

Ta-doped $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes: Phase stability and oxygen permeation in CO_2 atmosphere

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ABSTRACT

The chemical and structural stability of perovskite-derived $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) and $\text{Sr}(\text{Co}_{0.8}\text{Fe}_{0.2})_{0.9}\text{Ta}_{0.1}\text{O}_{3-\delta}$ (SCFTa) were investigated by both isothermal gravimetric and X-Ray diffraction. It was shown that the reaction between SCF and CO_2 at elevated temperature is almost negligible when Ta is doped to SCF. XPS analysis shows that the basicity of SCFTa is less than that of SCF, which may contribute to the enhanced stability of SCFTa in CO_2 atmosphere. Ta^{5+} also increases the perovskite phase stability of SCF in low oxygen partial pressure ($p\text{O}_2 < 10^{-2}$ atm), which was proven by the disappearance of a strong shrinkage signal during dilatometric thermal expansion measurements. In the oxygen permeation measurement, the flux of SCFTa was slightly lower than that of SCF when an air–helium gradient was applied over the membrane, but it remained almost the same when pure CO_2 was introduced as sweeping gas, while, the oxygen permeation flux of SCF dropped drastically at first and decreased to zero after 60 h in CO_2 atmosphere.

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1. Introduction

One of the reasons for global warming is the massive anthropogenic emission of CO_2 , which arises mainly from use of fossil fuels. It has been proposed that burning fossil fuels with CO_2 -diluted O_2 produces a concentrated CO_2 gas stream and thus enables efficient CO_2 capture [1,2]. To improve the economic competitiveness of this oxyfuel combustion technique, there are substantial efforts in developing ceramic oxygen separation membranes that have a potential to reduce the oxygen production cost by one third over the present cryogenic air separation process [3]. It is reported that in the Advanced Zero Emission Power Plant (AZEP) technique the O_2/CO_2 mixture, necessary for combustion, could be supplied by using CO_2 as sweeping gas for the transport of oxygen through a Mixed Ionic and Electronic Conductor (MIEC) membrane [4–6]. The MIEC usually has the oxygen deficient perovskite structure ($\text{ABO}_{3-\delta}$), in which oxygen ions are transported via hopping of oxygen vacancies, while electrons are conducted along the B–O–B network. Several new materials have been explored from which $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) is regarded as one of the most promising material. However, SCF has

been reported to undergo a phase transition from cubic perovskite to orthorhombic brownmillerite below 790 °C. Moreover, because of the presence of the alkaline-earth element Sr, SCF is very sensitive to acidic gasses like CO_2 . Yi et al. showed that exposure of SCF to an atmosphere containing 5% CO_2 at 810 °C resulted in the decomposition and partial failure of the membrane [7]. Zeng et al. also found that SCF completely decomposed after annealing in CO_2 at 950 °C [8].

Recently, high valence ions such as Ti^{4+} and Ta^{5+} have been reported to have positive effect on the phase stability and CO_2 tolerance of some MIECs. Zeng et al. have found that Ti doping considerably decreased the reaction between CO_2 and SCF [8], while Wang's group has been reported that introduction of Ta into $\text{SrCoO}_{3-\delta}$ improves phase stability and reversibility in air [9], and Ta containing $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Ta}_{0.1}\text{O}_{3-\delta}$ also exhibits high stability, high permeability and a low thermal expansion coefficient [10]. Bi et al. also found that partial substitution of Ce by Ta strongly increased the chemical stability of $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ against CO_2 [11], and they claimed that the relatively high electronegativity of Ta decreased the basicity of $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$, and consequently increased the chemical stability in a CO_2 environment. So it is reasonable to make the assumption that partial substitution of the B-site Co and Fe in SCF by Ta may increase its phase stability and CO_2 tolerance.

In this work, 10% of the Co and Fe cations in SCF were substituted by Ta, aiming to increase to the stability of SCF in CO_2 atmosphere. Both isothermal gravimetric and XRD were used to study the effect of Ta doping on phase stability, while oxygen permeation measurements were performed to examine permeation performance under operating conditions.

