into CO_2 , and therewith to improve the purity of captured CO_2 . The inlet temperatures are set to 300°C for the high temperature

Figure 7.4. Simplified process scheme of OTM integration into natural gas-fired IRCC power plant with pre-combustion layout.

water gas shift reactor and to 200 °C for the low-temperature water gas shift reactor, respectively. Water is condensed by cooling the stream, and the pressure is decreased from 40 bar to 16 bar in an expander to match the gas turbine inlet pressure of the other processes. Carbon dioxide is separated from hydrogen by an absorption-based process such as the Selexol process, equal to CO₂/H₂ separation in the other process designs. Hydrogen and some residual methane and CO are led to the gas turbine, in which they are combusted. The turbine inlet temperature is adjusted to 1125 °C using oxygen-depleted air from the OTM (at 413 °C) and additional compressed fresh air. The heat of the combustion products is used to superheat the saturated steam. In this process, a single pressure (70 bar) steam cycle was chosen, in which the pressure was high enough to supply steam to the ATR. Compared to using the triple-pressure steam cycle of the pre-combustion and oxyfuel IGCC in the IRCC process, the simplicity of the single pressure cycle leads to a lower investment and a marginally lower energy-efficiency.

The furnace used to pre-heat the autothermal reformer feed is not integrated into the rest of the plant. That is, combustion products of this furnace are sent to a stack, with the purpose to keep the CO₂ emission per MWh of produced electricity comparable to that of other assessed processes (see Table 9 for details). By mixing the combustion products of this furnace with the autothermal reformer products, the produced CO₂ would be captured and a zero-emission plant could be designed. This would however require an extra compressor, as the ATR products are at a much higher pressure than the combustion products, and would introduce unwanted N₂ into the stream of ATR products. Another option would be to pre-heat the ATR feed using an oxygen-fired furnace. This may be a good solution to design a zero-emission plant, but it comes with relatively high costs due to the increased pure oxygen demand (POD).

7.3.4. NGCC with oxyfuel carbon capture

Figure 7.5 shows a simplified process scheme of a Natural Gas Combined Cycle (NGCC) power plant as simulated in this study. The gas turbine combustor is fed with natural gas which is cleaned from sulphur in an equal way as in the IRCC process (again, not included in the simulation). CO_2 is used as OTM sweep gas and takes along oxygen to the gas turbine. The heat in the gas turbine outlet stream, mainly consisting of the combustion products CO_2 and H_2O , is used to produce superheated steam in an HRSG. Upon further cooling, H_2O is condensed out from the flue gas in a flash vessel. The resulting CO_2 is split in three fractions: one fraction (6 mol%) is compressed for storage or utilization, a second fraction (3 mol%) is heated to 850°C in a heat exchanger and a furnace, and used as sweep gas for the oxygen transport membrane, and the largest, third fraction is used as an inert gas to limit the gas turbine inlet temperature to the design specification of 1125°C . Like in the pre-combustion IRCC, a single-pressure steam cycle is used and an external furnace is used to pre-heat the OTM feed. Again, flue gases of the external furnace are sent to the stack, and not all CO_2 is captured to minimize differences between the process schemes.

Figure 7.5. Simplified process scheme of OTM integration into NGCC power plant with oxyfuel combustion layout.

The oxyfuel NGCC process described here partly resembles the Allam cycle⁴⁵, since both use CO₂ as the main gas turbine working fluid, and both have a large CO₂ recycle stream. The main difference is that CO₂ in the Allam cycle process remains in a supercritical state, while it is in the gaseous state in the NGCC process described here and shown in Figure 7.5.

7.4 Methods and assumptions

The Puertollano plant was simulated in such a way that the real plant is resembled as closely as possible with the available data. In the reference process simulation, plant sections that are not (much) affected by carbon capture and the incorporation of OTMs have been simplified, including for example the electrical power generation and conversion, the Claus plant, and the flue gas treatment. A similar approach is used for the other process designs.

The net energy efficiency η_{HHV} with which a plant converts fuel into electricity is calculated with Eq. 7.1, in which the input energy E_{in} is based on higher heating value (HHV) of the fuel. The gross amount of produced electricity is given by E_{out} , and the ancillary energy consumption E_a is the amount of energy required to drive plant equipment. Finally, the net energy production E_{net} is equal to the numerator in Eq. 7.1:

$$\eta_{\text{HHV}} = \frac{E_{\text{out}} - E_a}{E_{\text{in}}} \quad (7.1)$$

In analogy to wastewater treatment, the total oxygen demand (TOD) could be defined as the amount of oxygen required in all plant sections together to achieve full oxidation. Full oxidation of methane, along the reaction given by Eq. 7.2, requires 2 mol of oxygen per mol of methane, or 4 kg of oxygen per kg of methane.

For the coal and pet-coke mixture, the amount of oxygen required for full oxidation depends on the exact composition. Nitrogen and ash are assumed to be inert, carbon,

hydrogen, and sulphur are assumed to be fully oxidized, and oxygen present in coal to be used for the oxidation. The stoichiometric oxygen mass required to completely oxidize coal is calculated by

$$\frac{8}{3} * m_C + 8 m_H + m_S - m_O \quad (7.3)$$

with m_C , m_H , m_S , and m_O representing the mass fraction of carbon, hydrogen, sulphur and oxygen in coal expressed in weight percent. In the reference process as well as all pre-combustion processes, excess oxygen (11% - 14 % excess) is present in the gas turbine input gas. Nitrogen for cooling the turbine blades is supplied by air, thus taking in extra oxygen as well. For the oxyfuel processes, cooling is provided by CO_2 , and stoichiometric combustion is assumed. Nevertheless, the concentration of partly oxidized combustion products in the compressed CO_2 and flue gas streams is below 0.1% in all processes, and is therefore of negligible influence on the final energy efficiency of the process designs.

7.4.1. Oxygen permeation model and process equipment & design

First, regarding the oxygen transport membranes and the model used to calculate the oxygen flux through the membranes:

- We do not aim to provide a detailed model for oxygen transport through the OTM; diffusion is the only transport resistance taken into account. The oxygen flux through membranes could in reality also be limited by the surface exchange kinetics, concentration polarization in porous supports, and oxygen diffusion in the feed and sweep gases. Which of these effects leads to the strongest limitation on oxygen permeation depends on the membrane material and microstructure, gas flow rates and flow regimes around the membrane and in the porous support, as well as operating conditions. For a comprehensive overview of these effects, the reader is referred to literature ⁴⁶. The solid state diffusion model used in this study, as well as the input parameters that have been used, are described in A7.3.

- The expected degradation of the oxygen flux over time is taken into account when calculating the required membrane area. The expected flux at the end of the membrane lifetime is described by $J_{O_2, \text{end}} = J_{O_2, \text{init}} * (1 - r_d)^{t/1000}$, with t the amount of accumulated operating hours until membrane replacement and r_d the relative decrease of the oxygen flux over 1000 h. The value of r_d is taken from long-term experiments with SOFCs⁴⁷. The required membrane area to supply enough oxygen to the power plant during the complete membrane service life is then calculated by $A_{\text{adjusted}} = \frac{J_{O_2, \text{end}}}{J_{O_2, \text{init}}} A_{\text{model}}$, with A_{model} the required membrane area as calculated by the OTM model, and A_{adjusted} the membrane area corrected for ageing.

Second, regarding process equipment and design:

- All coal-fired power plants have an equal coal and pet-coke mixture input of 727 MW_{HHV}, as stated in Section 7.2.3. In the oxyfuel as well as the pre-combustion IGCC, the membrane feed is heated using natural gas, the heat input required to reach the feed temperature of 850 °C is not equal. The IRCC and NGCC plants have a natural gas input flow of 0.75 kmol s⁻¹ to the gas turbine, and a secondary natural gas input to the OTM feed furnace. Due to the feed temperature reached by heat exchanging, the heat rate of the secondary furnace and therewith of the whole process varies among the different plants.
- Types of equipment which are under development, but not considered deployable technology, are not included in any of the processes if the design allows that. OTMs and oxyfuel combustion may not be considered to be mature technologies, and are the only non-mature technologies used in the designs here. This choice leaves room for future optimization of the presented designs as soon as more advanced equipment becomes available.
- Heat exchangers are used to pre-heat the OTM feed stream to temperatures between 385 and 790 °C. The chosen heat exchanger feed temperatures are limited by the availability of high temperature process streams. Furthermore, the yield

strength and costs of materials used for heat exchangers are taken into account when choosing these temperatures. Extra heat required to increase the OTM feed temperature to 850 °C is added to the pre-heated feed in a natural gas-fired furnace.

- In the coal-based designs, NO, NO₂, NH₃, HCN, S, SO₂, SO₃, H₂S and COS are separated from the syngas in a single piece of equipment (component splitter) at 235 °C. In practice, this purification process requires several pieces of equipment. Details of the syngas purification are out of the scope of this paper and are not taken into account when calculating the plant efficiency and LCOE. Furthermore, the equipment required for separating H₂ and CO₂ in pre-combustion processes is simulated in a side project of this study, for which the pre-combustion IGCC design was used. The separation process which ranks highest in terms of energy efficiency and cost is a single-step Selexol process (as detailed in Section 3.1), which is implemented as a black box into the main simulation. In the natural gas-based designs, a feed of pure methane is assumed, and therefore no feed gas cleaning is simulated.
- The maximum temperature of superheated steam is set to 550 °C, a value taken directly from the specifications of the Puertollano plant. This temperature could however not be reached in all simulated designs. Furthermore, the gas turbine inlet temperature (TIT) is limited to 1125 °C to comply with the limit of the gas turbine used in Puertollano (Siemens V94.3 class E). Literature shows that the plant efficiency increases strongly with an increasing TIT^{48,49}. It may thus be expected that the plants simulated here reach a lower efficiency than some plants described in literature and plants that are built currently or in the future.
- CO₂ is compressed from 1 to 74 bar in a four-stage integrally geared compressor with inter-stage cooling. Using chilled water, the CO₂ is cooled further to 15 °C, at which it condenses. Finally, a pump is used to compress the liquid CO₂ to a final pressure of 120 bar. Considering that the volume of CO₂ available for sale will

increase with the number of carbon capture projects, and that the number of projects will increase steeply, a selling price of 1/3rd of the lowest 'breakeven cost' for capturing CO₂ (\$9 t⁻¹ for Coal-to-Liquids and Gas-to-Liquids processes ⁵⁰) is assumed. The revenue per ton of produced CO₂ is thus assumed to be less than half the cost to emit the same amount of CO₂.

- The Soave-Redlich-Kwong equation of state was applied as thermodynamic model for the steam cycle in the simulations, and the Peng–Robinson equation of state was used elsewhere.
- During periods in which an OTM-based process is not operated, it may be beneficial to maintain the OTM temperature at its normal working temperature. This would decrease the risk for failure due to heat gradient induced stress experienced during heating or cooling of membranes. Furthermore, maintaining a constant temperature could help to decrease the startup time of an OTM-based process. For a further study it would be useful to evaluate whether an additional ASU for use during plant startup would be economically attractive. In that case, oxygen production and carbon capture may start after the gasification and gas turbine are brought up to speed with the ASU.
- The operating capacity factor, defined as the ratio between productive hours divided by total number of hours in a time period, is taken as 85% (7446 productive hours per year) for estimating costs of coal-fired plants, a number based on the estimation of maximum availability of a new IGCC plant based on the Puertollano design ^{26,51}. For gas-fired plants, the operating capacity factor was set to 90%. Their higher capacity factor is justified by not having to handle solids, which causes many of the availability issues in an IGCC ⁵¹.

7.4.2. Economic evaluation

The LCOE is calculated by means of a net present value (NPV) analysis based on a method described in literature ⁵². The LCOE is the parameter for which the set of equations in the NPV analysis, described in detail in Appendix A7, is solved. This is done such that the NPV after 20 years of production equals zero, represented mathematically by

$$\text{NPV}_{20}(\text{LCOE}) = 0 \quad (7.4)$$

To compare the LCOE for the studied designs, assumptions for variables required in the calculation have been standardized as much as possible. Table 7.3 gives an overview of some of the most crucial values, together with a short description of the information source and if available the literature reference. The reference year 2014 is used for all capital expenditures calculations in this study if no other year is specifically noted. Based on the results of plant design simulations, the size of each piece of equipment was assessed. For common types of equipment, the purchase cost was calculated from cost correlations based on sizing variables obtained from literature ⁵³. Hand factors were used to calculate the installed cost ⁵³. For more complex equipment, for example the gasifier, reformer, and gas turbine, purchase price values were estimated by experts in personal correspondence. Location factors were not accounted for, whereas inflation was taken into account by correcting the CapEx with the Chemical Engineering Plant Cost Index (CEPCI) ⁵⁴, and using that as a basis for most other cost calculations. Values used for sizing variables, Hand factors, and the CEPCI are specified in A7.4. The total depreciable cost (TDC) consists of the total installed cost of equipment inside battery limits (ISBL) and surcharges for

- Modification outside the plant infrastructure (OSBL = 20% of ISBL);
- Engineering, procurement and construction (10% of the sum of ISBL and OSBL);
- and Contingency charges (10% of the sum of ISBL and OSBL).

Raw material expenditures are based on energy input and prices of materials stated in Table 7.3. Cost estimations for operations, maintenance, overhead, and taxes, are based on multiplication factors obtained from literature^{55,56}. Together with the costs of capital and depreciation, based on the period of depreciation, the operational expenditure (OpEx) is calculated.

Membranes represent a large share of the CapEx in all OTM-based designs, and by taking OpEx as a percentage of the CapEx, the membrane surface area significantly influences the OpEx. To dampen this effect, OpEx is calculated based on the total depreciable capital excluding OTMs and modules but including the assembly of stacks. In this way, pieces of equipment that may need inspection, maintenance, or operation, such as gaskets, pipes, valves, and instrumentation are taken into account for the OpEx. Furthermore, heat exchangers and air compressors present in the membrane island are also taken into account for the same reason. In contrast, OTMs and modules, which are replaced after 7 years but don't need maintenance in the meantime, are not taken into account for the OpEx.

With CapEx and OpEx information as input, and together with assumptions based on variables such as the plant capacity factor, depreciation periods, taxes, and discount factor, net present value (NPV) calculations were done for each design. Fixed costs of production (FCOP), variable costs of production (VCOP), and depreciation are the negative cash flows which are taken into account. The revenue is calculated by multiplying the amount of generated electricity by an assumed value for the LCOE. Taxes are calculated by multiplying the taxable income by the tax rate; the taxable income is the revenue minus FCOP, VCOP, and depreciation. Using Eqs. 7.4 – 7.6, the yearly cash flow, discounted yearly cash flow (DCF), and NPV are calculated, where d is the yearly discount factor (7.5%). By setting the NPV to zero for the plant service life, and solving the system iteratively, the LCOE required for break-even operation over 20 years is obtained. Calculations are explained in detail in the supplementary information A7.4 (CapEx), A7.5 (OpEx) and A7.6 (NPV).

Table 7.3. Overview of assumed values for variables used to calculate LCOE.

Variable	Value	Explanation / source
Coal and pet-coke price	\$3.31 GJHHV ⁻¹	ELCOGAS personal correspondence
Natural gas price	\$5.27 GJHHV ⁻¹	Mean daily Henry Hub industrial price in the period January 2001 to October 2017 ⁵⁸
€/€ ratio	1.25	2010 – 2017 average ⁵⁹
Plant service life n	20 years	
Discount factor d	7.5%	
Tax rate tr	25%	
CO ₂ revenue	\$3 ton ⁻¹	See Section 7.4.2.
CO ₂ emission allowance	\$6.98 ton ⁻¹	Mean daily EEX Primary auction spot price in the period 2013-2017 ⁶⁰
OTM price	\$1000 m ⁻²	Raw materials and membrane fabrication
Membrane module price	\$2000 m ⁻²	Raw materials and machining of metal housing, membrane sealing, leakage testing
Assembly of modules into trains	\$200 m ⁻²	Piping and instrumentation
Service life of OTMs	7 years	See Section 7.4.2
Service life of module and assembly	20 years	Equal to service life of the rest of the plant
OTM flux degradation rate r_d	0.3% / 1000 h	Based on SOFC results
IGCC capacity factor	85%	See Section 7.4.2
IRCC and NGCC capacity factor	90%	See Section 7.4.2
Reference year for financial calculations	2014	

$$C = \text{Revenue} - \text{Taxes paid} - \text{FCOP} - \text{VCOP} - \text{Investment} \quad (7.5)$$

$$\text{DCF}(y) = C(1 + d)^{-y} \quad (7.6)$$

$$\text{NPV}_n = \sum_{y=1}^n \text{DCF}(y) \quad (7.7)$$

Several IGCC power plants are commercially operated, and a small amount of data on the operating capacity factor is publicly available. Depending on the process design, the amount of major equipment breakdowns, and the maturity of the used technology, typically operating capacity factors of 75% - 90% have been achieved after three to five years of operation ⁵⁷. For future IGCC plants, a capacity factor (assumed availability) of 85% or higher would be realistic ⁵¹. Furthermore, since solid-handling plants typically have a higher downtime than gas-handling plants, we assumed in this study that the IRCC and NGCC plants could achieve a capacity factor of 90%. These values are in line with the values assumed by the IEA Greenhouse Gas R&D Programme ⁶¹.

7.4.3. Costs of CO₂ avoided and captured

Cost of CO₂ captured (C_c) and cost of CO₂ avoided (C_a), both expressed in \$ ton_{CO₂}⁻¹, are metrics that are often used in literature to compare costs among various power plant designs with carbon capture facilities ^{50,62-65}.

$$C_c = \frac{\text{LCOE} - \text{LCOE}_{\text{ref}}}{M_C - M_{C,\text{ref}}} \quad (7.8)$$

$$C_a = \frac{\text{LCOE} - \text{LCOE}_{\text{ref}}}{M_A - M_{A,\text{ref}}} \quad (7.9)$$

in which LCOE_{ref} and LCOE are the values for LCOE, expressed in \$ MWh⁻¹, obtained for the unabated reference process and the relevant carbon capturing process, respectively. $M_{C,\text{ref}}$ and M_C represent the specific mass of captured CO₂ in the reference and carbon capture scenario, respectively, and are expressed in kg MWh⁻¹. As the reference process does not carbon capture, $M_{C,\text{ref}}$ equals zero. $M_{A,\text{ref}}$ and M_A are as well expressed in kg MWh⁻¹ and represent the specific mass of CO₂ avoided in the reference and carbon

capture scenario, respectively. Again, the avoided mass of CO₂ equals zero in the unabated process.

7.4.4. Sensitivity analysis

Assessing costs relies for a large part on assumptions; assumptions are kept equal for all designs as much as reasonably possible. Nevertheless, an inaccuracy in an assumption could have a small effect on the outcome of the simulation in one case, and a large effect in another case. To determine which plausible inaccuracy would have the strongest effect on the LCOE, a sensitivity analysis is performed. This is done by perturbing the simulation input values, one by one, to the lower and upper bound of the range of plausible input values. After each input value adjustment, the value of the LCOE of the corresponding process is calculated by setting the NPV to 0. In this subchapter, the range of plausible input values is determined for each of the assessed parameters. Table 4 lists the operations used to calculate the lower and upper bounds of the ranges within which the parameters are assessed.. An overview of the expected values and the lower and upper bound values calculated using the operations shown in Table 4 is given in Appendix A7.

