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# Novel CO₂-stable dual phase membrane with high oxygen permeability

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5 **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.% $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ - 40 wt.% $Pr_{0.6}Sr_{0.4}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (CP-PSFC) dual phase membrane, which suggests that CP-PSFC is as a promising**
10 **membrane for industrial applications in the oxyfuel process for CO₂ capture.**

CO₂ capture and storage technologies in power plants have gained attention worldwide[1] since the combustion of fossil fuel is
15 considered to be the main contribution to CO₂ emissions. Oxygen transporting membranes (OTMs)[2] based on mixed electronic and ionic conductors, can supply 100 % purity oxygen to power stations for CO₂ capture according to the oxyfuel for CO₂ capture and storage.[3] The oxyfuel concept involves the combustion of
20 fossil fuels with an oxygen/exhaust gas mixture. The pure oxygen used in the oxyfuel process can be produced by the Linde cryogenic technique. However, by using OTMs, oxygen can be separated from air by using a part of the exhaust gas CO₂ as sweep gas. Oxygen production by using OTMs can reduce the
25 costs by 35 % and save 60 % energy compared to the conventional cryogenic process.[4] A part of the exhaust gas CO₂ is sequestrated, another part recycled and used as sweep gas for the oxygen separation through the OTMs. Thus, the OTMs for CO₂ capture in oxyfuel process should have not only good stability in
30 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]
35 Among OTMs, many cobalt-based single phase perovskite-type membranes such as $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ exhibit high oxygen permeability[8] since cobalt can provide a high concentration of mobile oxygen vacancies in the perovskite lattice over a wide temperature range.[9] However, under CO₂ atmosphere these
40 membranes lose immediately 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 structure stability and CO₂ resistance, made of a micro-scale mixture of well separated grains of the two
45 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.
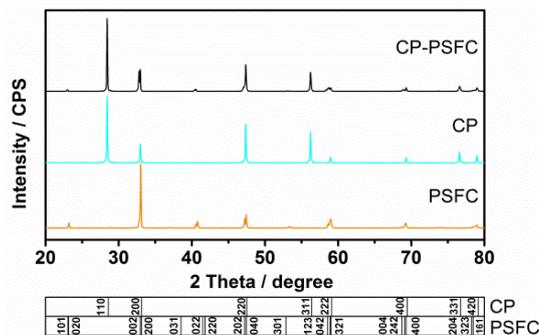


**Fig. 1** XRD patterns of the dual phase CP-PSFC membrane, and of the single phases CP and PSFC, all sintered at 1200 ºC in air for 5 h.

50 improved the oxygen permeability of their CO₂-stable dual phase membranes, such as $Ce_{0.8}Sm_{0.2}O_{1.9}$-$SmMn_{0.5}Co_{0.5}O_3$[12] and $Ce_{0.85}Sm_{0.15}O_{1.925}$-$Sm_{0.6}Sr_{0.4}FeO_3$,[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
55 Co-free CO₂-stable dual phase membranes, such as $NiFe_2O_4$-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (NF-CG),[14] $Fe_2O_3$-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (F-CG)[15] and $Ce_{0.9}Pr_{0.1}O_{2-\delta}$-$Pr_{0.6}Sr_{0.4}FeO_{3-\delta}$ (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
60 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 combined good CO₂ stability and high oxygen permeability.