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2. Experimental

$\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) and $\text{Sr}(\text{Co}_{0.8}\text{Fe}_{0.2})_{0.9}\text{Ta}_{0.1}\text{O}_{3-\delta}$ (SCFTa) powders were synthesized using an EDTA complexation/pyrolysis process [12]. Required quantities of SrCO_3 were dissolved in diluted nitric acid and appropriate amounts of $\text{Co}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$ solutions and EDTA (metal-cation: EDTA = 1:1) were added. The pH of the solution was adjusted to 2 with ammonia and finally Ta_2O_5 was added. The mixture was evaporated at 80°C while stirring until a viscous resin was obtained and subsequently heated on a hot plate, resulting in a rapid and vigor auto-ignition. The resultant powder was calcined at 1000°C for 5 h. The calcined powders were pressed uniaxially at 4 MPa into disk shapes, subsequently cold isostatically pressed at 300 MPa, and sintered in ambient air at 1200°C (SCF) or 1237°C (SCFTa) for 15 h.

Densities of the sintered samples were determined using Archimedes method in mercury. The phase composition was analyzed using XRD (Philips X'Pert Pro Super, Cu K α). The O1s XPS spectra of as-calcined powders were measured using an ESCALAB MK II, VG equipment, and analyzed with the Gaussian peaks software. Isothermal gravimetric analyses were carried out in a home-built apparatus equipped with an analytical balance. About 1 g of powder was placed in a quartz sample holder suspended from the bottom of the balance with a hooked quartz stick, and was heated in flowing air to 900°C . When the sample mass reached a constant value at 900°C , a CO_2 stream was introduced instead of air and the mass change was recorded and sampled by a computer.

Thermal expansion measurements were conducted using a dilatometer (NETZSCH DIL 402C) at a heating/cooling rate 3°C . First, sintered SCF and SCFTa samples were heated to 1000°C in nitrogen ($p\text{O}_2 \sim 10^{-4}$ atm) and then cooled to room temperature also in nitrogen. After that, the as-annealed samples were heated to 1000°C again in nitrogen and the thermal expansion was recorded.

The experimental setup for oxygen permeation measurements is schematically shown in Fig. 1. Disk-shaped samples with a diameter of 15 mm and a relative density >90% were polished to a thickness of 1 mm and ultrasonically cleaned in ethanol. The membranes were sealed to one end of an alumina tube at 1020°C using a glass ring as sealant. After sealing, the temperature was lowered to 900°C , and air was fed to one side of the sample (100 ml/min), while He or CO_2 (50 ml/min) was led over the other (permeate) side to carry away the permeated oxygen. The

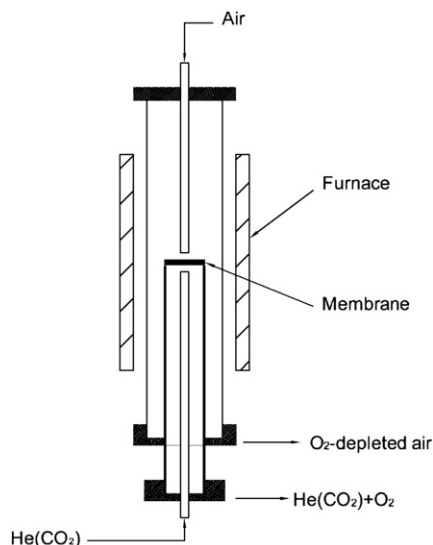


Fig. 1. Schematic diagram of the high temperature permeation setup.

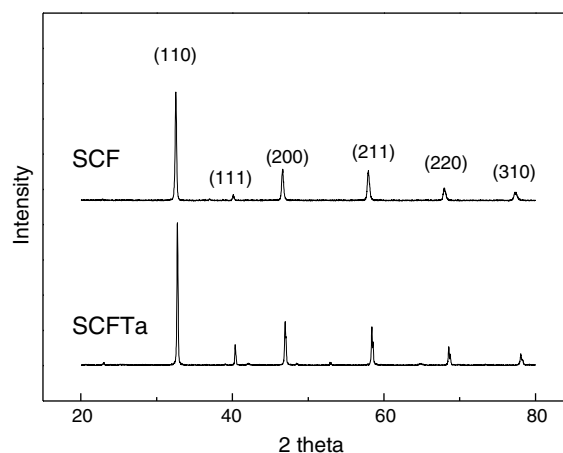


Fig. 2. XRD patterns of air-calcined SCF and SCFTa. All peaks are indexed in cubic setting.

composition of the effluent stream at the permeate side was analyzed by an online gas chromatograph (Ke Xiao instrument China GC-1690T). The oxygen flux was corrected for any oxygen leakage through the glass sealant or imperfection in the pellet by measuring the concentration of nitrogen in the effluent stream. The amount of leakage oxygen is typically less than 5% of the total amount of the permeated oxygen.