Table 4. Operations to determine upper and lower bounds of parameters in sensitivity analysis, with E the expected factor and σ the standard deviation.

Variable	Lower bound	Upper bound
Coal price	$-\sigma$	$+\sigma$
NG price	$-\sigma$	$+\sigma$
CO ₂ allowance cost	$+\sigma$	$-\sigma$
TDC _c	-30%	+30%
Membrane + module price	-50%	+200%
Membrane area	-20%	20%
OTM lifetime	+50%	-50%
Operating capacity factor	+5 pp	-15 pp

Expected fuel prices and standard deviations have been calculated based on literature data for the monthly-averaged Australian thermal coal price ⁶⁶, monthly Henry hub natural gas price for the period January 2001 through October 2017 ⁵⁸, and the daily EEX Primary auction spot price for CO₂ in the period Jan 7, 2013 through December 15, 2017 ⁶⁰. Most other variables that are subject to the sensitivity analysis could not be analyzed in the same way as the fuels, since no statistical data is available. Instead, lower and upper boundaries have been chosen based on assumptions.

Membrane and module prices for OTMs are not easily estimated, nor reported in detail in the literature. Variables such as the surface area per individual membrane, the membrane and module geometry, the placement in the module, the amount and type of steel required for the module, labor required for production of the modules time, and many more, could all influence the price of the membrane plus module. Due to this high number of unknown factors, the upper boundary price is 200% above the base value. Large-scale production of OTMs could lead to a lower price per unit of membrane area, a 50% decrease with respect to the base value is assumed in this study and taken as the lower bound for the sensitivity analysis. The value obtained in that case, \$1500 m⁻², is also the target price for an operational module mentioned by den Exter *et al.* ⁶⁸.

Furthermore, the LCOE may be sensitive to parameters related to the oxygen flux through the membranes. For example, the oxygen transport properties and long-term performance relate directly to the membrane material. Process conditions such as the feed and sweep gas pressure, membrane temperature, oxygen recovery rate, and sweep flow rate strongly influence the required membrane area. Module design in terms of gas flow, leakage, and mechanical strength need to be taken into account as well. Since OTMs have not been commercially operated, an error in any of the assessed variables could be expected. For this reason, the required membrane area is varied with +20% and -20% around the area calculated by the transport model. The service life of OTMs can be related to that of fuel cells. Solid Oxide Fuel Cells (SOFCs), which contain more different components than OTMs, have been operated for > 66,500 h (> 7.5 years) non-stop ⁴⁷.

Although the components are comparable, for OTMs no such proof-of-principle is known to the authors. Hence, the sensitivity analysis shows the influence of $\pm 50\%$ deviation in service life from the expected value of 7 years.

Lastly, as discussed by Casero *et al.*²⁶, plant availability and continuity of electricity demand and production are – for the Puertollano IGCC plant – some of the main factors determining the OpEx. The lower boundary of -15 pp is similar to the lowest reported values for comparable processes⁵⁷, while the factor of +5 pp represents a world-class capacity factor⁶⁹. For the natural gas based processes, the same values are taken as boundaries.

7.5 Results and discussion

s is within an accuracy of estimation of $\pm 30\%$, which is the value expected for a factorial analysis⁵³. The slightly higher TDC for the real plant likely originates from omitting the gas cleaning equipment in the simulation and from encountered issues with the coal gasification in the actual plant.

The specific TDC of the pre-combustion IRCC is close to that of the reference IGCC, even though the pre-combustion IRCC designs contains equipment to capture CO₂. Furthermore, the values of TDCe for coal-based processes are close to each other, and so are the values of TDCe for natural gas-based processes. When including the costs of OTMs and modules, the values of the specific TDC increase significantly for all membrane-based processes. For oxyfuel processes, this increase is more significant than for pre-combustion processes.

Table 7.5 shows an overview of key parameters for each of the processes. To enable direct comparison among different plants, TDC and OpEx values normalized to the net power production, further referred to as specific costs, are given next to the raw data. Values are analyzed in the forthcoming section, together with more detailed data.

The net efficiency of the reference process is calculated to be 39.5%_{HHV}, which is below the reported value of 41.1%_{HHV}²⁶. When considering that syngas purification is not taken into account in the simulation, the differences would become slightly larger still. Even though the reference plant contains some pieces of power-consuming equipment that have been neglected, the actual plant can thus operate more efficiently than the simulated plant. This is attributed to the lower level of detail and optimization and the lower integration level of air compressors (which could be shared between the oxygen production and gasification sections) in the simulation as compared to the reference plant. Furthermore, coal is used ‘as received’ in the simulation, while in the actual plant some drying is performed. Drying may have a positive influence on the plant efficiency.

The capital cost of construction (which is assumed to include the same costs as TDC) of the actual Puertollano plant was €₁₉₉₇ 601 million²⁶. Using CE₁₉₉₇ = 368⁵⁶ and CE₂₀₁₄ = 576.1⁵⁴, TDC equals €₂₀₁₄ 941 million and \$₂₀₁₄ 1177 million when escalated to the base year of this study. The TDC calculated for the simulated unabated IGCC is \$₂₀₁₄ 1055 million, without taking costs for gas cleaning into account. The difference between the TDC of the simulated and the actual process is within an accuracy of estimation of ± 30%, which is the value expected for a factorial analysis⁵³. The slightly higher TDC for the real plant likely originates from omitting the gas cleaning equipment in the simulation and from encountered issues with the coal gasification in the actual plant.

The specific TDC of the pre-combustion IRCC is close to that of the reference IGCC, even though the pre-combustion IRCC designs contains equipment to capture CO₂. Furthermore, the values of TDC_c for coal-based processes are close to each other, and so are the values of TDC_c for natural gas-based processes. When including the costs

Table 7.5. Overview of key parameters for each of the processes. Energy input is split into solid (pet-coke and coal) and gas (natural gas). TDC_c represents all depreciable capital not related to OTMs and modules, while TDC includes these.

Process	Energy input solid/gas [MW _{HHV}]	Net power production (E_{net}) [MW _e]	η_{HHV} [-]	TDC _c / TDC [10 ⁶ \$ ₂₀₁₄]	Specific TDC _c / specific TDC [\$ ₂₀₁₄ kW ⁻¹ _{gross installed}]	OpEx and specific OpEx [10 ⁶ \$ ₂₀₁₄ year ⁻¹] / [\$ ₂₀₁₄ MWh ⁻¹]
Puertollano reference	727 / 0	299	41.1%	1177 / -	3708 / -	247 / 111
IGCC w/o CC	727 / 0	287	39.5%	1055 / -	3674 / -	240 / 112
Oxyfuel IGCC	727 / 242	347	35.8%	1346 / 2166	3877 / 6241	321 / 124
Pre-combustion IGCC w/ ASU	727 / 0	238	32.7%	977 / -	4105 / -	217 / 122
Pre-combustion IGCC	727 / 15	228	30.7%	932 / 1277	4088 / 5600	220 / 129
Pre-combustion IRCC	0 / 753	285	37.8%	863 / 1077	3029 / 3781	254 / 113
Oxyfuel NGCC	0 / 853	331	38.8%	1022 / 1776	3087 / 5366	303 / 116

of OTMs and modules, the values of the specific TDC increase significantly for all membrane-based processes. For oxyfuel processes, this increase is more significant than for pre-combustion processes.

7.5.1. CapEx breakdown

Table 7.6 shows ISBL costs of all assessed processes, which are estimated with an accuracy of $\pm 30\%$. Due to differences in allocation of equipment to plant sections, large differences in ISBL costs between plant sections can be observed for the actual and simulated Puertollano IGCC plant w/o carbon capture. The total ISBL costs are however relatively close to each other, indicating that the assessment of TDC gives reasonable values. Values of the specific TDC given in are among the highest of specific TDC values of 15 pre-combustion IGCC processes listed in literature⁷⁰. After recalculation to the year 2014 using the relative CEPCI values^{54,71}, an expected value of the specific TDC of $\$_{2014} 2679 \text{ kW}^{-1}$ with a standard deviation of $\$_{2014} 934 \text{ kW}^{-1}$ was found based on gross installed capacity. Only one of the processes in literature showed a higher specific TDC than the pre-combustion IGCC process in this study. The least expensive process of these 15 showed a specific TDC 55% below that of the pre-combustion IGCC process with ASU-based oxygen supply simulated in this study ($\$_{2014} 4105 \text{ kW}^{-1}$), indicating that the error margins are wide. Discussed literature data are not obtained from actual plants but based on a literature review, cost models, prefeasibility studies, or expert opinions; hence, care should be taken when comparing assessed costs reported in literature with values obtained the current study.

The actual Puertollano plant required a specific TDC of $\text{€}_{1997} 1892 \text{ kW}^{-1}_{\text{gross installed}}$ ²⁶, the specific time-corrected TDC based on net power corresponds to $\$_{2014} 3708 \text{ kW}^{-1}_{\text{gross installed}}$. The calculated TDC of the simulated reference process is less than 1% lower. Casero *et al.* report about the learning curve and the high number of changes and replacements in the first few years of operation the Puertollano IGCC plant²⁶. It was one of the few IGCC plants using coal as a fuel, and also used a prototype gasifier and gas turbine. Based on that, the actual CapEx of the Puertollano plant is likely

Table 7.6. ISBL costs and TDC per plant section for each of the designs.

	IGCC w/o carbon capture		Simulated plants with carbon capture				
	Literature [10 ⁶ \$ ₂₀₁₄]	Simulation [10 ⁶ \$ ₂₀₁₄]	Oxyfuel IGCC [10 ⁶ \$ ₂₀₁₄]	Pre-comb. IGCC w/ ASU [10 ⁶ \$ ₂₀₁₄]	Pre-comb. IGCC w./ OTM [10 ⁶ \$ ₂₀₁₄]	Pre-comb. IRCC [10 ⁶ \$ ₂₀₁₄]	Oxyfuel NGCC [10 ⁶ \$ ₂₀₁₄]
Plant section							
Gasification or reforming	315	176	104	72	70	98	0
Membranes or ASU	44	109	859	156	374	230	819
CO ₂ separation and compression	0	0	50	46	46	47	32
Power island	214	250	295	209	200	176	186
Balance of plant	197	197	197	197	197	197	197
ISBL	769	732	1504	678	887	748	1233
TDC	1108	1055	2166	977	1277	1077	1776
TDC _e	1108	1055	1346	977	932	863	1022

higher than what would be expected based on equipment sizing and factorial analysis if contingency costs are not taken into account. This illustrates that the plant taken as reference for this study can be expected to show a high specific CapEx compared with more recently built nth-of-a-kind plants.

The design constraints applied in this study to comply with the Puertollano design, as discussed in Section 7.4.1, likely lead to relatively high specific TDC values in this study as well. Whereas this issue complicates the comparison between estimated specific TDC – and therefore all other cost-related variables – of the studied designs with literature values, comparisons between simulated values are unaffected.

7.5.2 Oxygen demand and operational expenses

With the oxygen permeation model used here, the averaged oxygen flux is around $1.1 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$ or $2.6 \cdot 10^{-2} \text{ Nml cm}^{-2} \text{ s}^{-1}$ for all processes (more values are shown in Table A7.3). The required membrane areas in the different processes depend on the amount of pure oxygen that needs to be produced, of which values are specified in Table 7.7. Design choices such as the stage-cut (the ratio between the permeate flow rate and feed flow rate), the sweep gas type, and the feed and sweep gas pressures influence the required membrane area. These design choices are kept equal as much as possible to focus on the effect of integrating OTMs into various processes rather than to fully optimize the conditions in each of the processes. Details of membrane specifications and design choices are available in Table A7.3.

Pure oxygen is used in coal gasification (IGCC) or natural gas reforming (IRCC), as well as in the combustion of syngas in the gas turbine (oxyfuel combustion processes). Oxyfuel combustion IGCC and NGCC have a higher specific total oxygen demand (sTOD) and specific pure oxygen demand (sPOD) than the pre-combustion based processes, since oxyfuel processes require pure oxygen for coal gasification as well as for syngas combustion. In pre-combustion processes, however, air is used as oxidant in the gas turbine. It provides a large part (~40%) of the total required oxygen, as the presence of nitrogen in the gas turbine does not negatively influence the CO₂ purity. For that

reason, the sPOD of pre-combustion processes is more than a factor 1.5 smaller than that of oxyfuel combustion processes, which is reflected by the large difference in membrane area and OTM-related CapEx.

Furthermore, in the pre-combustion IRCC process, 20% of the total oxygen flow is provided by steam in the autothermal reforming section. Therefore, the pure oxygen production by OTMs is 36% lower in the pre-combustion IRCC than in the pre-combustion IGCC process, which enables the pre-combustion IRCC to be the process requiring the smallest membrane area.

As shown in Table 7.6, the membrane island is the most capital-intensive part of all OTM-based processes. For the oxyfuel combustion cases, the membrane island remains among the most expensive parts of the plant even if the membranes and membrane modules would be obtained for free. This is due to the compressors and heat exchangers in the membrane island, which increases in size with an increasing demand of pure oxygen. In the coal-fired pre-combustion IGCC, the membrane island dominates the CapEx as well, but less strongly than for the oxyfuel designs. Using cryogenic distillation as oxygen supply for the pre-combustion IGCC, the total CapEx is assessed to be considerably lower than with OTMs. This however depends strongly on the assumed membrane-related parameters, such as the oxygen flux, costs for raw materials, machining, and the lifetime of the membranes.

As shown in Table 7.8, natural gas-based processes have higher specific fuel costs than coal/pet-coke based processes, as expected based on the 60% higher cost per unit of energy content (\$3.31 GJHHV⁻¹ for the coal/pet-coke mixture and \$5.27 GJHHV⁻¹ for natural gas). Coal and pet-coke are cheaper fuels than natural gas. Nevertheless, natural gas-based electricity production processes can show lower specific OpEx than coal-based processes, as demonstrated in Table 7.5.

The low specific OpEx of the pre-combustion IRCC process compared to other processes with carbon capture is due to the low CapEx, the high plant efficiency and low

Table 7.7. Total and pure oxygen demand, membrane area and oxygen flux in each of the processes. Values for required membrane areas are based on the oxygen flux through membranes of the maximum age (7 years).

Parameter	Process					
	IGCC w/o CC	Oxyfuel IGCC	Pre-comb. IGCC w/ ASU	Pre-comb. IGCC w/ OTM	Pre-comb IRCC	Oxyfuel NGCC
TOD [kmol s ⁻¹]	1.63	2.20	1.63	1.67	1.70	1.92
POD [kmol s ⁻¹]	0.67	1.56	0.67	0.67	0.43	1.54
sTOD [mol O ₂ kWh ⁻¹ _{net}]	20.95	22.77	25.27	26.90	21.85	21.29
sPOD [mol O ₂ kWh ⁻¹ _{net}]	8.40	17.32	10.13	11.05	5.46	16.71
Membrane area [10 ⁴ m ²]	-	19.0	-	7.98	4.95	17.5
Specific membrane area [m ² MW _a]		6.62·10 ²		3.35·10 ²	2.17·10 ²	6.13·10 ²
Mean membrane flux (newly installed) [10 ⁻⁷ mol cm ⁻² s ⁻¹]	-	1.06	-	1.05	1.05	1.06

demand of oxygen. However, the natural gas price is much more volatile than the coal price ⁷², leading to a larger expected fluctuation in OpEx. The effect of that fluctuation on the LCOE is discussed in the sensitivity analysis.

Furthermore, the oxyfuel IGCC process is the only process that uses significant quantities of both types of fuel. Whereas the coal/pet-coke mixture is used as the primary fuel, natural gas is used for pre-heating the membrane feed to 850 °C and accounts for 25% of the total energy input. The yearly natural gas expense is 35% of the total fuel expense, since natural gas is more expensive per unit of energy than coal and pet-coke. In the pre-combustion IGCC process, enough heat is available to bring the OTM feed to 780 °C by heat exchanging. In reality, the actual temperature of the OTM feed reached by heat exchanging partly depends on the material selection and design of the heat exchangers. Notwithstanding these choices, the amount of natural gas required for further heating is limited in comparison to the oxyfuel IGCC process. Due to the lower plant efficiency, however, the specific fuel cost is higher than that in the oxyfuel IGCC process.

Table 7.8. Fuel type and estimated cost for each of the designs.

Process	Coal/pet-coke input [PJ _{HHV} /year]	Natural gas input [PJ _{HHV} /year]	Specific fuel cost [€ MWh ⁻¹ produced]
IGCC w/o CC	19.5	0	30.2
Oxyfuel IGCC	19.5	6.49	38.2
Pre-combustion IGCC + ASU	19.5	0	36.4
Pre-combustion IGCC + OTM	19.5	0.41	39.3
Pre-combustion IRCC		21.4	50.1
Oxyfuel NGCC		24.2	48.9

The average yearly OpEx and specific OpEx for the reference IGCC plant were calculated to be \$293 million and \$112 MWh⁻¹, respectively (see Table 7.5). As shown in Figure 7.6, the specific OpEx of all other processes is higher, both due to the lower plant

efficiency caused by carbon capture and to the higher CapEx. Details of the OpEx calculation can be found in Appendix A7.5, in which detailed results are given for the pre-combustion IRCC plant.

Since coal-fired power plants process a solid, it is expected that they need more operations and maintenance staff than gas-fired plants. This is related to a higher chance of equipment or piping blockage, and increased wear due to erosion. In this study, it was assumed that the gasification section of coal-fired plants requires four operators per shift, while all other sections require two operators per section and shift. Labor costs for operations represent just 3–6% of the OpEx, and differences in labor costs between coal- and gas-fired plants are therefore small. Labor and materials costs of the maintenance department were taken as a percentage of the CapEx, and both represent a large share in the maintenance costs. The maintenance costs therefore differ considerably among the process designs, for example, the maintenance costs of the oxyfuel IGCC are 36% higher than the maintenance costs of the pre-combustion IRCC. Gas-fired plants show lower

Figure 7.6. Specific OpEx of all assessed processes.

maintenance costs per MWh of generated electricity than coal-fired plants, both due to their lower CapEx and their higher plant efficiency and net power production. The oxyfuel IGCC shows relatively low maintenance costs as well, due to its higher net power production compared to the pre-combustion IGCC processes.

7.5.3 Energy efficiency and LCOE

Figure 7.7 shows the two key metrics, plant efficiency and LCOE, for each of the assessed processes. The Puertollano IGCC base case without carbon capture (CC) shows the highest efficiency ($\eta_{\text{net}} = 39.5\%_{\text{HHV}}$), immediately followed by the oxyfuel combustion NGCC process. The oxyfuel IGCC process is 3.7 pp less efficient than the base case, less efficient, respectively. The natural gas-fired processes, while performing carbon capture, show efficiencies of $37.8\%_{\text{HHV}}$ for the IRCC process and $38.8\%_{\text{HHV}}$ for the NGCC whereas these steps are not required for natural gas-based processes, while the pre-combustion IGCC processes with ASU and OTMs are 6.8 pp and 8.8 pp. The higher number of process steps in coal-fired plants in which heat transfer or chemical reactions take place causes the efficiency of coal-fired plants to be lower than that of gas-fired plants.

