CERAMIC ION-CONDUCTING MEMBRANES FOR A SUSTAINABLE EUROPEAN ENERGY SYSTEM

Inaugural lecture given to mark the assumption of the position as Professor of Ion-Conducting Membranes at the University of Twente on Thursday 1th June by

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ABSTRACT:
The energy supply in Europe has changed in the past few decades from conventional technologies (fossil, nuclear) to more renewables (solar, wind) and the process is still going on. This leads to a high fluctuation of the energy supply and to times of over- and undercapacity. To ensure a sustainable and environmental friendly energy supply for the future, carbon capture technologies are necessary to reduce CO$_2$ emissions, and energy storage is needed to cover periods of low energy generation by renewables. The development of new batteries or the production of synthetic fuels is urgently required for energy storage.

Oxide ceramic membranes for the separation of oxygen or hydrogen from gas mixtures are of great interest for different applications due to their high efficiency and practically infinite selectivity. Supported membrane structures are envisaged for applications in oxygen and hydrogen generation for the corresponding gas supply, for example in power plants, glass, cement or steel production, as well as for chemical or petrochemical applications and for green energy generation (H$_2$).

In addition, ion-conducting ceramic membrane reactors make it possible to combine membrane separation processes directly with chemical reactions, leading to process intensification and, hence, benefits with regard to efficiency. Current research activities focus on membrane reactors due to their high intrinsic efficiency and great potential for the production of a large variety of commodity chemicals, energy carriers, and synthetic fuels. This includes the reduction of CO$_2$ emissions or the utilization of CO$_2$. Also environmental applications such as the disposal of NO$_x$ or H$_2$S are possible.
The following sections give an overview of the available energy conversion technologies, their advantages and disadvantages, and identify possible applications for membrane modules and reactors in this field. The function and transport of supported thin microstructured ion-conducting membranes are explained and the transport limitations are discussed. The potential manufacturing of larger planar components is shown with the example of the sequential tape casting process. Finally, an outlook for future research requirements is given and the synergies of a joint development between the University of Twente and Forschungszentrum Jülich GmbH are highlighted.

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ENERGY SUPPLY IN EUROPE
Energy generation and supply in Europe depends very strongly on the local structure and the social perspective in the different countries and the corresponding policies. In Germany, for example, in the last few decades the energy supply was predominantly based on nuclear power and fossil fuels, mainly lignite (brown coal) or hard coal (black coal) complemented by natural gas and small amounts of renewables. The major advantages of nuclear and fossil power plants are the low cost, the constant energy generation, and the reliable supply of fuels. Constant energy generation means that the amount of electricity produced is controlled by the installed capacity of the power plant, e.g. 500 MW, which is continuously supplied to the grid. The gap between supply and actual energy demand is covered by flexible natural-gas-fuelled power plants. In contrast, energy is stored in pumped-storage hydroelectric power plants. Major research in the field of fossil power plants focused on increasing efficiency in order to save costs and resources. One major disadvantage of nuclear energy is the waste disposal and storage problem, which has still not been solved. In addition, accidents can be extremely critical as demonstrated by Sellafield (GB/1957), Harrisburg (USA/1979), Chernobyl (USSR/1986) and Fukushima (JP/2011). As a result, directly after the accident in Fukushima, the German
Government decided to shut down older nuclear power plants and to phase out the remaining eight plants by 2022. The major disadvantage of fossil fuels is the emission of CO$_2$ into the environment, which is partly responsible for the greenhouse gas effect and global warming. Therefore, the European Commission took the decision of drastically reducing CO$_2$ emissions. Consequently, CO$_2$ capture and storage (CCS) from fossil power plants or other energy-intensive industries is under development. In addition to storage, attention has recently turned to considering possibilities for utilizing the captured CO$_2$.

Another consequence of phasing out nuclear and fossil power is that the lost capacity must be replaced by renewable energies, which has led to an extreme growth in this field in recent years. Renewables, such as wind power or solar energy, have the advantage of environmentally more friendly energy generation with low CO$_2$ emissions and in principle unlimited resources. The major disadvantages are the higher cost of electricity and the fact that energy generation fluctuates. Energy generation is independent of installed capacity, but highly dependent on climate and weather conditions, which are not controllable and not easy to predict. If no wind or sunshine is available, no power will be generated. This effect makes the energy supply much more complicated because energy is not easy to store on a large scale. Energy storage is required to cover these periods of low energy generation. Options are pumped-storage hydroelectric power stations, batteries or energy carrier (fuel) production during periods of high renewable power generation.