In this paper, we present the novel dual phase membrane, 60
65 wt.% $Ce_{0.9}Pr_{0.1}O_{2-\delta}$-40 wt.% $Pr_{0.6}Sr_{0.4}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (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
70 1200 ℃ for 5 h in air, the dual phase CP-PSFC membrane consists of only the cubic flourite 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
75 measurements (Fig. S2) between 30 and 1000 ℃ in an atmosphere of 50 vol% CO₂ / 50 vol% air. No carbonate formation was observed in the in-situ XRD patterns from 30 to 1000 ℃, which is in good agreement with the in-situ XRD finding in previous reports of the CP-PSF[16] and $La_{0.6}Sr_{0.4}$-
80 $Co_{0.8}Fe_{0.2}O_{3-\delta}$[18] under the similar experimental conditions. In this temperature range, the CP phase retains the cubic structure. Moreover, two phase transitions of the PSFC phase from the
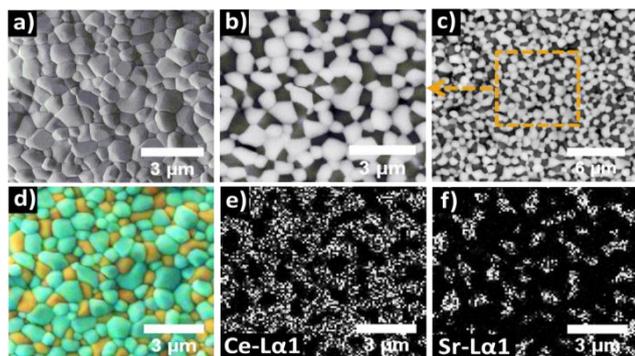
**Fig. 2** SEM (a), BSEM (b, c), and EDXS (d-f) images of the dual phase CP-PSFC membrane after sintered at 1200 °C for 5 h in air. In BSEM (b, c) for different magnifications, the dark grains represent PSFC, the light ones CP. Superimpositions of the Pr, Sr, Fe and Co (orange), and Pr and Ce (turquoise) signals have been used in Fig. 2(d). Element distribution of Ce in the CP grains (Fig. 2e) and Sr in the PSFC (Fig. 2f).

orthorhombic to the rhombohedral symmetry at ca. 600 °C and from the rhombohedral to the cubic symmetry at ca. 800 °C could be observed. However, the PSF phase without Co in the dual phase CP-PSF powder retains the orthorhombic symmetry under
5  the same conditions.[16] The phase transition from rhombohedral to cubic symmetry at high temperatures is in agreement with the finding for the comparable materials $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$[18] and $La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$.[19] The formation of the cubic structure of the PSFC phase at high temperatures is beneficial to the oxygen
10  permeability.[17, 20] Thus, the dual phase CP-PSFC material exhibits a stable co-existence of both the CP and the PSFC phases and a good tolerance against $CO_2$.

**Fig. 2** shows the scanning electron microscopy (SEM), back-scattered SEM (BSEM), and energy-dispersive X-ray
15  spectroscopy (EDXS) images of the dual phase CP-PSFC membrane after sintered at 1200 °C for 5 h in air. SEM (Fig. 2a) indicates that the membrane is dense. In the BSEM (Fig. 2b, c) at different magnifications, the grains of the two phases are well distributed forming a 3-dimensional percolation network with
20  clear grain boundaries, which is beneficial to the oxygen ion and electron transport through the membrane. The light grains in the BSEM are CP and the dark grains are PSFC since the contribution of the backscattered electrons to the SEM signal intensity is proportional to the atomic number. The grain size of
25  CP in these composite membranes is bigger than that of PSFC. The same information of phase distribution is provided by the EDXS (Fig. 2d-f) of the membrane. Fig. 2d shows the color version EDXS of the membrane where the turquoise color (dark in BSEM) is an overlap of the Ce and Pr signals, whereas the
30  orange color (light in BSEM) stems from an average of the Pr, Sr, Fe and Co signals. The EDXS elemental distributions of Ce in the CP grains (Fig. 2e) and of Sr in the PSFC grains (Fig. 2f) indicate the phase separation in the membrane and proof that no intermixing of Ce and Sr between the two phases exists.
35  The oxygen permeation fluxes through the dual phase CP-PSFC membrane as a function of temperature with pure He and $CO_2$ as sweep gases are shown in **Fig. 3**. For both the sweep gases He and $CO_2$, the oxygen permeation flux increases with increasing temperatures. By increasing the temperatures from 800 to 1000
40  °C, the oxygen permeation fluxes raise from 0.24 to 1.08 $cm^3(STP)min^{-1}cm^{-2}$ for using He and from 0.11 to 1.01 $cm^3(STP)min^{-1}cm^{-2}$ for using $CO_2$ as sweep gas. If pure $CO_2$ as sweep gas has been used, the oxygen permeation flux is only slightly lower than in the case when pure He was the sweep gas,
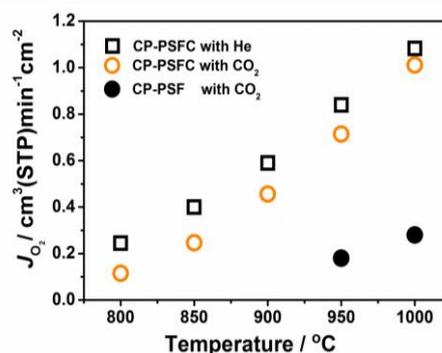