3. Results and discussion

3.1. Phase composition and thermal expansion

Fig. 2 shows the room temperature XRD patterns of as-calcined SCF and SCFTa powders. The XRD patterns can be indexed as cubic perovskite, and there is no evidence of second phase, indicating that a phase pure perovskite structure can be obtained by the synthesis method described above.

For SCF, it is well known that, during heating, a phase transition from the brownmillerite to the perovskite crystal structure occurs around 790°C when $p\text{O}_2$ is less than 10^{-2} atm [13–16], accompanied by a sudden volume decrease of more than 1% which may result in cracking of the membrane. Because of the sudden expansion during the formation of the perovskite crystal structure, analyzing the thermal expansion as function of temperature is a simple tool for detecting whether a membrane experiences this phase transition. Such a sudden expansion is even better visible when the derivative of the expansion as function of temperature is depicted. Thermal expansion measurements for both SCF and SCFTa were conducted and the results are shown in Fig. 3. A sudden large shrinkage for undoped SCF at around 760°C is observed which can be identified as the phase transition from the orthorhombic brownmillerite to the cubic perovskite structure. In previous work [17], we have found that addition of Zr increases the phase stability of SCF in a nitrogen atmosphere and decreases the volume change. However, still a small change in thermal expansion occurs when 4% Zr (the solubility limit in SCF) was added. While, no such shrinkage is observed for SCFTa (see Fig. 3), suggesting that Ta doping can completely prevent the phase transition.

3.2. Effect of Ta-doping on the reaction between SCF powders and CO_2

Isothermal gravimetric analysis of SCF and SCFTa powders in CO_2 atmosphere at 900°C are given in Fig. 4. The mass of the SCF powder immediately increased upon exposure to pure CO_2 at 900°C , resulting in a mass gain of 14.5% after 18 h. While the Ta-doped SCF powder

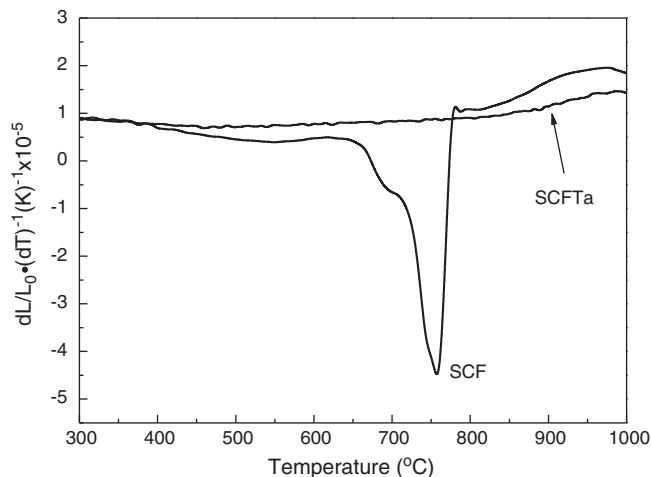
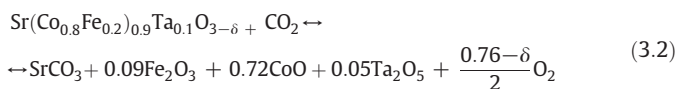
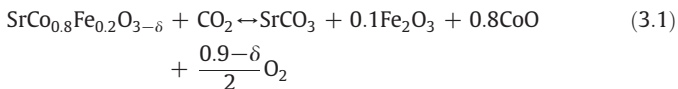


Fig. 3. Derivative of the expansion as function of temperature of SCF and SCFTa (in nitrogen).

showed a slight increase in mass of only 1.7% after 17 h of CO₂ exposure. Obviously, the reaction between SCF and CO₂ is largely restrained by the doping of Ta to SCF. After the isothermal gravimetric analysis, the samples were cooled to room temperature in CO₂ atmosphere and X-ray powder diffraction measurements were conducted to study the phase composition. The results given in Fig. 5 show that the SCF sample completely decomposed into strontium carbonates and iron/cobalt oxides, which is in accordance with the work of Rui et al. [18] and Yang and Lin [19]. For the Ta-doped SCF, only a small amount of SrCO₃ was present but this could be regarded as an extremely small amount, while the perovskite structure of SCFTa was largely preserved.

