



A novel CO₂-stable dual phase membrane with high oxygen permeability†

Cite this: *Chem. Commun.*, 2014, 50, 2451Received 16th October 2013,
Accepted 9th January 2014

DOI: 10.1039/c3cc47962e

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By cobalt-doping of the mixed conducting phase PSFC, a good combination of high CO₂ stability and high oxygen permeability is obtained for the 60 wt% Ce_{0.9}Pr_{0.1}O_{2-δ}-40 wt% Pr_{0.6}Sr_{0.4}Fe_{0.5}Co_{0.5}O_{3-δ} (CP-PSFC) dual phase membrane, which suggests that CP-PSFC is a promising membrane for industrial applications in the oxyfuel process for CO₂ capture.

CO₂ capture and storage technologies in power plants have gained attention worldwide¹ since the combustion of fossil fuel is considered to be the main contribution to CO₂ emissions. Oxygen transporting membranes (OTMs)² based on mixed electronic and ionic conductors, can supply oxygen of 100% purity to power stations for CO₂ capture according to the oxyfuel for CO₂ capture and storage.³ The oxyfuel concept involves the combustion of fossil fuels with an oxygen/exhaust gas mixture. The pure oxygen used in the oxyfuel process can be produced using the Linde cryogenic technique. However, by using OTMs, oxygen can be separated from air by using a part of the exhaust gas CO₂ as a sweep gas. Oxygen production by using OTMs can reduce the costs by 35% and save 60% energy compared to the conventional cryogenic process.⁴ A part of the exhaust gas CO₂ is sequestered, and another part is recycled and used as sweep gas for the oxygen separation through the OTMs. Thus, the OTMs for CO₂ capture in the oxyfuel process should have not only good stability in a CO₂ atmosphere but also high oxygen permeation performance at elevated temperatures. Moreover, OTMs can be used in many promising potential applications, such as in high-purity oxygen production,⁵ in catalytic membrane reactors,⁶ and as cathodes in solid oxide fuel cells (SOFCs).⁷

Among OTMs, many cobalt-based single phase perovskite-type membranes such as Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ} exhibit high oxygen permeability⁸ since cobalt can provide a high concentration of

mobile oxygen vacancies in the perovskite lattice over a wide temperature range.⁹ However, under a CO₂ atmosphere these membranes immediately lose their oxygen permeation flux, since the alkaline-earth metals on the A site of the perovskite framework form carbonates with CO₂.¹⁰ Recently, dual phase membranes with good structural stability and CO₂ resistance, made of a micro-scale mixture of well separated grains of the two phases of an oxygen ionic conductor and an electronic conductor, have attracted much attention for the application of the O₂ production in the oxyfuel concept. However, the low oxygen permeability of dual phase membranes needs to be improved to meet the industrial application requirements.¹¹ Zhu *et al.* improved the oxygen permeability of their CO₂-stable dual phase membranes, such as Ce_{0.8}Sm_{0.2}O_{1.9}-SmMn_{0.5}Co_{0.5}O₃¹² and Ce_{0.85}Sm_{0.15}O_{1.925}-Sm_{0.6}Sr_{0.4}FeO₃,¹³ by coating Co-containing porous layers on the membrane surface to enlarge the oxygen exchange surface. In our group, we have developed some novel Co-free CO₂-stable dual phase membranes, such as NiFe₂O₄-Ce_{0.9}Gd_{0.1}O_{2-δ} (NF-CG),¹⁴ Fe₂O₃-Ce_{0.9}Gd_{0.1}O_{2-δ} (F-CG)¹⁵ and Ce_{0.9}Pr_{0.1}O_{2-δ}-Pr_{0.6}Sr_{0.4}FeO_{3-δ} (CP-PSF).¹⁶ The CP-PSF membrane shows a good chemical stability under the harsh conditions of the POM reaction and in a CO₂ atmosphere at high temperatures.¹⁶ Thus, cobalt-doping of the PSF phase in the dual phase CP-PSF membrane can enhance the oxygen vacancy concentration in the membrane lattice, which should result in a combination of good CO₂ stability and high oxygen permeability.

In this paper, we present the novel dual phase membrane, 60 wt% Ce_{0.9}Pr_{0.1}O_{2-δ}-40 wt% Pr_{0.6}Sr_{0.4}Fe_{0.5}Co_{0.5}O_{3-δ} (abbreviated as CP-PSFC) prepared *via* a one-pot sol-gel synthesis method.¹⁷ In this dual phase system, the CP phase is mainly for ionic transport, and the PSFC phase for both electronic and ionic transport. The XRD pattern in Fig. 1 shows that after sintering at 1200 °C for 5 h in air, the dual phase CP-PSFC membrane consists of only the cubic fluorite CP phase (space group 225: *Fm3m*) and the orthorhombic distorted perovskite PSFC phase (space group 74: *Imma*). The phase stability of the dual phase CP-PSFC material against CO₂ was evaluated by *in situ* XRD measurements (Fig. S2, ESI†) between 30 and 1000 °C in an atmosphere of 50 vol% CO₂/50 vol% air. No carbonate formation was observed in the *in situ* XRD patterns

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† Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c3cc47962e