The efficiency of the reference process ($\eta_{\text{HV}} = 39.5\%$) is about 10 pp lower than that of a typical modern unabated IGCC power plant reported in literature ($\eta_{\text{HV}} = 49.1\%$)⁷³, of which about 7 pp can be ascribed to the low turbine inlet temperature used ($1125\text{ }^{\circ}\text{C}$ in this study, $1600\text{ }^{\circ}\text{C}$ in state-of-the-art process)⁷³. Other contributions include a lower gasifier temperature, lower steam temperature, and lower isentropic efficiency of compressors in the processes discussed in this work. Having based the design of all carbon capturing plants on the specifications of the old Puertollano plant, the efficiency of the processes described here is strongly affected by the low efficiency of the reference plant. Optimization of the design of processes with a TIT of $1600\text{ }^{\circ}\text{C}$ and OTM integration was not within the scope of this study, but would be interesting for future research. Due to the larger amount of heat available in such a plant, and therefore

Figure 7.7. Comparison of HHV-based plant efficiency and levelized cost of electricity (LCOE) for all simulated plant designs. Dots show the plant efficiency on the right y-axis, while columns show the LCOE on the left y-axis of the figure. The black column represents the simulated unabated Puertollano plant. The grey columns represent the other coal-fired designs, and the green columns represent the gas-fired designs. On the x-axis, ASU denotes oxygen supply by cryogenic distillation; in the other carbon-capturing processes OTMs are used to supply oxygen.

the lower required heating duty in an external furnace, it could be expected that the efficiency of OTM-based processes would increase significantly with an increased TIT.

The unabated reference plant shows the lowest LCOE among all processes. Furthermore, three clear trends can be distinguished. First, the OTM-based IGCC process produces more expensive electricity than the ASU-based IGCC process, which is likely due to the large contribution of membranes and modules to the total CapEx.

Second, oxyfuel combustion processes produce electricity at higher costs than pre-combustion processes, even though the efficiencies of oxyfuel processes are higher. Again, this is attributed to the high CapEx associated with membranes and modules. Third, natural gas based processes show lower costs than their coal-based counterparts, even though their specific feedstock costs are higher. This is due to the higher CapEx and lower net efficiency of coal-based processes, as well as the high CapEx-intensity of all processes in general.

Zooming in further, the lowest LCOE among abated processes is found for the pre-combustion IRCC, and the highest for the oxyfuel IGCC process. These processes also require the smallest and largest membrane area, respectively. The importance of the sPOD on the LCOE is illustrated by Figure 7.8, in which 68% of the variability in the LCOE is explained by the variability in POD.

Figure 7.8. Specific pure oxygen demand as predictor variable for LCOE.

7.5.4 Costs of CO₂ avoided and captured

Table 7.9 shows the amounts of produced, captured, emitted and avoided CO₂ per unit of produced electricity, the relative amount of CO₂ captured, as well as the cost of CO₂ avoided and cost of CO₂ captured. The costs of CO₂ avoided are between \$41 ton_{CO₂}⁻¹ for the pre-combustion IRCC and \$146 ton_{CO₂}⁻¹ for the oxyfuel IGCC. The cost of captured CO₂ is in all cases much higher than the expected selling price of \$3 ton_{CO₂}⁻¹, hence the selling price of CO₂ is expected not to influence the economic viability of the discussed processes. The cost of captured CO₂ is the highest (\$173 ton_{CO₂}⁻¹) for the oxyfuel NGCC, due to both the relatively small amount of CO₂ captured and the relatively high LCOE.

The influence of the reference plant LCOE on the costs per ton of CO₂ avoided is strong, as shown in literature ⁷⁴. If an old subcritical pulverized coal power plant would be taken as the reference plant, with twice as low LCOE and 50% higher specific CO₂ production than the Puertollano IGCC, the costs of CO₂ captured and avoided of the assessed process would be much closer to each other. The factor 3.6 difference between the cost of CO₂ avoided of the oxyfuel IGCC and pre-combustion IRCC would decrease to a factor 1.7, which might make it a less important factor to consider when making decisions on which type of plant to build.

Table 9. Overview of carbon capture performance of assessed designs. Values of the amounts of CO₂ produced, captured (M_C), emitted (M_E), and avoided (M_A) are given, as well as the relative amount of CO₂ which is captured. Values of the cost of CO₂ captured (C_C) and cost of CO₂ avoided (C_A) are shown as well.

Process	CO ₂ produced [kg MWh ⁻¹]	CO ₂ captured % of produced CO ₂	M_C [kg MWh ⁻¹]	M_E [kg MWh ⁻¹]	M_A [kg MWh ⁻¹]	C_C [\$ ton _{CO_{2,c}} ⁻¹]	C_A [\$ ton _{CO_{2,A}} ⁻¹]
IGCC w/o CC	817	0	0	817	0.0		
Oxyfuel IGCC	1127	84.0	911	217	600	96	146
Pre-combustion IGCC + ASU	1030	89.4	879	151	666	44	58
Pre-combustion IGCC + OTM	1077	89.4	911	166	651	80	112
Pre-combustion IRCC	546	75.4	355	191	626	73	41
Oxyfuel NGCC	496	78.4	360	136	681	173	91

7.5.5. OTM or ASU – case study in pre-combustion IGCC

Among the three coal-fired plants, pre-combustion carbon capture with cryogenic distillation (ASU) as method for oxygen production turns out to be both most efficient and least expensive. Compared to pre-combustion capture with OTM-based oxygen supply, the higher efficiency is mainly due to a more efficient supply of quench gas to the gas turbine in terms of gas volume and temperature. Large quantities of cold nitrogen are available from the cryogenic distillation, while the OTM-based pre-combustion design uses depleted air from the membrane together with additional compressed air, at temperatures of 280 – 320 °C. The quenching capacity of hot depleted air is less than that of cold nitrogen, causing an increase of about 10 MW in the required duty for additional compressed air and a decrease in efficiency of 2 pp. In literature, a similar comparison led to the opposite conclusion that an OTM-based coal-fired pre-combustion plant is 1 pp more efficient than the same plant with ASU-based oxygen supply ⁷⁷. In that case, the heat available in oxygen produced by OTMs was an advantage instead of a disadvantage, possibly due to the higher turbine inlet temperature compared with the current study.

From a cost perspective, the OTM is less attractive than the ASU as well. The investment required for the production of oxygen is 2.4 times higher with OTMs than with the ASU in the pre-combustion IGCC (ISBL investment of 374 M\$₂₀₁₄ and 156 M\$₂₀₁₄, respectively). Even if the membranes would be acquired at no cost, the higher efficiency of the ASU-based process would still cause the related LCOE to be lower than that of the OTM-based process.

Competition with energy produced with renewable sources

Electricity generation based on renewables is the logical competition of combined cycle processes with carbon capture when considering building new power stations with a small CO₂ footprint. Mean LCOE values for onshore wind farms entering service in 2019 (\$₂₀₁₄ 80 MWh⁻¹) or for solar power from large, ground-mounted photovoltaic cells (\$₂₀₁₄ 130 MWh⁻¹) ⁷⁸, are lower than that of the pre-combustion IRCC (\$₂₀₁₄ 177 MWh⁻¹), which shows the lowest LCOE among the OTM-based processes.

However, solar and wind power are non-dispatchable technologies: electricity is not produced on demand. A more fair comparison would also include the costs of (short-term) energy storage, for example using batteries, chemicals, heat, or pressure. In a recent study, the levelized cost of storage was calculated to be €₂₀₁₅ 50 – €90 MWh⁻¹ using pumped storage hydroelectricity, €₂₀₁₅ 70 – 120 MWh⁻¹ for compressed air energy storage, and more expensive for all other systems⁷⁹. Although not all generated wind and solar energy needs to be stored, adding (part of) the LCOS to the LCOE would bring the costs of sun power and wind power close to that of IRCC and IGCC with pre-combustion carbon capture. Taking into account that not all geological locations are well suitable for wind based or solar based electricity production, IGCC and IRCC power plants with carbon capture could be viable options to serve as baseload plants. Another interesting option is to combine biobased IGCC with carbon capture, resulting in processes with a negative CO₂ emission⁸⁰. Such IGCC power plants with a biobased feedstock could serve as baseload plants, and could be used next to peak load plants such as solar farms or wind farms. According to literature, the economics of this process strongly depends on the price of biomass⁸⁰⁻⁸¹. Likewise, a pre-combustion IRCC process using bio-methane as a feedstock could be designed. For each set of demands, an individual evaluation will be required to determine which type of power plant should be built.

Membrane sweep options

As described in Sections 3.2 – 3.5, different process designs require different membrane sweep gases. First of all, in oxyfuel designs the membrane sweep gas should not contain nitrogen. Nitrogen in the sweep gas ends up in the compressed CO₂, since no separation takes place further downstream. Presence of nitrogen negatively affects the CO₂ purity and the compression duty. Two viable sweep gas options for oxyfuel processes are CO₂ and steam; steam turned out to be best solution in this study in terms of heat integration. For deciding which sweep gas would be preferred, the stability of OTMs in the respective atmosphere is not taken into account. However, Bucher and Sitte showed that sweeping with steam could severely degrade OTMs made from LSCF⁸². On the other hand, LSCF membranes stable in a steam sweep – on relatively short time scales as

compared to power plant overhaul schedules – have been reported as well⁸³. For the effect of sweeping with CO₂ on the membrane service life, the same is true: depending on the membrane material, operating temperature and pressure, as well as the presence of impurities, the OTM material might or might not be stable. Dual-phase composite membranes are more resistant to acidic gases, and may present a viable alternative to perovskite oxides⁸⁴⁻⁸⁵. Another factor to take into account is that volatile chromia species could be present in the sweep vapor due to contact with chromium-containing steels at high temperatures. This might lead to degradation of OTMs as well, as shown for LSCF in the case of a combined CO₂ and steam sweep⁸⁶. Using air as sweep gas, like in the pre-combustion IGCC process in this study, might reduce the reactivity between membrane and sweep gas. Due to the high nitrogen concentration in air, this strategy would not work for oxyfuel combustion processes. In oxyfuel processes, the best solution may be either to use membranes stable with the applied sweep gas or to use a three-end layout.

OTM operating temperature

The operating temperature of OTMs was fixed to 850 °C. From a materials science point-of-view, an ideal operating temperature is a compromise between a high oxygen flux, which increases with increasing temperature, and a good long-term stability, which typically decreases with temperature. High temperatures are not desirable from a process engineering point of view, since they complicate heat exchange processes and cause a need for more expensive process equipment materials.

The availability of heat is insufficient to raise the OTM feed temperature to 850 °C in all studied plants. OTM feed streams therefore require pre-heating with a methane-fired furnace. Not only is the increase in LCOE due to pre-heating significant, but it also requires coal-fired plants to always use a secondary fuel. A preliminary result obtained in this study indicates that OTMs operating at a temperature below roughly 600 – 650 °C could eliminate the need for such a furnace, depending strongly on the outlet temperature of the gas turbine. A higher TIT results in a higher outlet temperature, which subsequently allows for more heat being exchanged between combustion products and OTM feed. Furthermore, the membrane surface area is one of the main cost drivers in

OTM-based power plants, and a low oxygen flux is therefore of large impact on the LCOE. The oxygen flux through an LSCF OTM would decrease with about two orders of magnitude upon decreasing the temperature from 850 °C to 600 °C⁸⁷, thus requiring a comparable increase in membrane area. Using currently known OTM materials, the LCOE increases strongly upon such a temperature decrease. This was confirmed for the oxyfuel IGCC process, for which the LCOE increased with a factor 40 to more than \$₂₀₁₄ 8000 upon decreasing the operating temperature to 600 °C, due to the increase in membrane area discussed previously. To operate in an economically viable way at this intermediate temperature, future materials with a flux roughly equal to the current materials' flux at 850 °C and good stability in atmospheres containing CO₂, SO₂, and steam are required. Materials such as Ruddlesden-Popper structured materials, which have shown a low polarization resistance in impedance spectroscopy experiments at 600 °C⁸⁸, or less conventional molten carbonate based materials which have shown high ionic conductivity at equal temperature⁸⁹ may be better candidates for OTMs at temperatures around 600 °C, but seem to be far from industrial operation still.

7.5.6 Evaluation of parameter sensitivities on LCOE

Figure 7.9 shows the results of the sensitivity analysis, indicating the assessed sensitivity of the LCOE of each of the processes on the parameters discussed in Section 7.4.4. The impact of the parameters on the LCOE decreases from the top to the bottom of the graph. For example, price fluctuations of natural gas and the CO₂ allowance price are shown to have the highest and lowest impact on LCOE for the pre-combustion IRCC design, respectively. The base LCOE values shown in Fig. 7.9 are equal to the values in Fig. 7.7 and represent the LCOE if the most likely values for all parameters are used for the calculation. The variations of parameters are discussed in Section 7.4.4. Values of assessed variations are displayed left and right of the bars in Fig. 7., and are used to indicate the spread in LCOE as a result of these variations. In this graph, variations of parameters are expressed in percent points, percentages relative to the

Figure 7.9. Sensitivity of LCOE to various parameters in all assessed processes.

Figure 7.9 - Continued. Sensitivity of LCOE to various parameters in all assessed processes.

expected value, and the standard deviation
the upper and lower bounds is given in A7.7.

σ . An overview

The LCOEs of oxyfuel combustion IGCC and NGCC are highly sensitive to the costs of membranes and modules, due to their comparatively large required membrane area. In contrast to the results of our study, Maas *et al.* ⁶³ showed that the costs of membranes represent only a few percent of the LCOE when using three-end OTMs in an oxyfuel IGCC ⁶³, whereas the membrane island of the oxyfuel IGCC in this study represents more than half of the CapEx of that process (Table 7.6). Besides some differences in process architecture and amount of produced power, different assumptions related to OTMs should account for the observed large difference in the assessed impact of OTMs on the LCOE. For example, the membrane area per MW_{el} installed and the estimated CapEx of OTMs are a factor 4 and a factor 6 higher in our study, respectively, giving a factor 24 difference in membrane investment. To improve the accuracy of the LCOE of OTM-based processes, and to decrease the differences between studies, more accurate data on initial and long-term OTM performance, costs of fabricating membranes, modules, and systems, and on OTM service life are required.

The operating capacity factor has a strong effect on the LCOE as well, according both to Figure 7.9 and to literature about the real Puertollano plant ²⁶. This is highly relevant, as the actual number of operating hours may be much lower than the theoretically possible number for both coal- and natural gas-fired plants. The increasing penetration of non-dispatchable renewables in the electricity market causes the supply to become more volatile.

Processes of which the LCOE is more sensitive to the capacity factor are likely also more sensitive to volatility of the electricity market. Due to the lower startup time of natural gas-fired combined cycle plants (120 – 280 min cold start ⁷⁵) than of coal/pet-coke fired IGCC plants (12 – 72 h cold start ²⁶), the number of shutdown and startup cycles per time unit will have less impact on the capacity factor of the former. Furthermore, during startup of the coal/pet-coke fired IGCC, natural gas has to be used

as fuel for the gas turbine ²⁶, thereby increasing the LCOE (this effect was neglected in the sensitivity analysis). Both factors make the IRCC more attractive compared to the other processes than it appears from Fig. 7.7. For the oxyfuel NGCC, the level of integration is higher, as a large part of the produced CO₂ is recycled back into the gas turbine and used as sweep for OTMs. Therefore, a long startup time may be expected for the NGCC as well. Alternatively, an extra air compressor may be installed to provide air as coolant to the gas turbine. In case the air compression for the gas turbine and oxygen supply section is fully integrated (a single compressor is used to deliver compressed air to both plant sections), a cold plant start takes longer than if it is only partially or not at all integrated. Integrated compressors therefore penalize peak load plants. The capacity factor was reported to be extremely important for the finances of the Puertollano plant ²⁶. For future IGCC plants, the influence of design choices on the capacity factor therefore requires thorough evaluation.

Common to all designs is the high sensitivity to inaccuracies in the estimation of the TDC. This is due to the high capital intensity of fossil fuel powered plants that perform carbon capture ⁷⁶. OTMs and modules have not been taken into account for calculations of TDC. Yet, the relative sizes and capacities of compressors and heat exchangers in the membrane island depend on the specific pure oxygen demand and are taken into account for TDC calculations. Nevertheless, pre-combustion processes are slightly more sensitive towards inaccuracy in TDC calculations than oxyfuel processes.

Fuel costs are of high impact on the LCOE of pre-combustion processes, but of lower impact on the LCOE of oxyfuel combustion processes. In absolute terms, the impact of varying fuel costs by one standard deviation in the positive and negative direction is comparable for all processes (\$23 – \$38 MWh⁻¹). Due to the high impact of membrane-related parameters on the LCOE, oxyfuel combustion processes are relatively less sensitive to variations in fuel costs than the other processes.

The CO₂ allowance price does not have a strong influence on the LCOE in any of the processes. Although a weak impact may be expected for the plants that perform

carbon capture, it is remarkable that the impact of the CO₂ allowance price on the LCOE of the reference unabated IGCC process is the lowest among all assessed factors. This can be seen as an indication that the price of CO₂ allowances needs to increase significantly to become a decisive factor. An allowance cost of \$40 ton_{CO₂}⁻¹ (equal to 20% above the expected value of \$6.98 ton_{CO₂}⁻¹) was sufficient in the study of Maas *et al.* to find a lower LCOE for all carbon capturing processes than of the base case⁶³. In our study however, the CO₂ allowance cost needs to be at least \$45 ton_{CO₂}⁻¹ to let the pre-combustion IRCC show a lower LCOE than the unabated reference process. Only above an allowance cost of \$130 ton_{CO₂}⁻¹, the LCOE of all carbon capturing processes were found to be lower than that of the reference process. As these are unrealistic prices at least at the short term, the effect of the CO₂ allowance price on the costs of power plants using OTMs to supply oxygen is not decisive in any of the assessed cases.

7.5.7. Discussion

Among the three coal-fired plants, pre-combustion carbon capture with cryogenic distillation (ASU) as method for oxygen production turns out to be both most efficient and least expensive. Compared to pre-combustion capture with OTM-based oxygen supply, the higher efficiency is mainly due to a more efficient supply of quench gas to the gas turbine in terms of gas volume and temperature. Large quantities of cold nitrogen are available from the cryogenic distillation, while the OTM-based pre-combustion design uses depleted air from the membrane together with additional compressed air, at temperatures of 280 – 320 °C. The quenching capacity of hot depleted air is less than that of cold nitrogen, causing an increase of about 10 MW in the required duty for additional compressed air and a decrease in efficiency of 2 pp. In literature, a similar comparison led to the opposite conclusion that an OTM-based coal-fired pre-combustion plant is 1 pp more efficient than the same plant with ASU-based oxygen supply⁷⁷. In that case, the heat available in oxygen produced by OTMs was an advantage instead of a disadvantage, possibly due to the higher turbine inlet temperature compared with the current study.

From a cost perspective, the OTM is less attractive than the ASU as well. The investment required for the production of oxygen is 2.4 times higher with OTMs than with the ASU in the pre-combustion IGCC (ISBL investment of 374 M\$₂₀₁₄ and 156 M\$₂₀₁₄, respectively). Even if the membranes would be acquired at no cost, the higher efficiency of the ASU-based process would still cause the related LCOE to be lower than that of the OTM-based process.