The following figures show energy generation in Germany at different periods as an example.
Constant power generation over a period of one month by nuclear or lignite in a fossil-fuelled power plant shown in Figure 1 covers the “base load”, which is the amount of energy always needed that must always be available. Figure 2 shows the energy supplied in May 2016 by renewables and conventional power plants. Figure 3 shows an extreme period, when only a low amount of wind and sunshine was available. Figure 2 shows a high fluctuation of renewable energy generation over the course of a day. This must currently be compensated by fossil power plants, which means that a number of them are operated flexibly without a constant energy supply, in contrast to past operation modes. This flexible operation is a critical issue for some materials and shortens the lifetime of the power plants.

In summary, to guarantee a reliable and sustainable power supply, two measures are mandatory, 1) carbon capture and storage or (better) utilization, and 2) energy storage on different time scales (short- to mid-term), which in addition to novel battery concepts also requires chemical energy carriers such as hydrogen, methane, methanol.
POTENTIAL APPLICATIONS FOR CERAMIC GAS SEPARATION MEMBRANES

Carbon Capture for Utilization or Storage (CCU/CCS)

In a conventional coal-fired power plant, the coal is combusted with air which leads to a flue gas consisting of approx. 85% N\textsubscript{2} and 15% CO\textsubscript{2} and H\textsubscript{2}O. Separation of the CO\textsubscript{2} from this flue gas was originally planned to be implemented by a chemical washing process, which leads to high costs and efficiency losses, and thus to an increasing amount of coal being combusted. In addition, the first chemical solution to be applied, monoethanolamine, is not easy to dispose of and displays high degradation rates. This led to the development of oxyfuel power plants. The major difference to a conventional “post-combustion” power plant is the combustion of the coal/gas with a mixture of pure oxygen and CO\textsubscript{2} from recycled flue gas instead of air. This leads to a flue gas with a high concentration of CO\textsubscript{2} (and H\textsubscript{2}O) without N\textsubscript{2}, which is ready for storage (CCS) or further use (CCU). Oxygen is produced commercially by a cryogenic step, in which air is cooled down to -190°C where the liquefaction of oxygen takes place. The cooling step has a high energy demand so that membranes for the separation of oxygen could be an interesting alternative. The reduction or elimination of CO\textsubscript{2} emissions originating from electricity generation plants fuelled by coal or gas is a major target in the current socio-economic, environmental and political situation involving discussions on how to reduce greenhouse gas emissions such as CO\textsubscript{2}. To reduce CO\textsubscript{2} emissions by 50 to 60% by 2050, as proposed by the EU and other industrial countries, a significant contribution is
required from carbon capture and storage (CCS). One way to achieve such a reduction is the introduction of gas separation techniques making use of membrane technology, which is associated with significantly lower efficiency losses compared with conventional separation technologies. CO₂, O₂ and H₂ separation is achieved by selective membranes with high permeability, so that CO₂ is obtained in a readily condensable form. Although membranes are already being used for material separation in other fields (e.g. the chemical industry), membranes for separating the technically relevant gases in fossil power plants are still far from being suitable for industrial applications. Strategies for novel membranes mean that research and technology development focuses on materials science and technology [2]. In addition, there is an urgent need for the reduction of greenhouse gases in other sectors such as the cement industry or steel industry.

One method for carbon capture is the oxyfuel process shown in Figure 4. The fuel is combusted with a mixture of pure oxygen and recirculated flue gas. A possible integration of a membrane is shown in Figure 4.

In the Ideal case, the flue gas contains only CO₂ and water. After condensation of the water, the CO₂ is ready for storage or further use.
MEMBRANE REACTORS FOR THE GENERATION OF ENERGY CARRIERS
A catalytic ceramic membrane reactor (CMR) is a device in which a separation process through the membrane is combined with a chemical reaction that takes place at one or both sides of the membrane. This integral coupling of both processes, separation and reaction, generates synergies between them. Often the two functions are located in the same housing [3].