**Fig. 3** Oxygen permeation fluxes through the dual phase CP-PSFC and CP-PSF[25] membranes as a function of temperature with pure He and $CO_2$ as sweep gas. Conditions for CP-PSFC: 150 $cm^3(STP)min^{-1}$ air as feed gas, 50 $cm^3(STP)min^{-1}$ He or $CO_2$ as sweep gas; Membrane thickness: 0.6 mm. Conditions for CP-PSF:[16] 150 $cm^3(STP)min^{-1}$ air as feed gas, 30 $cm^3(STP)min^{-1}$ $CO_2$ as sweep gas; Membrane thickness: 0.5 mm.

45  which is in good agreement with the observation in previous reports.[13, 14, 21] The reason of this experimental finding can be attributed to the weaker adsorptive interaction of He in comparison with $CO_2$ with the membrane surface, as the influence of He on the oxygen exchange reaction is less than that
50  of $CO_2$.[12, 14, 22, 23] Furthermore, it is also found that the difference of the oxygen permeation flux between He and $CO_2$ as sweep gases is bigger at lower temperatures and becomes smaller at higher temperatures, which can be ascribed to the decreasing adsorptive interaction with increasing temperatures. In
55  comparison with the Co-free dual phase CP-PSF membrane at 950 and 1000 °C,[16] the oxygen permeation fluxes of the Co-containing dual phase CP-PSFC membrane are increased by approximately the factor of 3, which is a clear indication for an increased concentration of mobile oxygen vacancies by Co-
60  doping which enhances significantly the oxygen permeability of the PSFC phase.

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
65  surface thus enhancing the exchange reaction), and the operation conditions (type of sweep gas, temperature, or the oxygen partial pressure). **Tab. S1** contains the oxygen permeation fluxes of several OTMs evaluated with $CO_2$ as sweep gas at ca. 950 °C. As shown in Tab. S1, our dual phase CP-PSFC membrane exhibits
70  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 relative thick membrane (0.6 mm) without any coating on the membrane's surface. It is believed that the oxygen permeability
75  of our CP-PSFC membrane can be further improved by reducing the membrane thickness as a hollow fiber membrane[23, 24] or an asymmetric membrane,[25] or by coating for a membrane surface enlargement.[12, 13]

**Fig. 4** presents the long-term oxygen permeation operation of two
80  dual phase CP-PSFC membranes M1 and M2. For CP-PSFC membrane M1, when He is used as 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
85  $cm^3(STP)min^{-1}cm^{-2}$ (inset in Fig. 4). When pure $CO_2$ was used instead of He as sweep gas, the oxygen permeation flux only slightly decreased to the lower value of 0.70 $cm^3(STP)min^{-1}cm^{-2}$. This oxygen permeation flux was found to be constant during the whole oxygen permeation operation by using pure $CO_2$ as sweep
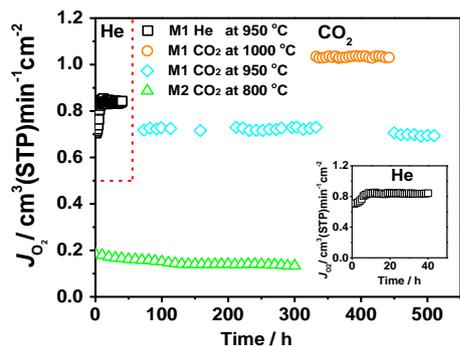
**Fig. 4** Long-term oxygen permeation operation of two dual phase CP-PSFC membranes M1 and M2 with pure He or $CO_2$ as sweep gases at different temperatures. The inset magnifies the oxygen permeation operation with pure He as sweep gas at 950 ℃. Conditions: 150 $cm^3$ $min^{-1}$ air as feed gas, 50 $cm^3$ $min^{-1}$ He or $CO_2$ as sweep gas; Membrane thickness: 0.6 mm.