Electricity generation based on renewables is the logical competition of combined cycle processes with carbon capture when considering building new power stations with a small CO₂ footprint. Mean LCOE values for onshore wind farms entering service in 2019 (\$₂₀₁₄ 80 MWh⁻¹) or for solar power from large, ground-mounted photovoltaic cells (\$₂₀₁₄ 130 MWh⁻¹)⁷⁸, are lower than that of the pre-combustion IRCC (\$₂₀₁₄ 177 MWh⁻¹), which shows the lowest LCOE among the OTM-based processes. However, solar and wind power are non-dispatchable technologies: electricity is not produced on demand. A more fair comparison would also include the costs of (short-term) energy storage, for example using batteries, chemicals, heat, or pressure. In a recent study, the levelized cost of storage was calculated to be €₂₀₁₅50 - €90 MWh⁻¹ using pumped storage hydroelectricity, €₂₀₁₅ 70 - 120 MWh⁻¹ for compressed air energy storage, and more expensive for all other systems⁷⁹. Although not all generated wind and solar energy needs to be stored, adding (part of) the LCOS to the LCOE would bring the costs of sun power and wind power close to that of IRCC and IGCC with pre-combustion carbon capture. Taking into account that not all geological locations are well suitable for wind based or solar based electricity production, IGCC and IRCC power plants with carbon capture could be viable options to serve as baseload plants. Another interesting option is to combine biobased IGCC with carbon capture, resulting in processes with a negative CO₂ emission⁸⁰. Such IGCC power plants with a biobased feedstock could serve as baseload plants, and could be used next to peak load plants such as solar farms or wind farms. According to literature, the economics of this process strongly depends on the price of biomass⁸⁰⁻⁸¹. Likewise, a pre-combustion IRCC process using bio-methane as a

feedstock could be designed. For each set of demands, an individual evaluation will be required to determine which type of power plant should be built.

As described in Section 7.3, different process designs require different membrane sweep gases. First of all, in oxyfuel designs the membrane sweep gas should not contain nitrogen. Nitrogen in the sweep gas ends up in the compressed CO₂, since no separation takes place further downstream. Presence of nitrogen negatively affects the CO₂ purity and the compression duty. Two viable sweep gas options for oxyfuel processes are CO₂ and steam; steam turned out to be best solution in this study in terms of heat integration. For deciding which sweep gas would be preferred, the stability of OTMs in the respective atmosphere is not taken into account. However, Bucher and Sitte showed that sweeping with steam could severely degrade OTMs made from LSCF⁸². On the other hand, LSCF membranes stable in a steam sweep – on relatively short time scales as compared to power plant overhaul schedules – have been reported as well⁸³. For the effect of sweeping with CO₂ on the membrane service life, the same is true: depending on the membrane material, operating temperature and pressure, as well as the presence of impurities, the OTM material might or might not be stable. Dual-phase composite membranes are more resistant to acidic gases, and may present a viable alternative to perovskite oxides⁸⁴⁻⁸⁵. Another factor to take into account is that volatile chromia species could be present in the sweep vapor due to contact with chromium-containing steels at high temperatures. This might lead to degradation of OTMs as well, as shown for LSCF in the case of a combined CO₂ and steam sweep⁸⁶. Using air as sweep gas, like in the pre-combustion IGCC process in this study, might reduce the reactivity between membrane and sweep gas. Due to the high nitrogen concentration in air, this strategy would not work for oxyfuel combustion processes. In oxyfuel processes, the best solution may be either to use membranes stable with the applied sweep gas or to use a three-end layout.

The operating temperature of OTMs was fixed to 850 °C. From a materials science point-of-view, an ideal operating temperature is a compromise between a high oxygen flux, which increases with increasing temperature, and a good long-term stability, which

typically decreases with temperature. High temperatures are not desirable from a process engineering point of view, since they complicate heat exchange processes and cause a need for more expensive process equipment materials.

The availability of heat is insufficient to raise the OTM feed temperature to 850 °C in all studied plants. OTM feed streams therefore require pre-heating with a methane-fired furnace. Not only is the increase in LCOE due to pre-heating significant, but it also requires coal-fired plants to always use a secondary fuel. A preliminary result obtained in this study indicates that OTMs operating at a temperature below roughly 600 – 650 °C could eliminate the need for such a furnace, depending strongly on the outlet temperature of the gas turbine. A higher TIT results in a higher outlet temperature, which subsequently allows for more heat being exchanged between combustion products and OTM feed. Furthermore, the membrane surface area is one of the main cost drivers in OTM-based power plants, and a low oxygen flux is therefore of large impact on the LCOE. The oxygen flux through an LSCF OTM would decrease with about two orders of magnitude upon decreasing the temperature from 850 °C to 600 °C⁸⁷, thus requiring a comparable increase in membrane area. Using currently known OTM materials, the LCOE increases strongly upon such a temperature decrease. This was confirmed for the oxyfuel IGCC process, for which the LCOE increased with a factor 40 to more than \$₂₀₁₄ 8000 upon decreasing the operating temperature to 600 °C, due to the increase in membrane area discussed previously. To operate in an economically viable way at this intermediate temperature, future materials with a flux roughly equal to the current materials' flux at 850 °C and good stability in atmospheres containing CO₂, SO₂, and steam are required. Materials such as Ruddlesden-Popper structured materials, which have shown a low polarization resistance in impedance spectroscopy experiments at 600 °C⁸⁸, or less conventional molten carbonate based materials which have shown high ionic conductivity at equal temperature⁸⁹ may be better candidates for OTMs at temperatures around 600 °C, but seem to be far from industrial operation still.

7.1 Conclusions

In this chapter, the integration of oxygen transport membranes (OTMs) into four different power plant processes has been studied. Discussed processes include coal-fired integrated gasification combined cycle (IGCC) plants with pre-combustion and oxyfuel combustion technology, natural gas-fired integrated reforming combined cycle (IRCC) with pre-combustion carbon capture, and natural gas combined cycle (NGCC) power with oxyfuel combustion carbon capture. Oxygen production by cryogenic distillation and by OTMs have been compared for the pre-combustion IGCC process.

Among the assessed carbon capturing plants, the oxyfuel combustion NGCC plant shows the highest efficiency (38.8%_{HHV}). High efficiency and low costs do not necessarily go together, as it is also the second most expensive among the carbon capturing processes discussed here. The pre-combustion IRCC process shows the lowest LCOE (\$177 MWh⁻¹) and the lowest cost per ton of CO₂ avoided (\$41 ton_{CO₂,A}⁻¹), while the efficiency is only 1 pp lower than that of the NGCC. The pre-combustion IRCC process is likely the most attractive process to combine with OTMs among the processes discussed here because of its low OTM area, lowest LCOE and relatively high energy efficiency.

With the assumptions made in this study, OTM-based oxygen supply is not more efficient and neither less expensive than oxygen supply by cryogenic distillation. The energy efficiencies of the pre-combustion IGCC with ASU and OTM are 32.9%_{HHV} and 30.9%_{HHV}, respectively. This 2 pp difference in energy-efficiency is mainly attributed to a more efficient use of the gas turbine in the ASU-based process. Without restricting the turbine inlet temperature (TIT) to 1125 °C, the advantage in energy-efficiency of the ASU-based process would likely disappear.

The LCOE of OTM-based processes depends strongly on the costs of membranes and modules. Whereas oxyfuel combustion processes require pure oxygen in coal gasification or natural gas reforming as well as in the gas turbine, pre-combustion processes require it only in the coal gasification or natural gas reforming sections. Hence,

for oxyfuel combustion processes the dependency of LCOE on membrane and module costs and area is stronger than for pre-combustion processes. The use of steam as oxidant in the pre-combustion IRCC further decreases the pure oxygen demand (POD) as compared with the pre-combustion IGCC process, and thereby as well the membrane area and the resulting LCOE. All in all, the specific pure oxygen demand differs by more than a factor 3 between the pre-combustion IRCC and oxyfuel IGCC processes (5.46 vs 17.32 mol pure O₂ kWh⁻¹), which is the main reason for the 26% lower LCOE of the former.

7.6.1. Outlook

A promising idea is to step away from using steam to drive a generator in IGCC plants. In an Allam cycle, supercritical CO₂ is used rather than steam as energy transport medium. The efficiency of Allam-cycle based plants is projected to be much closer to the Carnot efficiency than that of steam-based cycles^{45,90}. It is predicted that with the Allam cycle, both the capital investment and the operating costs could be lowered significantly compared to other power generation processes that operate CCS^{65,91}. In comparison with the most profitable modern generation coal-fired power plants that do not capture CO₂, the LCOE seems to be on par⁹¹, and in comparison with other carbon capturing processes, the estimated efficiency is high while the capture rate is high too⁹². However, this process has matured even less than other CCS processes. Gas turbines that operate with supercritical CO₂ as the working fluid are still in the prototype phase⁹³. In future research, it would be interesting to investigate the efficiency and economic viability of Allam cycle power plants with OTMs as oxygen supply technology.

References

1. G.S. Booras, S.C. Smelser. *An engineering and economic evaluation of CO₂ removal from fossil-fuel-fired power plants*. Energy. 1991; 16(11), pp. 1295-1305.
2. *The Global Status of CCS: 2016 Summary Report*. Global CCS Institute; 2016, <http://hub.globalccsinstitute.com/sites/default/files/publications/201158/global-status-ccs-2016-summary-report.pdf>

3. M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, *et al.* *Carbon capture and storage update*. Energy Environ. Sci. 2014; 7(1), pp. 130-189.
4. A.-M. Cormos, C.-C. Cormos. *Techno-economic evaluations of post-combustion CO₂ capture from sub- and super-critical circulated fluidised bed combustion (CFBC) power plants*. Appl. Therm. Eng. 2017; 127(Supplement C), pp. 106-115.
5. K.J. Borgert, E.S. Rubin. *Oxyfuel Combustion: Technical and Economic Considerations for the Development of Carbon Capture from Pulverized Coal Power Plants*. Energy Procedia. 2013; 37, pp. 1291-1300.
6. M. Kanniche, Y. Le Moullec, O. Authier, H. Hagi, D. Bontemps, T. Neveux, M. Louis-Louisy. *Up-to-date CO₂ Capture in Thermal Power Plants*. Energy Procedia. 2017; 114(Supplement C), pp. 95-103.
7. S. Goldenberg. Can Kemper become the first US power plant to use 'clean coal'? *The Guardian* 2014. <https://www.theguardian.com/environment/2014/mar/12/kemper-us-power-plant-coal-carbon>
8. J. Conca. The Largest Clean Coal Power Plant In America Turns To Natural Gas. *Forbes*. 2017. <https://www.forbes.com/sites/jamesconca/2017/07/11/the-largest-clean-coal-power-plant-in-america-turns-to-natural-gas/>.
9. O. Eiken, P. Ringrose, C. Hermanrud, B. Nazarian, T.A. Torp, L. Høier. *Lessons learned from 14 years of CCS operations: Sleipner, In Salah and Snøhvit*. Energy Procedia. 2011; 4, pp. 5541-5548.
10. C. Li, K. Zhang, Y. Wang, C. Guo, F. Maggi. *Experimental and numerical analysis of reservoir performance for geological CO₂ storage in the Ordos Basin in China*. Int. J. Greenh. Gas Con. 2016; 45, pp. 216-232.
11. P. Zakkour, M. Haines. *Permitting issues for CO₂ capture, transport and geological storage: A review of Europe, USA, Canada and Australia*. Int. J. Greenh. Gas Con. 2007; 1(1), pp. 94-100.
12. B.W. Terwel, E. ter Mors, D.D.L. Daamen. *It's not only about safety: Beliefs and attitudes of 811 local residents regarding a CCS project in Barendrecht*. Int. J. Greenh. Gas Con. 2012; 9, pp. 41-51.
13. NRG Energy, Inc. Petra Nova. <http://www.nrg.com/generation/projects/petra-nova/>. Accessed October 30, 2017.
14. SaskPower. Capturing Carbon and the World's Attention. <http://www.saskpower.com/our-power-future/carbon-capture-and-storage/capturing-carbon-and-the-worlds-attention/>. Accessed October 30, 2017.

15. Global CCS institute. Large Scale CCS facilities. <http://www.globalccsinstitute.com/projects/large-scale-ccs-projects>. Accessed 30 October, 2017.
16. M.A. Nemitallah, M.A. Habib, H.M. Badr, S.A. Said, A. Jamal, R. Ben-Mansour, E.M.A. Mokheimer, K. Mezghani. *Oxy-fuel combustion technology: current status, applications, and trends*. Int. J. Energ Res. 2017; 41(12), pp. 1670-1708.
17. B. Belaisaoui, Y. Le Moullec, H. Hagi, E. Favre. *Energy Efficiency of Oxygen Enriched Air Production Technologies: Cryogeny vs Membranes*. Energy Procedia. 2014; 63, pp. 497-503.
18. C. Kunze, S. De, H. Spliethoff. *A novel IGCC plant with membrane oxygen separation and carbon capture by carbonation–calcinations loop*. Int. J. Greenh. Gas Con. 2011; 5(5), pp. 1176-1183.
19. *Final Report Summary - DEMOYS (Dense membranes for efficient oxygen and hydrogen separation)*. 2013, http://cordis.europa.eu/result/rcn/158884_en.html
20. S.M. Kelly, S. Chakravarti, R.F. Drnevich, Inventors; Praxair Technology, Inc., assignee. Method and system for oxygen transport membrane enhanced integrated gasifier combined cycle (IGCC). US patent PCT/US2015/025052. 22 Oct, 2015.
21. S.M. Kelly, G.M. Christie, C. Robinson, J.R. Wilson, J.E. Gonzalez, U.R. Doraswami, Inventors; Praxair Technology, Inc., assignee. Ceramic oxygen transport membrane array, reforming reactor and valve assembly. US patent PCT/US2014/059463. 20 Aug, 2015.
22. Z. Lu, P.J. Plonczak, J.A. Lane, Inventors; Praxair Technology, Inc., assignee. Composite oxygen transport membrane. 2017.
23. S. Troy, A. Schreiber, P. Zapp. *Life cycle assessment of membrane-based carbon capture and storage*. Clean Technologies and Environmental Policy. 2016; 18(6), pp. 1641-1654.
24. G. Cau, V. Tola, P. Deiana. *Comparative performance assessment of USC and IGCC power plants integrated with CO₂ capture systems*. Fuel. 2014; 116, pp. 820-833.
25. R. Hoya, C. Fushimi. *Thermal efficiency of advanced integrated coal gasification combined cycle power generation systems with low-temperature gasifier, gas cleaning and CO₂ capturing units*. Fuel Processing Technology. 2017; 164, pp. 80-91.
26. P. Casero, P. Coca, F. García-Peña, N. Hervás. *20 - Case Study: ELCOGAS Puertollano IGCC power plant, Spain. Integrated Gasification Combined Cycle (IGCC) Technologies*. Woodhead Publishing; 2017:753-775.
27. E. de Visser, C. Hendriks, M. Barrio, M.J. Mølnvik, G. de Koeijer, S. Liljemark, Y. Le Gallo. *Dynamis CO₂ quality recommendations*. Int. J. Greenh. Gas Con. 2008; 2(4), pp. 478-484.

28. R. Anantharaman, O. Bolland. *Integration of Oxygen Transport Membranes in an IGCC power plant with CO₂ capture*. Chemical Engineering Transactions. 2011; 25, pp. 25-30.
29. D. Grainger, M.-B. Hägg. *Techno-economic evaluation of a PVAm CO₂-selective membrane in an IGCC power plant with CO₂ capture*. Fuel. 2008; 87(1), pp. 14-24.
30. P.E. Campbell, J.T. McMullan, B.C. Williams. *Concept for a competitive coal fired integrated gasification combined cycle power plant*. Fuel. 2000; 79(9), pp. 1031-1040.
31. P. Schley, M. Beck, M. Uhrig, *et al.* *Measurements of the Calorific Value of Methane with the New GERG Reference Calorimeter*. International Journal of Thermophysics. 2010; 31(4), pp. 665-679.
32. *The Air Gases Nitrogen, Oxygen and Argon. Industrial Gases Processing*: Wiley-VCH Verlag GmbH & Co. KGaA; 2008:9-109.
33. A. Schreiber, J. Marx, P. Zapp. *Environmental assessment of a membrane-based air separation for a coal-fired oxyfuel power plant*. Journal of Membrane Science. 2013; 440(Supplement C), pp. 122-133.
34. L. Duan, S. Sun, L. Yue, W. Qu, J. Bian. *Study on different zero CO₂ emission IGCC systems with CO₂ capture by integrating OTM*. Int. J. Energ Res. 2016; 40(10), pp. 1410-1427.
35. H. Stadler, F. Beggel, M. Habermehl, B. Persigehl, R. Kneer, M. Modigell, P. Jeschke. *Oxyfuel coal combustion by efficient integration of oxygen transport membranes*. Int. J. Greenh. Gas Con. 2011; 5(1), pp. 7-15.
36. S. Engels, F. Beggel, M. Modigell, H. Stadler. *Simulation of a membrane unit for oxyfuel power plants under consideration of realistic BSCF membrane properties*. J. Membr. Sci. 2010; 359(1), pp. 93-101.
37. J. Sunarso, S. Baumann, J.M. Serra, W.A. Meulenbergh, S. Liu, Y.S. Lin, J.C. Diniz da Costa. *Mixed ionic-electronic conducting (MIEC) ceramic-based membranes for oxygen separation*. J. Membr. Sci. 2008; 320(1-2), pp. 13-41.
38. M. Brisotto, F. Cernuschi, F. Drago, C. Lenardi, P. Rosa, C. Meneghini, M. Merlini, C. Rinaldi. *High temperature stability of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} and La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-δ} oxygen separation perovskite membranes*. J. Eur. Ceram. Soc. 2016; 36(7), pp. 1679-1690.
39. V. Esposito, M. Søgaaard, P.V. Hendriksen. *Chemical stability of La_{0.6}Sr_{0.4}CoO_{3-δ} in oxygen permeation applications under exposure to N₂ and CO₂*. Solid State Ionics. 2012; 227, pp. 46-56.
40. G. Pećanac, S. Baumann, J. Malzbender. *Mechanical properties and lifetime predictions for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} membrane material*. J. Membr. Sci. 2011; 385-386, pp. 263-268.