Different general concepts are possible for membrane reactors. These concepts, i.e. extractor, distributor and contractor, are described very well in [3] [4]. In particular, the extractor and distributor concepts are relevant for the processes described here.

![Figure 5: a) extractor and b) distributor concepts [3].](image)

The extractor concept (5a) is mostly used to remove a product from a reaction mixture. In our example, components A and B react to C and D, and D is removed from the mixture by permeation through the membrane. D might be the desired product or an undesired by-product. Major advantages are the shift of the reaction equilibrium to the product side, the prevention of undesired side reactions, and the lack of additional cleaning steps. The distributor concept (Figure 5b) is mostly used for the controlled supply of a reactant to the reaction. In 5b, the educt B is supplied to the educt A reacting to form the desired product C. The major advantages are the exclusion of unwanted reactants such as D in 5b and the homogeneous distribution of the reactant B to the catalytic reaction under ideal conditions (temperature, pressure) avoiding undesired side reactions at, for example, lower temperatures. The synergy of combining separation and reaction steps leads to enhanced efficiency known as process intensification, which has great potential for the synthesis of commodity chemicals,
energy carriers, or synthetic fuels. Moreover, different reactions on both sides of the membrane can be coupled. This means that the permeating reactant, e.g. oxygen or hydrogen, might not only come from simple gas mixtures such as air or syngas, but also from decomposition of (in part hazardous) gases such as CO$_2$, H$_2$O, NO$_x$, H$_2$S. These gases ideally come from industrial waste streams, e.g. carbon capture and utilization (CCU), to reduce greenhouse gas emissions and to reach the goals of limiting climate change. Producing valuable products from “waste” [5, 6, 7] obviously creates added value and makes industry more sustainable. Also the use of waste heat from combustion processes improves efficiency and, hence, sustainability. For the future, the use of concentrated solar energy is a promising alternative for energy input into chemical production systems [8] and can also be combined with a membrane reactor system. In conclusion, ceramic membrane reactors have the potential to play an important role in this context, although the coupling of reactions makes the systems even more complex and a thorough systems analysis is necessary.

The following examples, concentrate on membrane reactor concepts using ceramic ion-conducting gas separation membranes. The major advantage of this type of membrane is the infinite selectivity for the targeted gas due to the solid-state transport of the respective ions, here oxygen or hydrogen (i.e. protons). The driving force for the separation process is the chemical potential (i.e. partial pressure in a gas phase) gradient of the permeating gas across the membrane. The transport, i.e. diffusion, through the dense ceramic membrane layer is a thermally activated process requiring temperatures between 400 and 1000°C [9] [10] [11] [12]. At the high partial pressure side, the permeable ions form at catalytic surfaces, resulting in a multi-step process including ionization, dissociation and finally incorporation into the crystal lattice. The ions or defects diffuse through the membrane layer and recombine at the low partial pressure side releasing the electrons again. Also the combination of oxygen ion and proton conduction in one material is possible (co-ionic conductor) and can also be used for membrane reactors [13]. Purely ionic conductors transport only ions such as O$_2^-$ or H$^+$ (or both). They have negligible electronic conductivity. Therefore, a voltage is created across the membrane. An external circuit is necessary to ensure a continuous ion flux. The most popular application for such a membrane is for a solid oxide fuel cell or gas sensors. In reverse mode, a voltage can also be applied thus driving the ion flux through the membrane and resulting in, for example, solid oxide electrolyser cells. The major advantage of this concept is the ability to tune
the ion flux by the applied voltage, which is at the same time the major drawback due to the need for electrodes and electrical energy. Since this is a special class of membrane reactors widely investigated in the framework of power-to-X technologies [14] [15], it is outside the scope of the present review. Here, we concentrate on mixed ionic-electronic conductors (MIEC). They have both ionic and electronic conductivity at the same time. The charge compensation takes place in the membrane. In this case, only heat and a gradient in the chemical potential of oxygen or hydrogen are needed. To ensure a high flux through the membrane, several transport mechanisms have to be considered [16]: (i) Solid-state diffusion through the dense membrane comprising bulk and grain boundary resistances is always reciprocally proportional to the membrane thickness. Therefore, the development of thin membrane layers is necessary, which for mechanical reasons need to be supported by thicker porous layers. In the case of very thin membrane layers, (ii) surface exchange kinetics become rate-limiting and comprise all the steps for ionization and dissociation of the gas molecules as well as incorporation of the ionic species in the crystal lattice, Finally, (iii) concentration polarization effects occur in the gas phase and particularly in the porous supports due to slow transport of the gas molecules through the pore network comprising, for example, convection, molecular diffusion, and Knudsen diffusion depending on the support microstructure and the actual permeation rate. In conclusion, the resulting permeation rate strongly depends on material properties, microstructure, and process parameters. The transport in the different layers is described in Figure 10 in the following chapter.