gas at 950 ℃ for 400 h. when the operation temperature was elevated to 1000 ℃, the oxygen permeation flux increased significantly to the higher value of 1.01 $cm^3(STP)min^{-1}cm^{-2}$ and was constant for at least 100 h. Whereas the CP-PSFC membrane
5   M1 shows a phase transition from rhombohedral to cubic (Fig. S2) and a fast activation step over 10 h only at the higher temperature of 950 ℃, when cooling the CP-PSFC membrane M2 from 950 to 800 ℃, a phase transition from cubic to orthorhombic takes place (Fig. S2). After this phase transition, a slow activation step
10   takes place over ca. 100 h at the lower temperature of 800 ℃. As a result of (i) the phase transformation, and (ii) the lower permeation temperature, for the CP-PSFC membrane M2 with pure $CO_2$ as sweep gas at 800 ℃, the oxygen permeation flux decreases slowly from 0.19 to 0.13 $cm^3(STP)min^{-1}cm^{-2}$ in the first
15   100 h. After this phase transformation and the activation step, the oxygen permeation flux reaches a steady-state for 200 h. For the membrane M1 and M2 after the long-term oxygen permeation operation, no carbonate formation was observed in the XRD patterns (Fig. S3 and S5). No carbon species enrichment was
20   found on the strontium positions in the EDXS images of the membranes M1 and M2 surfaces (Fig. S6 and S7) and cross-sections (Fig. S4 and S8) which excludes a $SrCO_3$ formation. This long-term operations suggest that our dual phase CP-PSFC membrane exhibits an excellent stability in $CO_2$ and shows a high
25   oxygen permeation performance.

In summary, we prepared a novel $CO_2$-stable dual phase 60 wt.% $Ce_{0.9}Pr_{0.1}O_{2-\delta}$-40 wt.% $Pr_{0.6}Sr_{0.4}Fe_{0.5}Co_{0.5}O_{3-\delta}$ (CP-PSFC) membrane with Co-doping of the PSF phase for a high oxygen permeability. Cobalt-doping of the PSF phase can enhance the
30   oxygen vacancy concentration in the membrane lattice and stabilize the cubic structure above 800 ℃ which is beneficial for the oxygen permeability. The in-situ XRD and the long-term operations demonstrated that the CP-PSFC dual phase membrane shows a very good tolerance against $CO_2$. Moreover, the very
35   high oxygen permeation flux of 0.70 and 1.01 $cm^3(STP)min^{-1}cm^{-2}$ were found to be constant at 950 and 1000 ℃ during the long-term operation over at least 400 h. The dual phase CP-PSFC membrane with excellent $CO_2$ stability and high oxygen permeation performance is a promising membrane material for
40   industrial applications in the oxyfuel process for $CO_2$ capture.