The general reaction between SCF or SCFTa and CO₂ can be written as follows [20]:



If δ is assumed to be 0.5, as mentioned in ref. [21], it can be calculated from these chemical reactions in combination with the

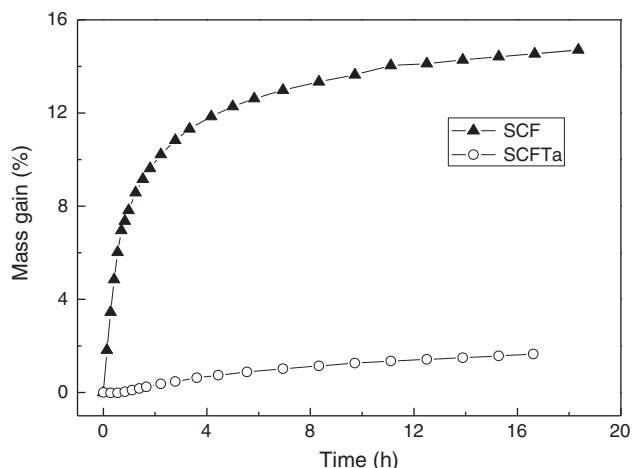


Fig. 4. Mass change of SCF and SCFTa powder samples upon exposure to CO₂ at 900 °C.

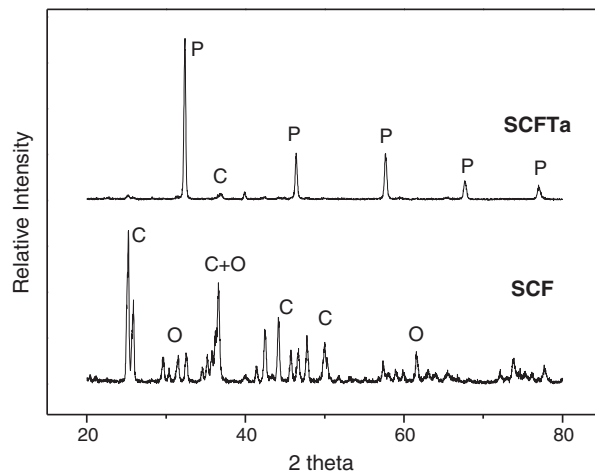


Fig. 5. XRD patterns of SCF and SCFTa after isothermal gravimetric analysis in CO₂ atmosphere at 900 °C for 19 and 17 h respectively and subsequently cooled to room temperature in CO₂. P: perovskite; C: SrCO₃; O: metal-oxides.

mass loss as determined by isothermal gravimetric analysis (Fig. 2) that over 85% (mol) of SCF has decomposed, while this decomposition is less than 8% for SCFTa. Generally, the chemical reactions as given in Formulae (3.1) and (3.2) can be regarded as a Lewis acid–base reaction, where CO₂ acts as the acid while the metal oxides represent the solid base [11]. The intensity of this reaction is determined by the basicity of the metal oxides, and it is well known that the basicity of a metal oxide is defined as the ability of these species to donate electrons to an adsorbed molecule (in this case CO₂). In general, the O1s binding energy (O1s BE), which is related to the charge density around the oxide ions, is usually used as a measure for the basicity of metal oxides [22,23]. A higher O1s BE means a lower charge density and consequently it is harder for the oxides to donate electrons to the adsorbed molecule. In this work, the O1s BE of SCF and SCFTa were measured by X-ray Photoelectron Spectroscopy (XPS). The XPS spectra of the O1s BE signals are shown in Fig. 6, and all specific data are summarized in Table 1.

The peak at 531.4 eV is assigned to oxygen adsorbed on the particle surface [24], which is identical for both SCF and SCFTa. However, the peak for lattice oxygen of SCFTa in XPS shifts to a higher value by 0.4 eV compared with pure SCF, indicating that the electron donating capacity of SCFTa is less and consequently its basic character is weaker than that of SCF. One possible reason for the lower basicity of SCFTa is

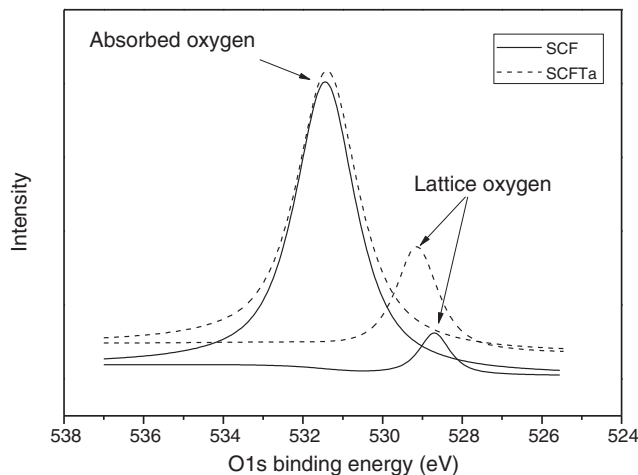


Fig. 6. O1s binding energy of lattice oxide ions and absorbed oxygen of SCF and SCFTa powders as determined by XPS.