The challenges involved in the development and operation of such membrane reactors arise from the harsh environments (high temperature and potentially reducing or corrosive atmospheres) requiring sufficient stability of the materials and reaction performance. Therefore, selective materials with long-term stability, including catalysts, must be developed in order to optimize the energy and cost efficiency of the overall process. The quantitative description of membrane reactor performance is very complex because many parameters can be used for evaluation, particularly when a product mixture is desired, e.g. syngas. No uniform method has yet been established in the literature. Nevertheless, relevant parameters for rating membrane reactors are (i) selectivity (with respect to the desired product), (ii) conversion rate (of the educt), and (iii) yield. The selectivity quantifies how much desired product is formed in relation to all the products, including undesired by-products. The conversion rate corresponds to
the relative amount of a reactant which has reacted, and the yield describes how much of a desired product is formed, which can be described as conversion times selectivity. Moreover, the faradaic efficiency is sometimes used, which describes the contingent of transported electrons participating in the reaction. This is particularly applicable in current-assisted modes to rate the efficiency of a process and quantify the need for electric power. In the past few years, various review articles have been published on the use of membrane reactors, but they have mostly concentrated on one certain topic (e.g. CO₂ utilization) [5] or a single educt (e.g. CH₄) [17]. Figure 6 shows one example of a membrane reactor concept, the catalytic partial oxidation of methane for syngas production. Syngas is an important intermediate product for fuel production or production of chemicals, as shown in Figure 6.

**Figure 6: Production of syngas in a membrane reactor by partial oxidation of methane.**
Figure 8 gives a broad overview of different processes and products. The applications for the proton-conducting hydrogen transport membrane are shown in green, and the applications for oxygen transport membranes in blue. At this point, it is not possible to assess the economic potential of particular processes because most of the developments are still on a laboratory scale and need further improvement on the scientific and technological level.

*Figure 7: Possibilities for the industrial use of syngas [18].*
Figure 8: Summary of selected processes where oxygen- and hydrogen-permeable membranes are applicable.
CERAMIC ION-CONDUCTING MEMBRANES

Ceramic membranes can be classified in two groups: dense ceramic membranes which separate gases by the diffusion of ions through their lattice and porous membranes where the separation is performed by size exclusion of the molecules by means of small pores or free volume in the lattice.

Porous membrane systems are graded structures on ceramic or metallic supports. Gas is transported through these membranes to the free volume in the lattice of the material. Materials used for microporous or mesoporous systems are oxides, such as SiO$_2$ or ZrO$_2$, or zeolites based on aluminosilicates. Polymers are another possibility for use in gas separation at ambient temperatures. In addition, dense palladium-based metal membranes can be used for hydrogen separation. Oxygen- or hydrogen-ion-conducting membranes are of great interest for dense ( gastight) ceramic membranes. The membrane classes are shown in Figure 9a and b.

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<tr>
<th>Microporous ($d_{pore} &lt; 2$ nm)</th>
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<td>amorphous SiO$_2$, 3D network of [SiO$_4$] tetrahedrons</td>
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Figure 9a: Separation of gases by porous and polymer membranes.
Potential membrane materials for mixed ionic-electronic conducting (MIEC) ceramics enable oxygen or hydrogen transport as a result of bulk diffusion of ionic species (oxygen ions or protons) and electrons. The transport process is driven by the oxygen or hydrogen partial pressure gradient across the membrane and takes place at temperatures between 500-900°C. High-performance membranes are being developed consisting of a 20-50 µm thick membrane layer on a porous support with varying thicknesses in the range of 400 – 700 µm. In addition, porous catalytic layers can be applied in order to facilitate the incorporation and removal of the ions at the membrane surfaces. Examples of materials for oxygen-separating membranes are rare earth or alkaline earth cobaltites and ferrites with a perovskite structure. Possible materials for hydrogen-separating membranes are doped lanthanum tungstates or barium cerate or zirconate solid solutions, which have a defective fluorite or perovskite structure.