41. B. Liu, Q. Zong, X. Du, Z. Zhang, T. Xiao, H. AlMegren. *Novel sour water gas shift catalyst (SWGS) for lean steam to gas ratio applications*. Fuel Processing Technology. 2015; 134, pp. 65-72.
42. A.V. Rayer, A. Henni, P. Tontiwachwuthikul. *High pressure physical solubility of carbon dioxide (CO₂) in mixed polyethylene glycol dimethyl ethers (Genosorb 1753)*. The Canadian Journal of Chemical Engineering. 2012; 90(3), pp. 576-583.
43. J. Mletzko, S. Ehlers, A. Kather. *Comparison of Natural Gas Combined Cycle Power Plants with Post Combustion and Oxyfuel Technology at Different CO₂ Capture Rates*. Energy Procedia. 2016; 86(Supplement C), pp. 2-11.
44. R. Reimert, F. Marschner, H.J. Renner, W. Boll, E. Supp, M. Brejc, W. Liebner, G. Schaub. *Gas Production, 2. Processes*. Ullmann's Encyclopedia of Industrial Chemistry 2011.
45. R. Allam, S. Martin, B. Forrest, et al. *Demonstration of the Allam Cycle: An Update on the Development Status of a High Efficiency Supercritical Carbon Dioxide Power Process Employing Full Carbon Capture*. Energy Procedia. 2017; 114(Supplement C), pp. 5948-5966.
46. U. Unije, R. Mücke, P. Niehoff, S. Baumann, R. Vaßen, O. Guillon. *Simulation of the effect of the porous support on flux through an asymmetric oxygen transport membrane*. J. Membr. Sci. 2017; 524, pp. 334-343.
47. L. Blum, P. Batfalsky, Q. Fang, L.G.J. de Haart, J. Malzbender, N. Margaritis, N.H. Menzler, R. Peters. *SOFC Stack and System Development at Forschungszentrum Jülich*. J. Electrochem. Soc. 2015; 162(10), pp. F1199-F1205.
48. Sanjay. *Investigation of effect of variation of cycle parameters on thermodynamic performance of gas-steam combined cycle*. Energy. 2011; 36(1), pp. 157-167.
49. A. Giuffrida, S. Moiola, M.C. Romano, G. Lozza. *Lignite-fired air-blown IGCC systems with pre-combustion CO₂ capture*. Int. J. Energ Res. 2016; 40(6), pp. 831-845.
50. W.M. Summers, S.E. Herron, A. Zoelle. *Cost of Capturing CO₂ from Industrial Sources* National Energy Technology Laboratory (NETL); 2014, <https://www.netl.doe.gov/research/energy-analysis/search-publications/vuedetails?id=1836>
51. J. Philips. *Integrated Gasification Combined Cycle (IGCC) Design Considerations for High Availability*. Palo Alto CA, USA: Electric Power Research Institute (EPRI); 2007, 1. <https://www.epri.com/#/pages/product/1012226/>
52. J. Anderson, A. Fennell. *Calculate financial indicators to guide investments*. Chem. Eng. Prog. 2013; (Sept.), pp. 34-40.

53. G. Towler, R. Sinnott. *Chapter 7 – Capital Cost Estimating. Chemical Engineering Design (Second Edition)*. Boston: Butterworth-Heinemann; 2013:307-354.
54. M.M. El-Halwagi. *Sustainable Design Through Process Integration: Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement*. Waltham, USA: Elsevier Science; 2017.
55. W.D. Seider, J.D. Seader, D.R. Lewin. *Product & Process Design Principles: Synthesis, Analysis and Evaluation*. Third ed: John Wiley & Sons; 2009.
56. R.K. Sinnott, G. Towler. *Chemical engineering design: SI Edition*. Elsevier; 2009.
57. U.S. Energy Information Administration. United States Natural Gas Industrial Price. <https://www.eia.gov/dnav/ng/hist/n3035us3m.htm>. Accessed January 14, 2018.
58. EZB. EZB. Euro (EUR) to U.S. dollar (USD) annual average exchange rate from 1999 to 2017. *Statista – The Statistics Portal* <https://www.statista.com/statistics/412794/euro-to-u-s-dollar-annual-average-exchange-rate/>. Accessed January 14, 2018.
59. European Energy Exchange AG. Results EUA Primary Auction Spot. <https://www.eex.com/en/market-data/environmental-markets/auction-market/european-emission-allowances-auction/european-emission-allowances-auction-download>. Accessed December 22, 2017.
60. C. Wolfersdorf, B. Meyer. *The current status and future prospects for IGCC systems. Integrated Gasification Combined Cycle (IGCC) Technologies*: Woodhead Publishing; 2017:847-889.
61. J. Davison. *Criteria for technical and economic assessment of plants with low CO₂ emissions*. IEA Greenhouse Gas R&D Programme (IEA GHG); May 2009 2009, 2009/TR3.
62. J. Davison. *Performance and costs of power plants with capture and storage of CO₂*. *Energy*. 2007; 32(7), pp. 1163-1176.
63. P. Maas, N. Nauels, L. Zhao, P. Markewitz, V. Scherer, M. Modigell, D. Stolten, J.F. Hake. *Energetic and economic evaluation of membrane-based carbon capture routes for power plant processes*. *Int. J. Greenh. Gas Con.* 2016; 44(Supplement C), pp. 124-139.
64. P. Mathieu, O. Bolland. *Comparison of Costs for Natural gas Power Generation with CO₂ Capture*. *Energy Procedia*. 2013; 37(Supplement C), pp. 2406-2419.
65. Y. Le Moullec. *Conceptual study of a high efficiency coal-fired power plant with CO₂ capture using a supercritical CO₂ Brayton cycle*. *Energy*. 2013; 49, pp. 32-46.
66. I.M. Fund. IMF Primary Commodity Prices. <http://www.imf.org/external/np/res/commmod/index.aspx>. Accessed January 22, 2018.
67. F.A. Holland, J.K. Wilkinson. *Process Economics*. In: Perry R. H., ed. *Perry's Chemical Engineers' Handbook – International Edition*. 7th ed 1997.

68. M.J. den Exter, W.G. Haije, J.F. Vente. *Viability of ITM Technology for Oxygen Production and Oxidation Processes: Material, System, and Process Aspects*. In: Bose Arun C., ed. *Inorganic Membranes for Energy and Environmental Applications*: Springer New York; 2009:27-51.
69. L. Fleischman, R. Cleetus, J. Deyette, S. Clemmer, S. Frenkel. *Ripe for Retirement: An Economic Analysis of the U.S. Coal Fleet*. The Electricity Journal. 2013; 26(10), pp. 51-63.
70. E. Tzimas. *The Cost of Carbon Capture and Storage Demonstration Projects in Europe* European Commission Joint Research Centre Institute for Energy 2009, <http://dx.doi.org/10.2790/18793>
71. S. Jenkins. Economic Indicators: CEPCI. *Chemical Engineering*. 2015. <http://www.chemengonline.com/economic-indicators-cepci/>.
72. L.M. Abadie. *Operating flexibility at power plants: A market valuation*. International Journal of Electrical Power & Energy Systems. 2015; 64, pp. 41-49.
73. A. Ryzhkov, T. Bogatova, S. Gordeev. *Technological solutions for an advanced IGCC plant*. Fuel. 2018; 214(Supplement C), pp. 63-72.
74. D. Simbeck, D. Beecy. *The CCS paradox: The much higher CO₂ avoidance costs of existing versus new fossil fuel power plants*. Energy Procedia. 2011; 4, pp. 1917-1924.
75. M.A. Gonzalez-Salazar, T. Kirsten, L. Prchlik. *Review of the operational flexibility and emissions of gas- and coal-fired power plants in a future with growing renewables*. Renew. Sust. Energ. Rev. 2018; 82(Part 1), pp. 1497-1513.
76. H. Lion, S. Jan Christoph. *The role of capital costs in decarbonizing the electricity sector*. Environ. Res. Lett. 2016; 11(11), pp. 114010.
77. Tonziello, J.; Vellini, M., Oxygen production technologies for IGCC power plants with CO₂ capture. *Energy Procedia* **2011**, 4 (Supplement C), 637-644.
78. *Levelized Cost and Levelized Avoided Cost of New Generation Resources in the Annual Energy Outlook 2014*; U.S. Energy Information Administration: 2014.
79. Jülch, V., Comparison of electricity storage options using levelized cost of storage (LCOS) method. *Applied Energy* **2016**, 183 (Supplement C), 1594-1606.
80. Bhave, A.; Taylor, R. H. S.; Fennell, P.; Livingston, W. R.; Shah, N.; Dowell, N. M.; Dennis, J.; Kraft, M.; Pourkashanian, M.; Insa, M.; Jones, J.; Burdett, N.; Bauen, A.; Beal, C.; Smallbone, A.; Akroyd, J., Screening and techno-economic assessment of biomass-based power generation with CCS technologies to meet 2050 CO₂ targets. *Applied Energy* **2017**, 190, 481-489.

81. Sofia, D.; Coca Llano, P.; Giuliano, A.; Iborra Hernández, M.; García Peña, F.; Barletta, D., Co-gasification of coal–petcoke and biomass in the Puertollano IGCC power plant. *Chemical Engineering Research and Design* **2014**, 92 (8), 1428–1440.
82. Bucher, E.; Sitte, W., Long-term stability of the oxygen exchange properties of $(\text{La,Sr})_{1-x}(\text{Co,Fe})\text{O}_{3-\delta}$ in dry and wet atmospheres. *Solid State Ionics* **2011**, 192 (1), 480–482.
83. Wang, R.; Meng, B.; Meng, X.; Tan, X.; Sunarso, J.; Liu, L.; Liu, S., Highly stable $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fibre membrane for air separation swept by steam or steam mixture. *Journal of Membrane Science* **2015**, 479, 232–239.
84. Ramasamy, M.; Persoon, E. S.; Baumann, S.; Schroeder, M.; Schulze-Küppers, F.; Görtz, D.; Bhawe, R.; Bram, M.; Meulenberg, W. A., Structural and chemical stability of high performance $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ – FeCo_2O_4 dual phase oxygen transport membranes. *Journal of Membrane Science* **2017**, 544, 278–286.
85. Bermudez, J. M.; Garcia-Fayos, J.; Reina, T. R.; Reed, G.; Persoon, E. S.; Görtz, D.; Schroeder, M.; Millan, M.; Serra, J. M., Thermochemical stability of $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ and NiFe_2O_4 – $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$ under real conditions for its application in oxygen transport membranes for oxyfuel combustion. *Journal of Membrane Science* **2018**.
86. Benson, S. J.; Waller, D.; Kilner, J. A., Degradation of LSCF6428 in Carbon Dioxide and Water Atmospheres. *Journal of The Electrochemical Society* **1999**, 146 (4), 1305 – 1309.
87. Serra, J. M.; Garcia-Fayos, J.; Baumann, S.; Schulze-Kueppers, F.; Meulenberg, W. A., Oxygen permeation through tape-cast asymmetric all- $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membranes. *Journal of Membrane Science* **2013**, 447, 297–305.
88. Vibhu, V.; Rougier, A.; Nicollet, C.; Flura, A.; Fourcade, S.; Penin, N.; Grenier, J. C.; Bassat, J. M., $\text{Pr}_4\text{Ni}_3\text{O}_{10+\delta}$: A new promising oxygen electrode material for solid oxide fuel cells. *Journal of Power Sources* **2016**, 317, 184–193.
89. Belousov, V. V., Next-Generation Electrochemical Energy Materials for Intermediate Temperature Molten Oxide Fuel Cells and Ion Transport Molten Oxide Membranes. *Accounts of Chemical Research* **2017**, 50 (2), 273–280.
90. Ahn, Y.; Bae, S. J.; Kim, M.; Cho, S. K.; Baik, S.; Lee, J. I.; Cha, J. E., Review of supercritical CO_2 power cycle technology and current status of research and development. *Nuclear Engineering and Technology* **2015**, 47 (6), 647–661.
91. Service, R. F., Fossil power, guilt free. *Science* **2017**, 356 (6340), 796–799.
92. Weiland, N. T.; White, C. W., Techno-economic analysis of an integrated gasification direct-fired supercritical CO_2 power cycle. *Fuel* **2018**, 212, 613–625.

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93. Allison, T. C.; Moore, J.; Pelton, R.; Wilkes, J.; Ertas, B., Turbomachinery. In *Fundamentals and Applications of Supercritical Carbon Dioxide (sCO₂) Based Power Cycles*, Friedman, P.; Dennis, R., Eds. Woodhead Publishing: 2017; pp 147-215.

Appendix A7

Fuel analysis

The higher heating value (HHV) of the coal/pet-coke mixture used in all coal-fired plants can be calculated using the following empirical equation ⁹⁴:

$$\text{HHV} = 0.0211m_a + 0.3491m_c + 1.1783m_h + 0.0151m_n - 0.1034m_o + 0.1005m_s \quad (\text{A7.1.1})$$

in which m with subscripts a, c, h, n, o, and s represent the mass fractions of ash, carbon, hydrogen, nitrogen, oxygen, and sulphur, respectively. Values of these parameters are listed in Table A7.10.

The lower heating value (LHV) is calculated by taking the formation of water vapor into account,

$$\text{LHV} = \text{HHV} - m_w \Delta H_{\text{vap}} \quad (\text{A7.1.2})$$

$$m_w = M + 9H + \gamma_a w_a \quad (\text{A7.1.3})$$

in which m_w represents the mass of water formed upon combustion of coal, m_m the fraction of moisture in as-received coal expressed in kg H₂O / kg coal, ΔH_{vap} the latent heat of vaporization of water, γ_a the relative humidity of air used in the combustion process in the gas turbine, and w_a the air mass supplied in the combustion process per kg of coal. Furthermore, natural gas was assumed to consist of pure methane (CH₄). The HHV of methane is 890.6 kJ mol⁻¹ ⁹⁶, or 55.52 MJ kg⁻¹ when expressed in a mass-based unit.

Process designs and stream properties

Figure A7.2, displayed on the next page, shows the process flow diagram (PFD) of the simulated unabated reference Integrated Gasification Combined Cycle (IGCC) power plant. On the following pages, Table A7.2 indicates temperature, pressure, total flow, mass vapor fraction X , and composition of each of the streams. The labeling of the streams is denoted in the PFD; prefixes I, O, and S represent input, output, and internal streams,

Table A7.10. Properties of coal/pet-coke mixture and of its combustion. *Values resulting from proximate and ultimate analyses were obtained by personal correspondence with ELCOGAS.

	Unit	Value	Reference
Moisture	wt% of coal in proximate analysis	9.4	*
Ash	wt% of coal in ultimate analysis	22.85	
Carbon	wt% of coal in ultimate analysis	65.35	
Hydrogen	wt% of coal in ultimate analysis	3.09	
Nitrogen	wt% of coal in ultimate analysis	1.50	
Oxygen	wt% of coal in ultimate analysis	3.66	
Sulfur	wt% of coal in ultimate analysis	3.54	
γ_a	%	45	Assumed
w_a	kg air kg ⁻¹ coal	0.900	From Aspen Plus simulation
ΔH_{vap}	MJ kg ⁻¹	2.395	⁹⁵
HHV	MJ kg ⁻¹	26.94	
LHV	MJ kg ⁻¹	25.07	

respectively. Similar figures of the other process designs discussed in Chapter 7 will be made available online as supplementary information of the publication.

In Fig. A7.2, input streams are marked green and output streams are marked blue. A zero in Table A7.2 indicates the presence of the component with a molar fraction below 0.0005, and a dash (-) the total absence of a component. Molar fractions above 0.999 were truncated rather than rounded and trailing zeroes were removed from all values. Molar fractions were listed for the most abundant molecules only; hence, the sum of the shown fractions is not necessarily equal to unity. Streams which mainly contain impurities may show a sum of molar fractions far below unity. The composition of the coal/pet-coke mixture cannot be expressed by the fractions used in Table A7.2; instead, the reader is directed to Table A7.1 in which the specifications of the mixture are listed.

Fig. A7.2. IGCC w/o carbon capture

Table A7.2. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture							
Property	Unit	Stream					
Mol fraction		I1	I2	I3	I4	I5 (COAL)	I6
O ₂	[-]	0.209	0.85	-	-	n.a.	0.018
H ₂ O	[-]	-	-	1	-	n.a.	-
H ₂	[-]	-	-	-	-	n.a.	-
CO	[-]	-	-	-	-	n.a.	-
CO ₂	[-]	4E-4	-	-	-	n.a.	-
N ₂	[-]	0.781	0.145	-	1	n.a.	0.982
Ar	[-]	0.009	0.005	-	-	n.a.	-
Mass flow	kg s ⁻¹	463.9	25.71	0.145	2.54	29	67.23
X	[-]	1	1	0	1	0	1
Temperature	°C	15	85	195	60	15	359
Pressure	bar	1.013	23	34	25	1	18.4

Table A7.2 - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture						
Property	Unit	Stream				
Mol fraction		O1	O2	O3 (SLAG)	O4 (NO _x)	O5 (SO _x)
O ₂	[-]	0.209	0.104	-	-	-
H ₂ O	[-]	-	0.035	-	-	-
H ₂	[-]	-	0	-	-	-
CO	[-]	-	0	-	-	-
CO ₂	[-]	4E-4	0.092	-	-	-
N ₂	[-]	0.781	0.761	-	-	-
Ar	[-]	0.009	0.007	-	-	-
Mass flow	kg s ⁻¹	122.4	459	6.003	0.002	1.08
X	[-]	1	1	0	1	1
Temperature	°C	194.2	135	1493	235	235
Pressure	bar	14.2	0.96	25	24	24

Table A7.2. - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture									
Property	Unit	Stream							
Mol fraction		S1	S2	S3	S4	S5	S6	S7	S8
O ₂	[-]	0.209	0.209	0.209	0.209	0.209	0.209	0.209	0.209
H ₂ O	[-]	-	-	-	-	-	-	-	-
H ₂	[-]	-	-	-	-	-	-	-	-
CO	[-]	-	-	-	-	-	-	-	-
CO ₂	[-]	4E-4	4E-4	4E-4	4E-4	4E-4	4E-4	4E-4	4E-4
N ₂	[-]	0.781	0.781	0.781	0.781	0.781	0.781	0.781	0.781
Ar	[-]	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
Mass flow	kg s ⁻¹	154.5	154.5	154.9	154.5	154.5	154.9	463.9	463.9
X	[-]	1	1	1	1	1	1	1	1
Temperature	°C	15	15	15	194.2	194.2	194.2	194.2	35
Pressure	bar	1.013	1.013	1.013	4.2	4.2	4.2	4.2	4.2

Table A7.2. - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture									
Property	Unit	Stream							
Mol fraction		S9	S10	S11	S12	S13	S14	S15	S16
O ₂	[-]	0.209	0.209	0.209	0.209	0.209	0.209	0.209	0.209
H ₂ O	[-]	-	-	-	-	-	-	-	-
H ₂	[-]	-	-	-	-	-	-	-	-
CO	[-]	-	-	-	-	-	-	-	-
CO ₂	[-]	4E-4	4E-4	4E-4	4E-4	4E-4	4E-4	4E-4	4E-4
N ₂	[-]	0.781	0.781	0.781	0.781	0.781	0.781	0.781	0.781
Ar	[-]	0.009	0.009	0.009	0.009	0.009	0.009	0.009	0.009
Mass flow	kg s ⁻¹	154.5	154.5	154.9	154.5	154.5	154.9	463.9	341.5
X	[-]	1	1	1	1	1	1	1	1
Temperature	°C	35	35	35	194.2	194.2	194.2	194.2	194.2
Pressure	bar	4.2	4.2	4.2	14.2	14.2	14.2	14.2	14.2

Table A7.2. - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture									
Property	Unit	Stream							
Mol fraction		S17	S18	S19	S20	S21	S22	S23	S24
O ₂	[-]	-	-	-	-	-	-	-	-
H ₂ O	[-]	0.104	0.104	0.104	0.104	0.104	0.104	0.758	0.048
H ₂	[-]	0.035	0.035	0.035	0.035	0.035	0.035	0.009	0.241
CO	[-]	0	0	0	0	0	0	-	0.642
CO ₂	[-]	0	0	0	0	0	0	-	-
N ₂	[-]	0.092	0.092	0.092	0.092	0.092	0.092	-	-
Ar	[-]	0.761	0.761	0.761	0.761	0.761	0.761	0.228	0.022
Mass flow	kg s ⁻¹	459	459	459	459	459	459	28.4	29
X	[-]	1	1	1	1	1	1	1	0.078
Temperature	°C	1136	567	525	501.9	280	261.6	73.1	15
Pressure	bar	16	0.96	0.96	0.96	0.96	0.96	23	1