## Notes and references

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1.  R. S. Haszeldine, *Science*, 2009, 325, 1647-1652.
2.  S. P. S. Badwal and F. T. Ciacchi, *Adv. Mater.*, 2001, 13, 993-+; Y. Y. Liu, X. Y. Tan and K. Li, *Catal. Rev. - Sci. Eng.*, 2006, 48, 145-198; J. Sunarso, S. Baumann, J. M. Serra, W. A. Meulenberg, S. Liu,
60   Y. S. Lin and J. C. D. da Costa, *J. Membr. Sci.*, 2008, 320, 13-41.
3.  A. Leo, S. Liu and J. C. D. da Costa, *Int. J. Greenhouse Gas Control*, 2009, 3, 357-367; X. Y. Tan, K. Li, A. Thursfield and I. S. Metcalfe, *Catal. Today*, 2008, 131, 292-304.
4.  P. A. Armstrong, D. L. Bennet, E. P. T. Förster and E. E. van Stein,
65   Washington DC, USA, 3-6 October 2004.
5.  X. F. Zhu, S. M. Sun, Y. Cong and W. S. Yang, *J. Membr. Sci.*, 2009, 345, 47-52; F. Y. Liang, H. Q. Jiang, T. Schiestel and J. Caro, *Ind. Eng. Chem. Res.*, 2010, 49, 9377-9384; F. Y. Liang, H. Q. Jiang, H. X. Luo, R. Kriegel and J. Caro, *Catal. Today*, 2012, 193, 95-100.
70   6.  H. Q. Jiang, H. H. Wang, F. Y. Liang, S. Werth, T. Schiestel and J. Caro, *Angew. Chem. Int. Ed.*, 2009, 48, 2983-2986; Y. Y. Wei, W. S. Yang, J. Caro and H. H. Wang, *Chem. Eng. J.*, 2013, 220, 185-203.
7.  Z. P. Shao and S. M. Haile, *Nature*, 2004, 431, 170-173.
8.  Z. P. Shao, W. S. Yang, Y. Cong, H. Dong, J. H. Tong and G. X.
75   Xiong, *J. Membr. Sci.*, 2000, 172, 177-188; J. F. Vente, S. McIntosh, W. G. Haije and H. J. M. Bouwmeester, *J. Solid State Electrochem.*, 2006, 10, 581-588.
9.  R. Kriegel, R. Kircheisen and J. Töpfer, *Solid State Ionics*, 2010, 181, 64-70.
80   10.  M. Arnold, H. H. Wang and A. Feldhoff, *J. Membr. Sci.*, 2007, 293, 44-52; A. Waindich, A. Möbius and M. Müller, *J. Membr. Sci.*, 2009, 337, 182-187; S. Engels, F. Beggel, M. Modigell and H. Stadler, *J. Membr. Sci.*, 2010, 359, 93-101.
11.  B. C. H. Steele, *Curr. Opin. Solid State Mater. Sci.*, 1996, 1, 684-691.
85   12.  X. F. Zhu, H. Y. Liu, Y. Cong and W. S. Yang, *Chem. Commun.*, 2012, 48, 251-253.
13.  X. F. Zhu, M. R. Li, H. Liu, T. Y. Zhang, Y. Cong and W. S. Yang, *J. Membr. Sci.*, 2012, 394, 120-130.
14.  H. X. Luo, K. Efimov, H. Q. Jiang, A. Feldhoff, H. H. Wang and J.
90   Caro, *Angew. Chem., Int. Ed.*, 2011, 50, 759-763.
15.  H. X. Luo, H. Q. Jiang, K. Efimov, F. Y. Liang, H. H. Wang and J. Caro, *Ind. Eng. Chem. Res.*, 2011, 50, 13508-13517.
16.  H. X. Luo, H. Q. Jiang, T. Klande, Z. W. Cao, F. Liang, H. H. Wang and J. Caro, *Chem. Mater.*, 2012, 24, 2148-2154.
95   17.  F. Y. Liang, K. Partovi, H. Q. Jiang, H. X. Luo and J. Caro, *J. Mater. Chem. A*, 2013, 1, 746-751.
18.  T. Klande, O. Ravkina and A. Feldhoff, *J. Membr. Sci.*, 2013, 437, 122-130.
19.  K. Efimov, T. Klande, N. Juditzki and A. Feldhoff, *J. Membr. Sci.*,
100   2012, 389, 205-215.
20.  X. T. Liu, H. L. Zhao, J. Y. Yang, Y. Li, T. Chen, X. G. Lu, W. Z. Ding and F. S. Li, *J. Membr. Sci.*, 2011, 383, 235-240; X. F. Zhu, H. H. Wang and W. S. Yang, *Chem. Commun.*, 2004, 1130-1131.
21.  H. X. Luo, H. Q. Jiang, T. Klande, F. Y. Liang, Z. W. Cao, H. H.
105   Wang and J. Caro, *J. Membr. Sci.*, 2012, 423, 450-458.
22.  S. M. Fang, C. S. Chen and L. Winnubst, *Solid State Ionics*, 2011, 190, 46-52; J. E. tenElshof, H. J. M. Bouwmeester and H. Verweij, *Solid State Ionics*, 1996, 89, 81-92.
23.  W. Li, T. F. Tian, F. Y. Shi, Y. S. Wang and C. S. Chen, *Ind. Eng.*
110   *Chem. Res.*, 2009, 48, 5789-5793.
24.  W. Li, J. J. Liu and C. S. Chen, *J. Membr. Sci.*, 2009, 340, 266-271.
25.  S. Baumann, J. M. Serra, M. P. Lobera, S. Escolastico, F. Schulze-Kueppers and W. A. Meulenberg, *J. Membr. Sci.*, 2011, 377, 198-205; M. P. Lobera, J. M. Serra, S. P. Foghmoes, M. Sogaard and A. Kaiser,
115   *J. Membr. Sci.*, 2011, 385, 154-161.