In the following, the function of a supported asymmetric membrane is considered on a mixed ionic-electronic oxygen conductor for separating oxygen from air. The structure of such a membrane is shown in Figure 10. As Figure 11 shows, transport differs greatly in the different membrane layers. Bulk transport in the functional membrane layer is a diffusion process. The porous catalytic surfaces on both sides of the membrane facilitate incorporation of the oxygen into the material and the support only has to ensure the gas supply by viscous flow and molecular transport. The process with the lowest speed determines and limits the amount of oxygen transported. Research focuses on an understanding of transport mechanisms and on increasing the flux. In addition,
the material has to be stable (chemically, thermochemically and mechanically) for a long time during operation, which is the most important issue. With respect to commercial applications, low-cost materials and production methods are required for the membranes.

Figure 10: Schematic microstructure and working principle of asymmetric mixed ionic-electronic conductor.

Figure 11: Complex transport to asymmetric ion-conducting membrane structures [19] [16] [20].
One possibility for a continuous production of planar microstructured systems is the sequential tape casting process shown in Figure 12. First the membrane layer is cast on a polymer which has an optimal surface. In a second step, the support is cast onto the membrane. After co-firing of the system, the catalytic layers are, for example, printed or infiltrated into the support. This manufacturing route makes it possible to produce plates of 20 * 20 cm.

Figure 12: Tape casting of membrane structures.

Figure 13: Examples of final membrane components made by tape casting and lamination.
OUTLOOK

Gas separation membranes are used in membrane reactors under aggressive conditions (gas atmosphere, pressure, temperature). The great challenge is to find low-cost materials with long-term stability for the respective processes while simultaneously achieving economically acceptable performance (flux, separation factor). Many materials that display high stability have a low flux or vice versa. For this reason, a compromise must often be sought in materials development. That is to say, materials with adequate flux and acceptable stability must be employed. To achieve the required performance, it is necessary to specifically develop thermomechanically stable thin films with optimized microstructures. In adjusting the microstructure, attention must be paid above all to the grain size and morphology as well as to the selective modification of the grain boundary properties by doping and appropriate heat treatment.

Catalytically active layers with high surface areas are frequently also required in order to increase the flux. The catalyst, membrane material, and substrate must be adapted to each other and must not display any damaging reactions during operation. Furthermore, the selected module concepts and thin-film systems must be scalable and suitable for mass production. Depending on the design, different production methods can be taken into consideration including tape casting, extrusion, thermal spraying, and thin-film processes.

A number of promising new processes energy carrier generation can be found in the literature. However, there is often no data on efficiency, economic viability, and the related system integration. Above all, system integration and selective modification of the processes are extremely relevant for achieving economic efficiency. Implementing membranes in chemical reactors can shift the equilibrium and influence the effective reaction kinetics (including mass transport) by directly removing the product. In addition to the stability of the materials, the greatest challenges therefore lie in the selection of the most promising membrane reactor concepts and correctly evaluating them.

In this respect, future joint activities between the University of Twente and Forschungszentrum Jülich are focused on the above-mentioned topics. Material systems such as dual phase membranes with much higher stability in aggressive environments or lower partial pressures show a high potential for fulfilling the targets. In addition, microstructuring of the support to ensure better gas transport is required. One interesting method is freeze
casting. The pores are generated by ice crystals which are evaporated after the casting process. It is also very important to look at the economic benefits of different applications for membranes together with the different industries concerned. Finally the most relevant industrial applications must be identified and materials and membranes must be developed regarding their application environment. After assembling the modules a proof of concept is required in application relevant conditions. Teaching lectures at University of Twente will be given in the field of ceramic processing and ionic conducting membranes.
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