Table A7.2. - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture									
Property	Unit	Stream							
Mol fraction		S25	S26	S27	S28	S29	S30	S31	S32
O ₂	[-]	0	0	-	0	-	0	0	0
H ₂ O	[-]	0.044	0.044	1	0.044	1	0.044	0.044	0.044
H ₂	[-]	0.198	0.198	-	0.198	-	0.198	0.198	0.198
CO	[-]	0.606	0.606	-	0.606	-	0.606	0.606	0.606
CO ₂	[-]	0.037	0.037	-	0.037	-	0.037	0.037	0.037
N ₂	[-]	0.101	0.101	-	0.101	-	0.101	0.101	0.101
Ar	[-]	0.002	0.002	-	0.002	-	0.002	0.002	0.002
Mass flow	kg s ⁻¹	51.39	128.6	70.83	128.6	13.33	128.6	128.6	51.39
X	[-]	1	1	0	1	0	1	1	1
Temperature	°C	1493	766.5	307	370	195	235	235	235
Pressure	bar	25	24	126.5	24	34	24	24	24

Table A7.2 - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture									
Property	Unit	Stream							
Mol fraction		S33	S34	S35	S36	S37	S38	S39	S40
O ₂	[-]	0	0	-	-	-	-	-	-
H ₂ O	[-]	0.046	0.046	1	1	1	1	1	1
H ₂	[-]	0.2	0.2	-	-	-	-	-	-
CO	[-]	0.614	0.614	-	-	-	-	-	-
CO ₂	[-]	0.037	0.037	-	-	-	-	-	-
N ₂	[-]	0.102	0.102	-	-	-	-	-	-
Ar	[-]	0.002	0.002	-	-	-	-	-	-
Mass flow	kg s ⁻¹	50.31	50.31	70.83	13.33	13.33	84.17	70.83	70.83
X	[-]	1	1	0.725	0.831	1	1	1	1
Temperature	°C	126	260	327.8	240.6	505	356.9	511	329
Pressure	bar	24	24	126.5	34	33	33	124.5	33

Table A7.2 - continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture									
Property	Unit	Stream							
Mol fraction		S41	S42	S43	S44	S45	S46	S47	S48
O ₂	[-]	-	-	-	-	-	-	-	-
H ₂ O	[-]	1	1	1	1	1	1	1	1
H ₂	[-]	-	-	-	-	-	-	-	-
CO	[-]	-	-	-	-	-	-	-	-
CO ₂	[-]	-	-	-	-	-	-	-	-
N ₂	[-]	-	-	-	-	-	-	-	-
Ar	[-]	-	-	-	-	-	-	-	-
Mass flow	kg s ⁻¹	84.17	84.17	84.17	84.17	84.17	84.17	15.6	68.7
X	[-]	1	1	1	0	0	0	0	0
Temperature	°C	518	292.7	18.5	50.6	50.9	204.1	204.1	204.1
Pressure	bar	33	5	0.11	0.11	34	34	34	34

Table A7.2 – continued. Stream contents and properties in the unabated reference IGCC process.

IGCC w/o carbon capture						
Property	Unit	Stream				
Mol fraction		S49	S50	S51	S52	S53
C	[-]	-	-	-	-	-
O ₂	[-]	-	-	-	0	0
H ₂ O	[-]	1	1	1	0.044	0.044
H ₂	[-]	-	-	-	0.198	0.198
CO	[-]	-	-	-	0.606	0.606
CO ₂	[-]	-	-	-	0.037	0.037
N ₂	[-]	-	-	-	0.101	0.101
Ar	[-]	-	-	-	0.002	0.002
Mass flow	kg s ⁻¹	68.57	68.57	68.57	77.24	77.24
X	[-]	0	0.74	0	1	1
Temperature	°C	206.4	327.8	307	235	235
Pressure	bar	126.5	126.5	126.5	24	24

Discrete modeling of the oxygen flux through a planar OTM membrane

In the model used for modelling the oxygen flux through the planar OTM membrane, oxygen permeation is assumed to be fully governed by solid state diffusion through the membrane. Resistances due to oxygen surface exchange, gas phase diffusion of oxygen towards the membrane surface, and mixing of the gas in the module are considered to be insignificant relative to the resistance due to solid state diffusion. It is further assumed that no temperature gradients over the membrane exist. The governing equation describing diffusional transport of oxygen across the OTM membrane is the Wagner equation ⁹⁷,

$$J_{O_2} = \frac{RT}{4^2 F^2 a} \int_{\ln p'_{O_2}}^{\ln p''_{O_2}} \frac{\sigma_e \sigma_i}{\sigma_e + \sigma_i} d \ln p_{O_2} \quad (A7.3.1)$$

where T is the temperature, a the membrane thickness, σ_e and σ_i are the electronic and ionic conductivities, respectively, and p_{O_2} and p'_{O_2} the oxygen partial pressures maintained at the feed and permeate sides of the membrane, respectively. For the perovskite oxide

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428), the electronic conductivity prevails over the ionic conductivity, which allows simplification of Eq. A7.3.1 into

$$J_{O_2} = \frac{RT}{4^2 F^2 a} \int_{\ln p'_{O_2}}^{\ln p''_{O_2}} \sigma_i d \ln p_{O_2} \quad (\text{A7.3.2})$$

The ionic conductivity of LSCF6428 at conditions relevant to this study can be approximated by the power law expression

$$\sigma_i = \sigma_i^0 p_{O_2}^n \quad (\text{A7.3.3})$$

Substitution in Eq. A7.3.2 gives

$$J_{O_2} = \frac{RT \sigma_i^0}{(4F)^2 n a} (p_{O_2}^n - p'_{O_2}{}^n) \quad (\text{A7.3.4})$$

Oxygen permeation across the OTM can be schematically represented by Fig. A7.3. At either side of the membrane, the oxygen concentration at coordinate i along the flow direction is different from that at a nearby point $i+1$. Gas phase diffusion tends to equalize both concentrations. Assuming that no exchange of oxygen by gas phase diffusion occurs between ‘packages’ traveling along either side of the membrane, the mass balance equations at both sides membranes read

Figure A7.3. Schematic representation of the OTM after discretization. A countercurrent flow is assumed for feed and permeate gases.

$$\frac{\partial c(x, t)}{\partial t} = -\frac{\partial F(x, t)}{\partial V} - \frac{J_{O_2}(x, t) \partial A}{\partial V} \quad (\text{A7.3.5})$$

$$\frac{\partial c'(x, t)}{\partial t} = \frac{\partial F'(x, t)}{\partial V'} + \frac{J_{O_2}(x, t) \partial A}{\partial V'} \quad (\text{A7.3.6})$$

In these equations, c is the oxygen concentration in the gas phase, F the oxygen molar flow rate, A the incremental surface area, x the length coordinate, and t the time. The prime notation is used to denote the various parameters at the permeate side of the membrane. At steady-state conditions, Eqs. A7.3.5 and A7.3.6 simplify to

$$\frac{\partial F(x)}{\partial x} = b J_{O_2}(x) \quad (\text{A7.3.7})$$

$$\frac{\partial F'(x)}{\partial x} = -b J_{O_2}(x) \quad (\text{A7.3.8})$$

where b represents the width of the membrane.

Because of the difficulty in solving Eqs. A7.3.5 and A7.3.6 analytically, both equations were discretized and solved self-consistently by means of iteration (using Microsoft Excel). The discretized forms of both equations can be represented by

$$c(i, k + 1) = c(i, k) - \frac{F(i + 1, k) - F(i, k) + \Delta x b J_{O_2}(i, k)}{\Delta V} \Delta t \quad (\text{A7.3.9})$$

$$c'(i, k + 1) = c'(i, k) + \frac{F'(i + 1, k) - F'(i, k) + \Delta x b J_{O_2}(i, k)}{\Delta V'} \Delta t \quad (\text{A7.3.10})$$

The number of elements ranges between $i = 1$ and $i = N$.² The parameter Δt is the time step per iteration, the total passed time is $k\Delta t$. As a rule of thumb, the time step was chosen two orders of magnitudes smaller than the average residence time of the gas in the OTM unit. The concentration of oxygen at both sides of the membrane in any element was regarded as uniform. The oxygen flux $J_{O_2}(i, k)$ for element i after the k^{th} iteration is calculated using Eq. A7.3.4, which reads after discretization

² Note from Fig. SI3.1 and Eq. SI3.13 that virtual element number $N+1$ is used for defining the inlet molar flow rate at the permeate side of the membrane.

$$J_{O_2}(i, k) = \frac{RT\sigma_i^0}{(4F)^2na} (p_{O_2}(i, k)^n - p'_{O_2}(i, k)^n) \quad (A7.3.11)$$

where the oxygen partial pressures on either side of the membrane are calculated using the ideal gas law. The molar flow rates of oxygen at the inlets at both sides of the membrane are invariant with time and are calculated from (using the ideal gas law),

$$F(1) = \frac{Gp_{O_2(\text{inlet})}}{RT} \quad (A7.3.12)$$

$$F'(N+1) = \frac{G'p'_{O_2(\text{inlet})}}{RT} \quad (A7.3.13)$$

where the quantities G and G' are the total volumetric flow rates, and $p_{O_2(\text{inlet})}$ and $p'_{O_2(\text{inlet})}$ the corresponding oxygen partial pressures at the inlet of the feed and permeate side of the membrane, respectively. The molar flow rates for other elements are calculated from the mass balance equations,

$$F(i+1, k) = F(i, k) + \Delta x b J_{O_2}(i, k) \quad (A7.3.14)$$

$$F'(i+1, k) = F'(i, k) - \Delta x b J_{O_2}(i, k) \quad (A7.3.15)$$

Note that these equations are the discretized forms of Eqs. A7.3.7 and A7.3.8, and are strictly speaking only valid at steady state conditions. Once the iteration procedure has reached steady-state, the total oxygen flux through the OTM equals

$$J_{O_2, \text{tot}} = \frac{F(N+1) - F(1)}{A} = \frac{F'(1) - F'(N+1)}{A} \quad (A7.3.16)$$

Table A7.3. Parameters used in calculation of the oxygen flux through the OTM and calculated membrane area for each of the process designs.

Parameter	Unit	Process			
		Oxyfuel	Pre-combustion	Pre-combustion	Oxyfuel
		IGCC	IGCC	IRCC	NGCC
T	K	1123	1123	1123	1123
σ_i^0	S m ⁻¹	12.94	12.94	12.94	12.94
n	-	0.43	0.43	0.43	0.43
a	mm	0.1	0.1	0.1	0.1
b	m	10 ⁵	10 ⁵	10 ⁵	10 ⁵
θ	-	0.5	0.5	0.5	0.5
$J_{O_2, \text{tot}}$	kmol s ⁻¹	1.670	0.699	0.432	1.536
Feed side					
G	m ³ s ⁻¹	707.3	296.2	182.9	650.4
$p_{O_2(\text{inlet})}$	bar	2.1	2.1	2.1	2.1
Sweep side		Steam	Air	Steam	CO ₂
G'	m ³ s ⁻¹	196.5	82.31	51.84	180.7
$p'_{O_2(\text{inlet})}$	bar	1·10 ⁻⁵	0.21	1·10 ⁻⁵	1·10 ⁻⁵
$p'_{O_2(\text{outlet})}$	%	77.8	77.8	77.8	77.8
Calculated membrane area					
A_{tot}	m ²	116200	66400	41200	141800

Iterative calculations of the oxygen flux were performed for the OTM, operating at 1123 K, for a given thickness a , oxygen partial pressure at the permeate side outlet of the membrane $p'_{O_2(\text{outlet})}$, and stage cut θ . Corresponding values of σ_i^0 and n values were derived from experimental data of the oxygen flux through LSCF6428 membranes⁹⁸⁻¹⁰⁰. Values of G and G' were obtained from the Aspen Plus calculation used for simulation of the different process designs (See main text). The membrane area A was adapted until $F'(1)$ matched the Pure Oxygen Demand (POD) specified by the Aspen Plus simulation

for each of the process designs. Table A7.3 lists parameters used in the oxygen flux modeling and the calculated membrane areas needed for each of the process designs.

CapEx calculation

Estimations of the cost of purchased equipment C_p were performed with the parametric cost function ¹⁰¹

$$C_p = a + b \cdot S^n \quad (\text{A7.4.1})$$

Cost constants a (expressed in \$), b (expressed in the inverted unit of S multiplied by \$), and n (without unit), were obtained from literature ¹⁰¹. The unit in which the cost governing parameter S is expressed differs between equipment types, as the quantity that indicates the size of different equipment types differs as well. For example, the value of S of a blower is related to its gas flow rate, and the unit in which S is expressed is then $\text{m}^3 \text{h}^{-1}$. Values of S were directly obtained from the Aspen Plus simulations if available. For heat exchangers and flash and pressure vessels, the value of S could not be retrieved from the Aspen Plus simulation directly. The area of heat exchangers and coolers was calculated using

$$A = \frac{Q}{U \cdot LMTD} \quad (\text{A7.4.2})$$

with A the heat-exchanging area in m^2 , Q the duty in W , $LMTD$ the logarithmic mean temperature difference ¹⁰¹, and U the heat transfer coefficient in $\text{W m}^{-2} \text{K}^{-1}$. Values for the heat transfer coefficient depend on the hot and cold medium, and are 160, 65, and $30 \text{ W m}^{-2} \text{K}^{-1}$ for gas / liquid, gas / high pressure steam, and gas / gas media combinations, respectively ¹⁰². For all pressure vessels and flash vessels, the shell mass was taken as the cost governing parameter. The shell mass was calculated based on the volume, material type and wall thickness of the vessel. The shell surface area was determined based on the ratio between height and diameter (ranging between 2.5 and 6, increasing with pressure) and the required volume. Finally, for more complex equipment (gasifier, reformer, and gas turbine), values of C_p were estimated by experts in personal correspondence.

To calculate the cost of installed equipment, the cost of purchased equipment was multiplied by the installation factor H , following the method proposed by Hand¹⁰¹:

$$C_i = C_p H \quad (\text{A7.4.3})$$

Table A7.4.1 shows the values of the constants, which are valid for the year 2010 (at which the Chemical Engineering Plant Cost Index (CEPCI) was 550.8¹⁰³).

Table A7.4.1. Sizing variable S , cost constants a , b , and n , and installation factor H for commonly used categories of equipment. Reprinted from Ref. 100, with permission from Elsevier.

		S	a [\$ ₂₀₁₄]	b [various units]	n [-]	H [-]
Equipment type						
Boiler	steam production [kg h ⁻¹]		130,000	53	0.9	4
Blower	Gas flow rate [m ³ h ⁻¹]		4,450	57	0.8	2.5
Compressor, centrifugal	Driver power [kW]		580,000	20,000	0.6	2.5
Heat exchanger, shell and tube	Area [m ²]		28,000	54	1.2	3.5
Furnace	Duty [MW]		80,000	109,000	0.8	2
Pressure vessel, vertical	Shell mass [kg]		11,600	34	0.85	4
Pump, centrifugal	Flow rate [L s ⁻¹]		8,000	240	0.9	4
Condensing steam turbine	Power [kW]		-14,000	1,900	0.75	3.5
Cooling tower	Flow rate [L s ⁻¹]		170,000	1,500	0.9	1

The Inside Battery Limits (ISBL) cost was calculated according to ¹⁰¹:

$$\text{ISBL}[\$_{2014}] = \sum C_i \frac{\text{CEPCI}_{2014}}{\text{CEPCI}_{2010}} \quad (\text{A7.4a})$$

$$\text{ISBL}[\$_{2014}] = \text{ISBL}[\$_{1997}] \sum \frac{\text{CEPCI}_{2014}}{\text{CEPCI}_{1997}} \quad (\text{A7.4b})$$

in which CEPCI_y corresponds to the value of the index in the year y . Equation A7.4a was used to calculate the ISBL cost in the year 2014 of the processes simulated with Aspen Plus, while the ISBL cost of the Puertollano reference plant in the year 2014 was calculated using Eq. A7.4b and the literature ISBL value for the year 1997 ¹⁰⁴. Location factors were not accounted for, whereas inflation was corrected for by the CEPCI. Table A7.4.2 lists the CEPCI values for the years 1997, 2010, and 2014 which were used in the calculation of ISBL in the reference year 2014.

Table A7.4.2. CEPCI values used in this study.

Year	CEPCI index value	Source
1997	368	100
2010	550.8	102
2014	576.1	105

Table A7.4.3 shows the values of the ISBL cost per plant section, based on literature for the reference plant ¹⁰⁴ and based on calculations using Eqs. A7.4.1 – A7.4.4 for all processes simulated with Aspen Plus including the unabated reference IGCC process. The cost of auxiliary equipment (called balance of plant) was not derived from the simulations but assumed to be equal to that of the Puertollano IGCC plant for each of the processes. OTMs and modules were depreciated to zero value in seven years, which is the expected lifetime. However, the assembly (tubing, auxiliary equipment and instrumentation) related to oxygen production is assumed have the same lifetime as the rest of the plant (20 years).

The total ISBL cost including and excluding the cost of OTMs and modules are abbreviated as ISBL and ISBL_e, respectively. Both are shown in Table A7.4.3. The total depreciable capital (TDC) is calculated by ¹⁰¹

$$\begin{aligned} \text{TDC} &= \text{ISBL} + \text{OSBL} + \text{EPC} + \text{CC} \\ &= \text{ISBL} + 0.2 \cdot \text{ISBL} + 2 \cdot 0.1 \sum (\text{ISBL} + \text{OSBL}) \end{aligned} \quad (\text{A7.4.5})$$

Modifications outside the plant infrastructure (OSBL), Engineering, Procurement and Construction (EPC), and Contingency Charges (CC) were all calculated based on the ISBL cost. Note that the values used here are at the optimistic ends of the given ranges ¹⁰¹. Table A7.4.4. shows the values of the TDC for all process designs.

Table A7.4.3. ISBL cost of each of the processes, shown per plant section, Values including and excluding costs of OTMs and modules are given, expressed in 10⁶ \$₂₀₁₄.

Section	Process						
	IGCC w/o	IGCC w/o	Oxyfuel	Pre-combustion	Pre-combustion	Pre-combustion	Oxyfuel
	CC – lit. ¹⁰³	CC -	IGCC	IGCC w/ASU	IGCC w/OTM	IRCC	NGCC
	simulation						
Gasification & Reforming	315	176	104	72	70	98	-
Membrane island or ASU – incl./excl. OTMs and modules	44	109	859/289	156	374/135	230/81	819/295
CO ₂ separation & compression	-	-	50	46	46	47	32
Power Island	214	250	295	209	200	176	186
Balance of plant	197	197	197	197	197	197	197
Gas cleaning	-	-	-	-	-	-	-
ISBL / ISBL _e	769 / 769	732 / 732	1504 / 935	678 / 678	887 / 647	748 / 599	1233 / 710

Table A7.4.4. Total Depreciable Capital (TDC) including OTMs and modules, values expressed in 10⁶ \$₂₀₁₄.