Table 1
O1s binding energies of SCF and SCFTa.

	Absorbed oxygen (eV)	Lattice oxygen (eV)
SCF	531.4	528.7
SCFTa	531.4	529.1

that the Ta—O bond strength of 799.1 kJ/mol is much higher than that of Co—O (384.5 kJ/mol) and the Fe—O bond (390.4 kJ/mol) [25]. So, partial substitution of Co and Fe, as present on the B-sites of SCF, by Ta increases the average B—O bond strength and consequently decreases the surface charge density, leading to a decrease of the basicity of SCF.

3.3. Oxygen permeation

To examine the oxygen permeation performance of SCF and SCFTa membranes under operating conditions, i.e. in a CO₂ atmosphere, long term oxygen permeation measurements were performed at 900 °C under air/CO₂ gradient (air flow rate 100 ml/min). The results, as given in Fig. 7, showed a permeability of around 1×10^{-6} mol/cm²/s for SCF when helium (50 ml/min) was used as sweeping gas, which is in accordance with literature [15]. However, when CO₂ (50 ml/min) was introduced, the flux suddenly dropped to 7.2×10^{-7} mol/cm²/s, followed by a decrease to almost zero after 57 h of CO₂ exposure at the sweep side of the membrane. For SCFTa, it took almost 30 h to achieve a steady oxygen permeation flux in helium, which has also been found by Zhu and Yi in their work [26,27]. This could be due to readjusting of the lattice structure from the as-prepared state to a steady state under permeation conditions or to a reduction of the initial surface oxygen desorption rate. When CO₂ was introduced as sweeping gas instead of helium, the oxygen permeation flux dropped from 9×10^{-7} mol/cm²/s to 8.5×10^{-7} mol/cm²/s. This drop in permeation is much lower than that of SCF. Even more important is that the flux remained almost constant during the following 50 h (7.8×10^{-7} mol/cm²/s after 50 h). Overall, it is worthwhile to get a stable membrane at the expense of sacrificing a little of permeability because stability is of top importance in industry. The good performance of SCFTa undoubtedly suggests that SCFTa should be a promising material for oxygen production in the oxyfuel process.

4. Conclusion

The phase transition from perovskite to brownmillerite at low oxygen partial pressure ($p_{O_2} < 10^{-2}$ atm) can effectively be restrained by substitution of Co and Fe with 10% Ta at the B site of SrCo_{0.8}Fe_{0.2}O_{3- δ} (SCF). Oxygen permeation measurements were conducted and the results showed that the Ta-doped SCF possessed much better long-term stability in a CO₂ atmosphere than pure SCF. A possible reason is that Ta doping decreases the basicity of SCF, which restrains the acid–base reaction of CO₂ with SCF. Actually, the decrease of basicity has been proven by XPS analysis. To sum up, the good performance of SCFTa in reducing atmosphere as well as in CO₂ atmosphere makes this material an interesting candidate as membrane in the oxyfuel combustion process.

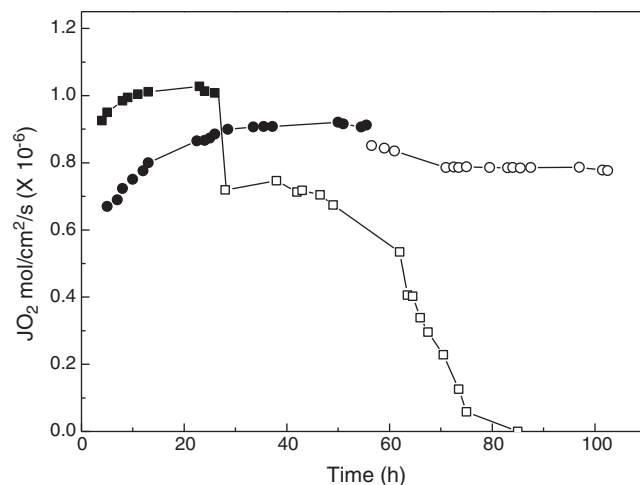


Fig. 7. Time dependence of oxygen permeation flux through 1 mm membranes at 900 °C; Sweep gas flow rate (He, CO₂): 50 ml/min ■: SCF in He; □: SCF in CO₂; ●: SCFTa in He; ○: SCFTa in CO₂.

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