The oxygen permeability of an OTM strongly depends on its composition, the membrane thickness, the coating of the membrane surface (catalytic coating or coating to enlarge the surface, thus enhancing the exchange reaction), and the operation conditions (type of sweep gas, temperature, or the oxygen partial pressure). Table S1 (ESI[†]) contains the oxygen permeation fluxes of several OTMs evaluated with CO₂ as the sweep gas at ca. 950 °C. As shown in Table S1 (ESI[†]), our dual phase CP–PSFC membrane exhibits the highest oxygen permeation flux compared to the other dual phase membranes. It should be noted that the fluxes measured on our dual phase CP–PSFC membrane were obtained for a relatively thick membrane (0.6 mm) without any coating on the membrane surface. It is believed that the oxygen permeability of our CP–PSFC membrane can be further improved by reducing the membrane thickness like a hollow fiber membrane^{23,24} or an asymmetric membrane,²⁵ or by coating for an enlargement of the membrane surface.^{12,13}

Fig. 4 presents the long-term oxygen permeation operation of two dual phase CP–PSFC membranes M1 and M2. For the CP–PSFC membrane M1, when He is used as the sweep gas at 950 °C, the oxygen permeation flux increases slowly during the activation time in the first 10 h. After this activation step, the oxygen permeation flux reaches steady-state with a constant value of 0.84 cm³ (STP) min⁻¹ cm⁻² (inset in Fig. 4). When pure CO₂ was used instead of He as the sweep gas, the oxygen permeation flux only slightly decreased to the lower value of 0.70 cm³ (STP) min⁻¹ cm⁻². This oxygen permeation flux was found to be constant during the whole oxygen permeation operation by using pure CO₂ as the sweep gas at 950 °C for 400 h. When the operation temperature was elevated to 1000 °C, the oxygen permeation flux increased significantly to the higher value of 1.01 cm³ (STP) min⁻¹ cm⁻² and was constant for at least 100 h. Whereas the CP–PSFC membrane M1 shows a phase transition from the rhombohedral to the cubic phase (Fig. S2, ESI[†]) and a fast activation step over 10 h only at the higher temperature of 950 °C, when cooling the CP–PSFC membrane M2 from 950 to 800 °C, a phase transition from the cubic to the orthorhombic phase takes place (Fig. S2, ESI[†]). After this phase transition, a slow activation step takes place over ca. 100 h at the lower

temperature of 800 °C. As a result of (i) the phase transformation, and (ii) the lower permeation temperature, for the CP–PSFC membrane M2 with pure CO₂ as the sweep gas at 800 °C, the oxygen permeation flux decreases slowly from 0.19 to 0.13 cm³ (STP) min⁻¹ cm⁻² in the first 100 h. After this phase transformation and the activation step, the oxygen permeation flux reaches a steady-state for 200 h. For the membranes M1 and M2 after the long-term oxygen permeation operation, no carbonate formation was observed in the XRD patterns (Fig. S3 and S5, ESI[†]). No carbon species enrichment was found at the strontium positions in the EDXS images on the surfaces of the membranes M1 and M2 (Fig. S6 and S7, ESI[†]) and their cross-sections (Fig. S4 and S8, ESI[†]), which excludes SrCO₃ formation. This long-term operations suggest that our dual phase CP–PSFC membrane exhibits an excellent stability in CO₂ and shows a high oxygen permeation performance.

In summary, we have prepared a novel CO₂-stable dual phase 60 wt% Ce_{0.9}Pr_{0.1}O_{2-δ}–40 wt% Pr_{0.6}Sr_{0.4}Fe_{0.5}Co_{0.5}O_{3-δ} (CP–PSFC) membrane with Co-doping of the PSF phase for high oxygen permeability. Cobalt-doping of the PSF phase can enhance the oxygen vacancy concentration in the membrane lattice and stabilize the cubic structure above 800 °C which is beneficial for oxygen permeability. The *in situ* XRD and the long-term operations demonstrate that the CP–PSFC dual phase membrane shows a very good tolerance against CO₂. Moreover, the very high oxygen permeation flux of 0.70 and 1.01 cm³ (STP) min⁻¹ cm⁻² were found to be constant at 950 and 1000 °C during the long-term operation for over at least 400 h. The dual phase CP–PSFC membrane with excellent CO₂ stability and high oxygen permeation performance is a promising membrane material for industrial applications in the oxyfuel process for CO₂ capture.

The EU is thanked for financing the 7th Framework Program of the IP Innovative Catalytic Technologies & Materials for the Next Gas to Liquid Processes (NEXT-GTL). The authors are thankful for the financial support by DFG 147/18-1 and to the Sino-German Center for Promoting Research (GZ 676). The authors thank Prof. Dr Feldhoff for stimulating discussions and F. Steinbach for technical support.

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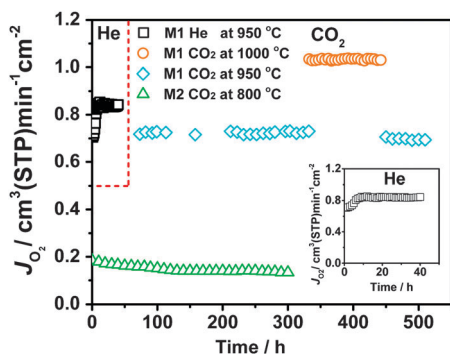


Fig. 4 Long-term oxygen permeation operation of two dual phase CP–PSFC membranes M1 and M2 with pure He or CO₂ as sweep gases at different temperatures. The inset magnifies the oxygen permeation operation with pure He as the sweep gas at 950 °C. Conditions: 150 cm³ min⁻¹ air as the feed gas, 50 cm³ min⁻¹ He or CO₂ as the sweep gas; membrane thickness: 0.6 mm.

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