Process								
Cost	IGCC w/o CC	IGCC w/o CC	Oxyfuel	Pre-combustion	Pre-combustion	Pre-combustion	Pre-combustion	Oxyfuel
type	literature	simulation	IGCC	IGCC + ASU	IGCC + OTM	IRCC	NGCC	
ISBL	769	732	1504	678	887	748	1233	
OSBL	154	146	301	136	177	150	247	
EPC	92	88	181	81	106	90	148	
CC	92	88	181	81	106	90	148	
TDC	1108	1055	2166	977	1277	1077	1776	

OpEx calculation

Table A7.5 shows the result of OpEx calculations for the pre-combustion IRCC process. Nomenclature used in this table is explained in Appendix A7.8. Costs of all types but feedstock and emissions were estimated based on values and equations from literature ^{101, 106}.

Fuel and utility costs have been discussed in Appendix A7.1. The CO₂ allowance price was calculated to be €₂₀₁₄5.58 t⁻¹CO₂ or \$₂₀₁₄6.98 t⁻¹ when recalculated into dollars, based on the mean daily price at the EEX spot primary market for CO₂ through the years 2013 – 2017 ¹⁰⁷. To calculate MW&B, the TDC excluding OTMs and modules but including membrane assembly was taken (further abbreviated to TDC_e). Omission of costs for OTMs and modules was justified by the assumption that OTMs do not to require any maintenance during their 7 years of service life, while the heat exchangers, compressors, piping and valves do require maintenance.

Table A7.5. Overview of OpEx for the pre-combustion IRCC process.

Category	Type	Value	Unit	Cost [10 ⁶ \$ ₂₀₁₄]
Variable costs				
Feedstock				
	Coal	3.31	€ GJHHV ⁻¹	0
	Pet-coke	1.53	€ GJHHV ⁻¹	0
	Natural gas	5.27	€ GJHHV ⁻¹	113
	Utilities	4.5	10 ⁶ \$	4.5
Emissions	CO ₂ allowance	6.98	\$ ton _{CO₂} ⁻¹	3.0
Fixed costs				
Operations				
	Direct wages and benefits (DW&B)	35	\$ h ⁻¹	3.6
	Supervision and engineering	15	% of DW&B	0.5
	Operating supplies and services	6	% of DW&B	0.2
	Technical assistance to manufacturing	60,000	\$/OSY	3.0
	Control laboratory	65,000	\$/OSY	3.3
Maintenance (M)				
	Wages and benefits (MW&B)	4.5	% of TDC _e	38.8
	Supervision and engineering	25	% of MW&B	9.7
	Materials and services	100	% of MW&B	38.8
	Maintenance overhead	5.0	% of MW&B	1.9
Operating overhead (O)				
	General plant overhead	7.1	% of SW&B	3.8
	Mechanical department services	2.4	% of SW&B	1.3
	Employee relations department	5.9	% of SW&B	3.1
	Business services	7.4	% of SW&B	3.9
Property taxes and insurance				
		2.0	% of TDC	21.5
OpEx				254

Net present value (NPV) analysis

The levelized cost of electricity (LCOE) is calculated by means of a net present value (NPV) analysis ¹⁰⁸ in which the LCOE is chosen such that the NPV after 20 years of production equals zero, represented mathematically by

$$\text{NPV}_{20}(\text{LCOE}) = 0 \quad (\text{A7.6.1})$$

To calculate the NPV, the annual cash flow C was determined for each of the 20 years ¹⁰⁸:

$$C = \text{Revenues} - \text{Taxes} - \text{FCOP} - \text{VCOP} - \text{Investment} \quad (\text{A7.6.2})$$

in which Variable Costs Of Production (VCOP) and fixed costs of production (FCOP) are defined by

$$\text{VCOP} = \text{Raw materials} + \text{Utilities} + \text{Emission allowances} \quad (\text{A7.6.3})$$

$$\text{FCOP} = \text{OpEx} - \text{VCOP} \quad (\text{A7.6.4})$$

Initial investments are done in the years -2 to 0, where 0 is the year of the production start. Equipment is assumed to have a lifetime of 20 years, equal to the analysis period of the NPV analysis. As the only exception, the OTMs and modules are replaced every seven years.

Table A7.6.1. Cost schedule during building and starting up.

Year	Costs	Revenue
-2	30% of TCI	0
-1	50% of TCI + 100% investment for OTMs, modules and assembly;	0
0	20% of TCI; FCOP; 30% of VCOP	30% of max. revenue
1	FCOP; 90% of VCOP	90% of max. revenue
2	FCOP; VCOP	Max. revenue

Table A7.6.1 shows the cost schedule for the first five years of the analysis, where the investment is expressed as a percentage of TCI.

Depreciation is a virtual expense which is not included in the cash flow, however, the taxable income is affected by deducting depreciation from the revenue. The yearly depreciation is calculated by taking 14.3% of TDC_m plus 5% of TDC_c ; the taxable income and the due taxes are calculated by

$$\text{Taxable Income} = \text{Revenues} - \text{FCOP} - \text{VCOP} - \text{Depreciation} \quad (\text{A7.6.5})$$

$$\text{Taxes paid} = \text{Taxable Income} \cdot tr \quad (\text{A7.6.6})$$

The tax rate tr is assumed to be 25%. The future values of the total cash flow is accounted for with a discount factor d of 0.075, the average of the values used by the International Energy Agency in their 2015 report¹⁰⁹. The discounted cash flow (DCF) in year y and the net present value for a plant lifetime of n years NPV_n can be calculated by:

$$\text{DCF}(y) = C(1 + d)^{-y} \quad (\text{A7.6.7})$$

$$\text{NPV}_n = \sum_{y=1}^n \text{DCF}(y) \quad (\text{A7.6.8})$$

The salvage value of all plant equipment is assumed to be equal to the decommissioning cost. The solver in Microsoft Excel is used to find the value of LCOE at which the value of NPV_{20} is exactly zero for each of the process designs. Table A7.6.2 shows the NPV analysis results for the pre-combustion IRCC process. The capital is fully depreciated in the year 2036, after 20 years of production. In the year 2023, 7 years after installing the first set of OTMs, the second set of membranes and modules is installed. This is accounted for by the investment in that year. The same investment is projected for the year 2030, in which the last set of membranes is installed. To obtain the values given in Table A7.6.2, valid for the pre-combustion IRCC, solving the system of equations gave $\text{LCOE} = \$ 178 \text{ MWh}^{-1}$.

Table A7.6.2. Results of the Net Present Value analysis for the pre-combustion IRCC plant. Years relative to the start of production (year 0) and actual years are both given.

Item [10 ⁶ \$ ₂₀₁₄]	Year, relative and absolute									
	-2	-1	0	1	2	3	4	5	6	7
	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
FCOP	0.0	0.0	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6
VCOP	0.0	0.0	35.2	105.5	117.2	117.2	117.2	117.2	117.2	117.2
Depreciation	0.0	0.0	65.8	65.8	65.8	65.8	65.8	65.8	65.8	65.8
Revenues	0.0	0.0	121.1	363.2	403.6	403.6	403.6	403.6	403.6	403.6
Taxable income	0.0	0.0	-116.4	55.4	84.1	84.1	84.1	84.1	84.1	84.1
Taxes paid	0.0	0.0	0.0	13.9	21.0	21.0	21.0	21.0	21.0	21.0
Investment	258.8	589.9	172.6	0.0	0.00	0.00	0.0	0.0	148.60	0.0
Total cash flow	-258.8	-589.9	-223.2	107.3	128.8	128.8	128.8	128.8	-19.8	128.8
Discounted cash flow	-258.8	-551.3	-194.9	87.6	98.3	91.8	85.8	80.2	-11.5	70.1
$NPV_y = \sum_{-2}^y DCF$	-258.8	-810.1	-1005.1	-917.4	-819.2	-727.3	-641.5	-561.2	-572.8	-502.7

Table A7.6.2 - Continued. Results of the Net Present Value analysis for the pre-combustion IRCC plant. Years relative to the start of production (year 0) and actual years are both given.

Item [10 ⁶ \$ ₂₀₁₄]	Year, relative and absolute														
	8	9	10	11	12	13	14	15	16	17	18	19			
	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036			
FCOP	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6			
VCOP	117.2	117.2	117.2	117.2	117.2	117.2	117.2	117.2	117.2	117.2	117.2	117.2			
Depreciation	65.8	65.8	65.8	65.8	65.8	65.8	65.8	65.8	65.8	65.8	65.8	65.8			
Revenues	403.6	403.6	403.6	403.6	403.6	403.6	403.6	403.6	403.6	403.6	403.6	403.6			
Taxable income	84.1	84.1	84.1	84.1	84.1	84.1	84.1	84.1	84.1	84.1	84.1	84.1			
Taxes paid	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0			
Investment	0.0	0.0	0.0	0.0	0.0	148.6	0.0	0.0	0.0	0.0	0.0	0.0			
Total cash flow	128.8	128.8	128.8	128.8	128.8	-19.8	128.8	128.8	128.8	128.8	128.8	128.8			
Discount factor	65.5	61.2	57.2	53.5	50.0	-7.2	43.6	40.8	38.1	35.6	33.3	31.1			
Discounted cash flow	-437.2	-376.0	-318.8	-265.3	-215.4	-222.6	-178.9	-138.1	-100.0	-64.4	-31.1	0.0			
$NPV_y = \sum_{-2}^y DCF$	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6	136.6			

Sensitivity analysis

In Tables A7.7.1 through A7.7.3, the lower bound, mean value, and upper bound of the variables assessed in the sensitivity analysis are shown. These values have been calculated by the operations indicated in Table 7.4 of the main text.

Table A7.7.1. Values of lower bounds of parameters analyzed in sensitivity analysis. The operation shows how the value is calculated, E represents the expected value, and σ the standard deviation.

Lower bound									
Item	Operation	Process							
		IGCC w/o	Oxyfuel	Pre-combustion	Pre-combustion	Pre-combustion	Pre-combustion	Oxyfuel	
		CC	IGCC	IGCC w/ASU	IGCC w/OTM	IRCC	NGCC		
Coal price [\$ GJHHV ⁻¹]	$E - \sigma$	1.79	1.79	1.79	1.79	n.a.	n.a.	n.a.	
NG price [\$ GJHHV ⁻¹]	$E - \sigma$	n.a.	3.70	n.a.	3.70	3.70	3.70	3.70	
CO ₂ allowance cost [\$ t ⁻¹]	$E - \sigma$	5.31	5.31	5.31	5.31	5.31	5.31	5.31	
TDC _c [M\$]	$E - 30\%$	738	942	683	652	604	715		
OTM + module price [\$ m ⁻²]	$E - 50\%$	n.a.	1500	n.a.	1500	1500	1500	1500	
Membrane area [m ²]	$E - 20\%$	n.a.	126400	n.a.	53120	32960	116160		
OTM lifetime [years]	$E + 50\%$	n.a.	10.5	n.a.	10.5	10.5	10.5	10.5	
Operating capacity factor [%]	$E + 5pp$	90	90	90	90	95	95	95	

Table A7.7.2. Expected values of parameters analyzed in sensitivity analysis.

Item	Expected value					
	Process					
	IGCC w/o CC	Oxyfuel IGCC	Pre-combustion IGCC w/ASU	Pre-combustion IGCC w/OTM	Pre-combustion IRCC	Oxyfuel NGCC
Coal price [\$ GJHHV ⁻¹]	3.31	3.31	3.31	3.31	n.a.	n.a.
NG price [\$ GJHHV ⁻¹]	n.a.	5.27	n.a.	5.27	5.27	5.27
CO ₂ allowance cost [\$ t ⁻¹]	6.98	6.98	6.98	6.98	6.98	6.98
TDC _e [M\$]	1055	1346	977	932	863	1022
OTM + module price [\$ m ⁻²]	n.a.	3000	n.a.	3000	3000	3000
Membrane area [m ²]	n.a.	158000	n.a.	66400	41200	145200
OTM lifetime [years]	n.a	7	n.a	7	7	7
Operating capacity factor [%]	85	85	85	85	90	90

Table A7.7.3. Upper bound of parameters analyzed in sensitivity analysis.

Upper bound						
Item	Operation	Process				
		IGCC w/o CC	Oxyfuel IGCC	Pre-combustion IGCC w/ASU	Pre-combustion IGCC w/OTM	Pre-combustion Oxyfuel NGCC
Coal price [\$ GJHHV ⁻¹]	$E + \sigma$	4.83	4.83	4.83	4.83	n.a.
NG price [\$ GJHHV ⁻¹]	$E + \sigma$	n.a.	7.71	n.a.	7.71	7.71
CO ₂ allowance cost [\$ t ⁻¹]	$E + \sigma$	8.65	8.65	8.65	8.65	8.65
TDC _c [M\$]	$E + 30\%$	1371	1749	1270	1212	1328
OTM + module price [\$ m ⁻²]	$E + 200\%$	n.a.	6000	n.a.	6000	6000
Membrane area [m ²]	$E + 20\%$	n.a.	189600	n.a	79680	174240
OTM lifetime [years]	$E - 50\%$	n.a.	3.5	n.a.	3.5	3.5
Operating capacity factor [%]	$E - 15\text{pp}$	70	70	70	70	75

Nomenclature and symbols

Table A7.8.1. List of abbreviations.

Section of		
Appendix A7	Abbreviation	Significance
2,4	ASU	Air Separation Unit (referring to cryogenic distillation)
4	CapEx	Capital Expenditures
4	CC	Contingency Charges
4	CEPCI	Chemical Engineering Plant Cost Index
6	DCF	Discounted cash flow
5	DW&B	Direct Wages and Benefits
4	EPC	Engineering, Procurement and Construction
5	EEX	European Energy Exchange
6	FCOP	Fixed Cost of Production
1	HHV	Higher Heating Value
4	ISBL	Inside Battery Limits
2,4	IGCC	Integrated Gasification Combined Cycle
2,4,5	IRCC	Integrated Reforming Combined Cycle
3	LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$
6	LCOE	Levelized Cost of Electricity
1	LHV	Lower Heating Value
6	MW&B	Maintenance Wages and Benefits
6	NG	Natural Gas
2,4	NGCC	Natural Gas Combined Cycle
6	NPV	Net Present Value
5,6	OpEx	Operating Expenditures
4	OSBL	Outside Battery Limits
4,6	OTM	Oxygen Transport Membrane
5	O&M	Sum of operations and maintenance costs
3	sPOD / POD	(specific) Pure Oxygen Demand
2	PFD	Process Flow Diagram
6	SW&B	Salaries, Wages and Benefits (DW&B+MW&B)

Table A7.8.1 – Continued. List of abbreviations.

Section of		
Appendix A7	Abbreviation	Significance
4,5	TDC	Total Depreciable Cost
5	TDC _e	Total Depreciable Cost excluding OTMs and modules, including costs related to the membrane assembly
6	TDC _m	Total Depreciable Cost of OTMs and modules
6	VCOP	Variable Cost of Production
2,4	w/o	without

Table A7.8.2. List of symbols.

Section of Appendix A7	Symbol	Unit	Significance
3	A	m^2	Surface area of membrane
4	A	m^2	Surface area of heat exchanger
4	$A_{\min}$	m^2	Minimum cross-sectional area of flash vessel
3	a	m	Membrane thickness
4	a	\$	Cost constant
4	b	Variable unit	Cost constant
3	b	m	Membrane width
3	c	mol m^{-3}	Oxygen concentration in gas phase
4	C_i	\$	Cost of installed equipment
4	C_p	\$	Cost of purchased equipment
6	C	M\$	Cash flow
6	d	[-]	Discount factor
3	F	C mol^{-1}	Faraday constant
3			Oxygen molar flow rate at position x and time t
	$F(x,t)$	mol s^{-1}	
3	$G(x,t)$	$\text{m}^3 \text{s}^{-1}$	Volumetric flow rate at position x and time t
1	ΔH_{vap}	MJ kg^{-1}	Latent heat of vaporization of water

Table A7.8.2 – Continued. List of symbols.

Section of Appendix A7	Symbol	Unit	Significance
4	H	[-]	Installation factor
3	i	[-]	Membrane element number in oxygen permeation model
3	J_{O_2}	$\text{mol cm}^{-2} \text{s}^{-1}$	Oxygen flux through membrane
3	J_{O_2}	$\text{mol cm}^{-2} \text{s}^{-1}$	Oxygen flux through membrane
3	k	[-]	Iteration number
4	$LMTD$	[-]	Logarithmic mean temperature difference
1	$m_a, m_c, m_h,$ m_n, m_o, m_s	wt%	Mass fractions of ash, carbon, hydrogen, nitrogen oxygen, and sulfur, respectively
1	m_w	kg kg^{-1}	Mass of water vapor formed upon combustion of pet-coke/coal mixture
6	n	year	Service life of plant
3	n	[-]	Power variable
4	n	[-]	Cost constant
3	N	[-]	Number of membrane elements in oxygen permeation model
3	p_{O_2}	bara	Oxygen partial pressure
4	Q	[MW]	Duty of heat exchanger
3	R	$\text{J mol}^{-1} \text{K}^{-1}$	Gas constant
3	S	mol s^{-1}	Total oxygen flux
4	S	Variable unit	Sizing variable ¹⁰⁰
3	t	s	Time
3	T	K	Temperature
4	U	$\text{W m}^{-2} \text{K}^{-1}$	Heat transfer coefficient
3	V	m^3	Volume

Table A7.8.2 – Continued. List of symbols.

Section of			
Appendix A7	Symbol	Unit	Significance
1	w_a	kg kg^{-1}	Total air mass, normalized to fuel mass, supplied for gasification, reforming, and combustion processes
3	x	m	Length coordinate in oxygen permeation model
1	γ_a	%	Relative humidity of air
3	θ	[-]	Stage cut
3	σ_o, σ_i	S cm^{-1}	Conductivity, electronic and ionic

References

94. Channiwala, S. A.; Parikh, P. P., A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel*, 2002, 81 (8), pp. 1051-1063.
95. Nag, P. K., *Power Plant Engineering*. 3rd ed.; McGraw-Hill Education (India) Pvt Limited: 2008. ISBN 9780070648159.
96. Schley, P.; Beck, M.; Uhrig, M.; Sarge, S. M.; Rauch, J.; Haloua, F.; Filtz, J. R.; Hay, B.; Yakoubi, M.; Escande, J.; Benito, A.; Cremonesi, P. L., *Measurements of the calorific value of methane with the new GERG reference calorimeter*. *International Journal of Thermophysics*, 2010, 31 (4), pp. 665-679.
97. Bouwmeester, H. J.; Burggraaf, A. J., Dense ceramic membranes for oxygen separation. In *The CRC handbook of solid state electrochemistry*, Gellings, P. J.; Bouwmeester, H. J. M., Eds. CRC Press: Boca Raton, 1997; p. 481. ISBN 978 0849389566.
98. Stevenson, J. W.; Armstrong, T. R.; Carneim, R. D.; Pederson, L. R.; Weber, W. J., *Electrochemical properties of mixed conducting perovskites $\text{La}_{1-x}\text{M}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($M = \text{Sr}, \text{Ba}, \text{Ca}$)*. *J. Electrochem. Soc.*, 1996, 143 (9), pp. 2722-2729.
99. Bidrawn, F.; Lee, S.; Vohs, J. M.; Gorte, R. J., The effect of Ca, Sr, and Ba doping on the ionic conductivity and cathode performance of LaFeO_3 . *J. Electrochem. Soc.*, 2008, 155 (7), pp. B660-B665.

100. Chen, W.; Nauels, N.; Bouwmeester, H. J. M.; Nijmeijer, A.; Winnubst, L., *An accurate way to determine the ionic conductivity of mixed ionic–electronic conducting (MIEC) ceramics*. J. Eur. Ceram. Soc., 2015, 35 (11), pp. 3075–3083.
101. Towler, G.; Sinnott, R., Chapter 7 - *Capital Cost Estimating*. In *Chemical Engineering Design (Second Edition)*, Butterworth-Heinemann: Boston, 2013; pp. 307–354. ISBN 9780080966601.
102. Towler, G.; Sinnott, R., Chapter 19 - *Heat-Transfer Equipment*. In *Chemical Engineering Design (Second Edition)*, Butterworth-Heinemann: Boston, 2013; pp. 1047–1205. ISBN 9780080966601.
103. El-Halwagi, M. M., *Sustainable Design Through Process Integration: Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement*. Elsevier Science: Waltham, USA, 2017. ISBN 9780080961613.
104. Casero, P.; Coca, P.; García-Peña, F.; Hervás, N., 20 - *Case study: ELCOGAS Puertollano IGCC power plant, Spain*. In *Integrated Gasification Combined Cycle (IGCC) Technologies*, Woodhead Publishing: 2017; pp. 753–775. ISBN 9780081001677.
105. Jenkins, S. Economic Indicators: CEPCI *Chemical Engineering* [Online], 2015. <http://www.chemengonline.com/economic-indicators-cepci/>.
106. Seider, W. D.; Seader, J. D.; Lewin, D. R., *Product & process design principles: synthesis, analysis and evaluation*. Third ed.; John Wiley & Sons: 2009. ISBN 978-0470048955.
107. Results EUA primary auction spot. <https://www.eex.com/en/market-data/environmental-markets/auction-market/european-emission-allowances-auction/european-emission-allowances-auction-download> (accessed December 22, 2017).
108. Anderson, J.; Fennell, A., *Calculate financial indicators to guide investments*. Chem. Eng. Prog., 2013, (Sept. issue), pp. 34–40.
109. Nuclear Energy Agency; International Energy Association, and Organisation for Economic Co-operation and Development, *Projected Costs of Generating Electricity 2015*. http://dx.doi.org/10.1787/cost_electricity-2015-en

CHAPTER 8

Reflections and perspectives

8.1 Introduction

The work described in this thesis all aims to develop Oxygen Transport Membranes (OTMs) for use in carbon capture processes. Ultimately, but within a limited time frame, OTMs should be economically viable and technologically mature enough to be considered as an industrially relevant technology. As discussed in the introduction, carbon capture is one of the technologies required to mitigate the temperature rise on earth. According to climate prediction models also discussed in the introduction, the likelihood of limiting the average temperature increase to 2 °C is low if we do not start to capture CO₂ within a few years and on a relevant scale. Whether or not the scale of carbon capture technology will be increased to the proposed levels is merely dependent on politics, as the required technology exists. For OTM technology to be relevant in the portfolio of carbon capture technologies, it needs to be at least on par with other technologies in terms of process economy and reliability within the same few years. We will not judge whether or not this is a realistic target, but rather focus on the current and foreseen challenges and indicate some possible solutions or directions. Here, the added value of the research presented in this thesis is discussed and put in perspective, and some directions are given for future research.

8.2 Reflections

During the trajectory of the PhD project, wide ranges of materials, measurement methods, and phenomena have been used and studied. To end up with the results displayed in this thesis, many more measurements were performed, which were in hindsight not the ideal ones due to various reasons.

8.2.1 Synthesis and sample preparation

In terms of synthesis and sample preparation, a few things need to be highlighted. First, the fabrication of dense pellets is required for many transport-related

characterization techniques, such as Electrical Conductivity Relaxation (ECR), oxygen permeation, and Pulse Isotopic Exchange (PIE) measurements. The fabrication of dense samples is not trivial for materials with poor sinter activities, for example due to the chosen calcination conditions or to insufficient milling and sieving. Calcination, which is performed to obtain a phase-pure powder with the desired crystal structure, may have to be performed at temperatures close to the temperature at which evaporation becomes significant. In such case, no sintering temperature yielding a dense sample may be found. Alternative sintering routes such as field-assisted sintering ¹, microwave-assisted sintering ², or hot isostatic pressing ³, or temperature profiles with a short time at the maximum temperature and fast heating and cooling rates may all be considered as alternative routes to achieve densification. Should time have permitted to do so, it might have been convenient to use such techniques, for example, in Chapter 4, in which it might have been possible to fabricate samples of better quality with a reduced number of trials.

Another sample preparation related issue concerns the fabrication of samples with nanoparticles at the surface. Such samples were claimed to show catalytic effects for the Oxygen Reduction Reaction ⁴. While performing such experiments, we encountered various challenges. First, the surface roughness of polished dense samples should be either quantified or manufactured with high reproducibility, both of which could have been given more attention. Automation of sample polishing and quantifying the surface roughness and its effect on the surface exchange rate should be considered before studying the effect of nanoparticle deposition on OTM surfaces. Second, the deposition of nanoparticles and the quantification of the deposited amount are not trivial either. Dip-coating, drop-coating, and spin-coating of dissolved metal nitrates with subsequent calcination are methods which enable the deposition of oxide or carbonate nanoparticles. Again, the reproducibility of these methods is not ideal due to them being (partly) manually operated. Metal nanoparticles can be deposited by sputtering, after which the particles can be pinned to the surface by a calcination treatment. Quantifying the number of deposited particles may be done by image analysis or by weight analysis, none of which proved easy and reliable. The more elegant and possibly more reproducible method to obtain nanoparticles atop a surface is exsolution ⁵⁻⁸. With this method, the composition of the sample together with thermodynamics and kinetics determine the presence, size, amount, and distribution of particles.

8.2.2 Optimization of measurements

Measurements form the main part of any research project. However, without a thorough plan, performing measurements will likely not yield the desired results. In such a plan, some key parts are the questions which should be answered by the experiments, the techniques required to measure the data, and the order and conditions in which experiments are performed. For the experiments described in this thesis, most of the optimization related to measurements was found in improving the data quality and reproducibility of measurements. Especially in the case of ECR and PIE experiments this was the case, as these techniques rely on custom-built setups. For example, to perform the ECR measurements described in Chapter 3, both the setup and the measurement method required adjustments. First, the temperature control had to be improved to decrease the overshoot on heating and cooling. This enabled to start a measurement sooner after a new temperature was established. Second, the sampling rate had to be increased to > 10 Hz in order to record a sufficient number of data points per relaxation event to enable fitting with the model. Third, to enable continuous measurements of 200 h or more, the setup had to be fully automated in terms of both hardware and software. Automation turned out to be both highly time-consuming to realize (~ 1 year) and very useful once it worked sufficiently well. Naturally, debugging and incorporating new ideas were done simultaneously with performing the experiments, and will never be fully complete.

Next to measurement automation, a key aspect in obtaining high quality ECR data is the sample itself. Typically, in case ECR data could not be fitted to the model properly, this was due to undesired sample-related effects. For example, surface restructuring, restructuring of the crystal during ageing at certain temperatures and $p\text{O}_2$, contamination of the sample surface, or the formation or propagation of (micro)cracks could all hamper the quality of obtained data. Whereas in some cases it could be sufficient to repeat the measurement with another specimen, in other cases it may be necessary to adjust the measurement order, maximum temperature, annealing time at a certain temperature.

8.2.3 Modeling and data analysis

After automation of the ECR measurements, a new method to analyze the data was required. As a data file is recorded for every single step in $p\text{O}_2$, the continuous

measurements during ~200 h in Chapter 3 generated 2400 data files per experiment (three oxidation and three reduction runs per hour). Previously, the data was treated manually, i.e. plotting, normalization, and fitting were performed manually in a file-by-file workflow. To increase the efficiency, a Matlab routine was written which can perform these steps automatically after the experimenter has specified a few parameters. After fitting of the files has completed, the experimenter just has to verify that the values of the fitting parameters are in a plausible range, that the data and fitting quality are both sufficient, and that the reproducibility is good. It is strongly advisable to start fitting the data while the measurement is running to save experimental time. Not only is the data quality more easily judged after fitting, but also could the user decide to perform additional experiments if the data obtained during part of an experiment is not satisfactory.

8.2.4 Applications

During the GREEN-CC project, which consisted of academic as well as industrial partners, one of the recurring questions was one related to strategical decisions: should we design an OTM in terms of materials, microstructure, and macrostructure based on the needs in a specific chemical process, or should we adapt the process conditions and design to the best possible OTM? Logically, this question has no definitive single answer, as an answer is heavily dependent on the role of the person answering the question. Both parties have to speak each other's language to find the best solution for the specific case. Possibly, the etc. Propitiously, in case OTMs remain an academic product rather than an industrial one, the knowledge obtained while performing research into OTMs is relevant for other applications, such as Solid Oxide Fuel Cell cathodes, electrolyzers, or perovskite-based catalysts.

8.3 Perspectives

The wide range of topics covered by this thesis, including synthesis aspects, the enhancement and understanding transport properties, the chemical stability of oxides in CO₂, as well as the design of carbon capture power plants based on OTMs, can be interpreted in various ways. Most notably, the large variety in the topics may indicate that there is still a significant amount of work to be performed OTMs can be applied in an

industrially viable way. First, some general topics will be discussed here, after which some reflections on specific chapters are given.

In the field of OTMs, the common mode towards progress seems to be the optimization of properties by endless substitution of certain cations for others. Materials become more and more complex as a larger number of different cations is used. However, a significant increase in oxygen flux at a concomitant decrease in operating temperature is asked for. Meanwhile, concessions in price and availability of raw materials, safety aspects, mechanical properties, and stability should be avoided as well, since most of these aspects are not sufficient for industrial scale use of OTMs yet. Tuning the materials' properties by substituting one cation for another may improve some of these parameters, but this is typically at the expense of other properties. The required large step may more likely be found by understanding the fundamentals, and designing the materials accordingly. Some inspiring publications based on this philosophy were published recently related to oxygen surface exchange processes ⁹⁻¹². While molecular dynamics simulations and density functional theory calculations may be of good use in understanding the fundamentals, it will remain challenging to translate their results into materials with improved properties. Meanwhile, materials scientists can continue to contribute to the fundamental understanding of oxygen transport, surface exchange kinetics, and stability by systematically investigating series of materials, as for example carried out by Wang *et al.* ¹³.

Based on the current status of the literature as well as on this thesis, the most urgent but likely also the most challenging problem for OTM technology is the oxygen flux as function of temperature. At high temperatures, typically 900 °C and above, the oxygen flux through selected mixed ionic-electronic conductors such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-6}$ (BSCF) is high. High temperatures however come at the expense of many other parameters which determine the amount and quality of produced oxygen. For example, the membrane sealing quality and stability ¹⁴, the compatibility with the steel or alloy membrane housing and the OTM itself in terms of thermal expansion and reactivity ¹⁵, the need for a type of steel or alloy which can withstand the high temperature under oxidative conditions ¹⁵, and the amount of heat available in a typical plant which is too little to reach the membrane operating temperature by heat integration (see Chapter 7).

Second to that, most materials that have shown the highest oxygen fluxes, such as BSCF or $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), typically come with unfavorable stability. Phenomena such as phase transitions, mechanical strength, and reactivity in atmospheres containing CO_2 , SO_2 , or steam, may limit the practical use of the materials with high oxygen fluxes. At the other side of the spectrum, some materials have been studied which show much better stability but also much smaller oxygen fluxes. Examples in this category are dual-phase composites which do not contain alkaline earth cations^{16,17}, or perovskite oxides with a high content of stable cations due to donor doping (for example containing Ta^{6+} or Nb^{5+})^{18,19}.

Further complications include issues related to the raw materials, including the safety aspects (for example, Co and Ni salts or oxides are often toxic or carcinogenic), the scarcity (many of the cations used in OTMs have been listed as critical raw materials by the EU²⁰), and the prices of some of the cations. Next to that, issues with the mechanical strength exist, such as the insufficient sinterability of some types of perovskite oxides, the largely different thermal expansion coefficient of some combinations of membrane, sealing, and housing, and degradation due to chemical reactions with gases, metals, or sealing materials. Finally, only very little results have been published regarding the reliable upscaling of membrane production in terms of the size of individual membranes and of total membrane area. Before production of OTMs can take place at an industrially relevant scale, the production process needs to be reliable.

References

1. O. Ravkina, J. Räthel, A. Feldhoff. *Influence of different sintering techniques on microstructure and phase composition of oxygen-transporting ceramic*. J. Eur. Ceram. Soc., 2015, 35(10), pp. 2833-2843.
2. Alammar, T.; Slowing, I.; Anderegg, J.; Mudring, A.-V., *Ionic-liquid-assisted microwave synthesis of solid solutions of $\text{Sr}_{1-x}\text{Ba}_x\text{SnO}_3$ perovskite for photocatalytic applications*. ChemSusChem 2017, 10(17), pp. 3387-3401.
3. Y. Takahashi and W. Shin. *$\text{LaSrAlFeO}_{3-\delta}$ oxygen ion conducting membranes sintered under different atmosphere and HIP*. J. Ceram. Soc. Jap. 2010, 118(12), pp. 1144-1149.

4. Chen, Y.; Chen, Y.; Ding, D. *et al.*, *A robust and active hybrid catalyst for facile oxygen reduction in solid oxide fuel cell*. Energy Environ. Sci., 2017, 10, pp. 964-971.
5. Hua, B.; Li, M.; Sun, Y.F.; Li, J.-H.; Luo, J.-L., *Enhancing perovskite electrocatalysis of solid oxide cells through controlled exsolution of nanoparticles*. ChemSusChem 2017, 10(17), pp. 3333-3341.
6. Papargyriou, D.; Irvine, J.T.S., *Nickel nanocatalyst exsolution from (La,Sr)(Cr,M,Ni)O₃ (M=Mn,Fe) perovskites for the fuel oxidation layer of Oxygen Transport Membranes*. Solid State Ionics, 2016, 288, pp. 120-123.
7. Neagu, D.; Tsekouras, G.; Miller, D.N.; Ménard, H.; Irvine J.T., *In situ growth of nanoparticles through control of non-stoichiometry*. Nat. Chem., 2013, 5(11), pp. 916-923.
8. Gao, Y.; Lu, Z.; You, T.L.; Wang, J.; Xie, L.; He, J.; Ciucci, F., *Energetics of nanoparticle exsolution from perovskite oxides*. J. Phys. Chem. Lett. 2018, 9(13), pp. 3772-3778.
9. Suntivich, J.; Gasteiger, H.A.; Yabuuchi, N.; Nakanishi, H.; Goodenough, J.B.; Shao-Horn, Y., *Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal-air batteries*. Nat. Chem., 2011, 3, pp. 546-550.
10. De Souza, R.A., *Limits to the rate of oxygen transport in mixed-conducting oxides*. J. Mater. Chem. A, 2017, 5, pp. 20334-20350
11. Chen, Y.; Chen, Y.; Ding, D. *et al.*, *A robust and active hybrid catalyst for facile oxygen reduction in solid oxide fuel cell*. Energy Environ. Sci., 2017, 10, pp. 964-971.
12. Chen, C.; Ciucci, F.; *Designing Fe-based oxygen catalysts by Density Functional Theory calculations*. Chem. Mater., 2016, 28(19), pp. 7058-7065.
13. Wang, J.; Saccoccio, M.; Chen, D. *et al.*, *The effect of A-site and B-site substitution on BaFeO_{3-δ}: An investigation as a cathode material for intermediate-temperature solid oxide fuel cells*. J. Power Sources, 2015, 297, pp. 511-518.
14. Borhan, I.; Gromada, M.; Nedelcu, G.G.; Leontie, L., *Influence of (CoO, CaO, B₂O₃) additives on thermal and dielectric properties of BaO-Al₂O₃-SiO₂ glass-ceramic sealant for OTM applications*. Ceram. Int., 2016, 42(8), pp. 10459-10468.

15. Pfaff, E.M.; Kaletsch, A.; Broeckmann, C., *Design of a Mixed Ionic/Electronic Conducting Oxygen Transport Membrane Pilot Module*. Chem. Eng. Tech., 2012, 35(3), pp. 455-463.
16. Balaguer, M.; García-Fayos, J.; Solís, C.; Serra, J.M., *Fast oxygen separation through SO_2 - and CO_2 -stable dual-phase membrane based on NiFe_2O_4 - $\text{Ce}_{0.8}\text{Tb}_{0.2}\text{O}_{2-\delta}$* . Chem. Mater., 2013, 25(24), pp. 4986-4993.
17. Ramasamy, M.; Persoon, E.S.; Baumann, S.; Schroeder, M.; Schulze-Küppers, F; Görtz, D.; Bhave, R.; Bram, M.; Meulenbergh, W.A., *Structural and chemical stability of high performance $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ - FeCo_2O_4 dual phase oxygen transport membranes*. J. Memb. Sci., 2017, 544, pp. 278-286.
18. Zhang, C.; Tian, H.; Yang, D.; Sunarso, J.; Liu, J.; Liu, S., *Enhanced CO_2 resistance for robust oxygen separation through tantalum-doped perovskite membranes*. ChemSusChem, 2016, 9(5), pp. 505-512.
19. Yi, J.; Schroeder, M.; Martin, M., *CO_2 -tolerant and cobalt-free $\text{SrFe}_{0.8}\text{Nb}_{0.2}\text{O}_{3-\delta}$ perovskite membrane for oxygen separation*. Chem. Mater., 2013, 25(6), pp. 815-817.
20. European Commission, *Study on the review of the list of critical raw materials*, published 13-09-2017, accessed 06-08-2018.
<http://ec.europa.eu/docsroom/documents/25421>

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About the author

Rian Ruhl was born on June 8th, 1989 in Heemstede, the Netherlands. After graduating from high school (Jac P. Thijssse College, Castricum), he went to the other side of the country, to study Chemical Engineering at the University of Twente. Next to the study, he participated in a variety of committees of the study association. His BSc thesis focused on the catalytic hydrogenation of phenol. During the MSc, he specialized in materials science and in the meantime organized a study tour to Argentina with fellow ChE students. He spent seven months in Novara, Italy, for an internship at AkzoNobel Chemicals SpA, during which he developed a reliability-centered maintenance program. His MSc thesis covered the synthesis and phase-transfer of upconverting nanoparticles for *in vivo* use, and was supervised by prof. dr.ir. J. Huskens.

In March 2014, Rian started his PhD in the Inorganic Membranes group headed by prof. A. Nijmeijer, and supervised by prof. H.J.M. Bouwmeester. His work formed part of the multidisciplinary EU-funded GREEN-CC project. During this PhD trajectory, he worked on topics ranging from materials science to process engineering, as described in this thesis. He participated in a summer school, several winter schools, and the Solid State Ionics conference in Padova, Italy. Next to the scientific part, he was involved in teaching electrochemistry to first-year BSc students and lab skills related to the fabrication and characterization of dense membranes to MSc students, and acted as the supervisor in the final projects of in total 9 BSc and MSc students.

Currently, the author works at Océ Technologies as Printing Process researcher. In this function, he seeks to understand how ink properties can be tuned, and how these relate to the droplet behavior and print quality.