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## Novel Ceria-based dual-phase membranes for oxyfuel CO<sub>2</sub> capture

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### Experimental

#### *Preparation of membranes*

The two dual-phase membranes 75wt.% Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> - 25wt.% SmMn<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> (SDC - SMC) and 75wt.% Ce<sub>0.8</sub>Sm<sub>0.2</sub>O<sub>1.9</sub> - 25wt.% Sm<sub>0.8</sub>Ca<sub>0.2</sub>Mn<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> (SDC - SMC) were derived from the solid-state one-pot method. After all the required amounts of the CeO<sub>2</sub>, Sm<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, MnO<sub>2</sub> and CaCO<sub>3</sub> were mixed and ball milled, the resulting mixtures were calcined at 1100 °C for 10 h, and then ball milled in ethanol. The calcinations and milling steps were repeated twice. Other perovskite oxides or fluorite oxides used in this paper were synthesized via EDTA-citric acid method as shown in the reference [1]. The powder less 400 mesh was used to prepare disks and bars under a pressure of ~200 MPa. The green disks and bars were sintered at 1400 °C and 1380 °C for 3 h for SDC - SMC and SDC - SCMC, respectively. The bars were sintered at 1500, 1200, 1200 °C for SDC, SMC and SCMC, respectively. All the dual-phase membrane samples employed to oxygen permeation test had relative density no less than 95%. After polished by SiC sand paper and cleaned in ethanol, both sides of membranes were coated with the SDC - SMC porous layer to improve the oxygen surface exchange rates. The slurry was made by mixing terpeneol and the as-prepared SDC - SMC powder with a weight ratio of 1:1. Porous layers were calcined at 1100 °C for 3 h. Thicknesses of porous layers were usually ~10 μm.

#### *Measurements of oxygen permeation fluxes*

Silver rings were used to seal membranes at 963 °C for oxygen permeation experiments. The effective inner surface areas of the membrane discs were controlled around 0.8 cm<sup>2</sup>. The operation temperature was controlled by a microprocessor temperature controller (Model AI-708, Xiamen Yuguang Electronics Technology Research Institute, China) within ±1 °C of the set points through a K-type thermocouple. Dried air (100 mL min<sup>-1</sup>) was used as the feed and high purity helium or CO<sub>2</sub> was used as purge gas on the other side of the membrane. Flow rates of the feed gases were

controlled by mass flow controllers (Models D07-7A/ZM, Beijing Jianzhong Machine Factory, China). Effluents were analyzed by a gas chromatograph (GC, Agilent 6890) equipped with 3 m-13 X column. Oxygen permeation fluxes through membranes were calculated based on the effluent flow rate and the concentration of oxygen in the effluents. Leakage due to the imperfect sealing was calculated by equation (1).

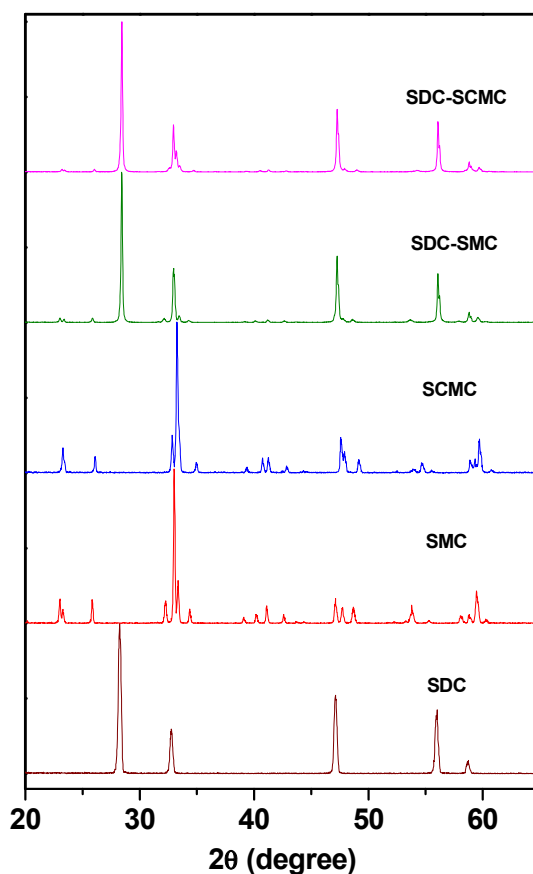
$$Leakage = \sqrt{\frac{28}{32}} \times \frac{0.21}{0.79} \times \frac{C_{N_2}}{C_{O_2}} \times 100\% \quad (1)$$

Where,  $C_{O_2}$  and  $C_{N_2}$  are concentrations of oxygen gas and nitrogen gas detected by GC, respectively. The leakages were no more than 1% for all the oxygen permeation experiments of dual-phase membranes, and had been subtracted when calculating oxygen permeation fluxes.

#### ***Characterization of membrane materials***

The total conductivities (four-probe DC) were measured with the bar-shaped samples about  $20 \times 5 \times 2 \text{ mm}^3$  in air by the four-probe method for the measurement of SMC and SCMC. A constant current of 10 mA was applied on the outside two probes by a galvanostat (Solartron 1287), and the voltage was measured by a multimeter (Keithley 2000). The total conductivities of the two dual-phase materials and SDC with much higher resistances than that of wires were tested by two-probe method. The phase structure of the membrane materials were determined by X-ray diffraction (XRD, Rigaku D/Max-RB, Cu K $\alpha$  radiation) in the  $2\theta$  range of  $20-80^\circ$  with a step width of  $0.02^\circ$ . Surface morphologies of membranes and local areas EDX analysis (spot size  $\sim 1 \mu\text{m}$ ) was observed on a scanning electronic microscopy (SEM, Quanta 200 FEG, FEI Company) operated at 20 kV. The thermal gravimetric (TG) analysis of the two dual-phase materials under  $N_2$  and  $CO_2$  atmosphere was conducted on a thermal analyzer (Pyris Diamond TG/DTA) with gas flow rate of  $100 \text{ mL min}^{-1}$ . The samples were heated from room temperature to  $850^\circ\text{C}$  under  $N_2$  atmosphere with a rate of  $10^\circ\text{C min}^{-1}$  and kept at this temperature for 2 h, then the gas was switched to  $CO_2$  and kept at the temperature for another 2 h.

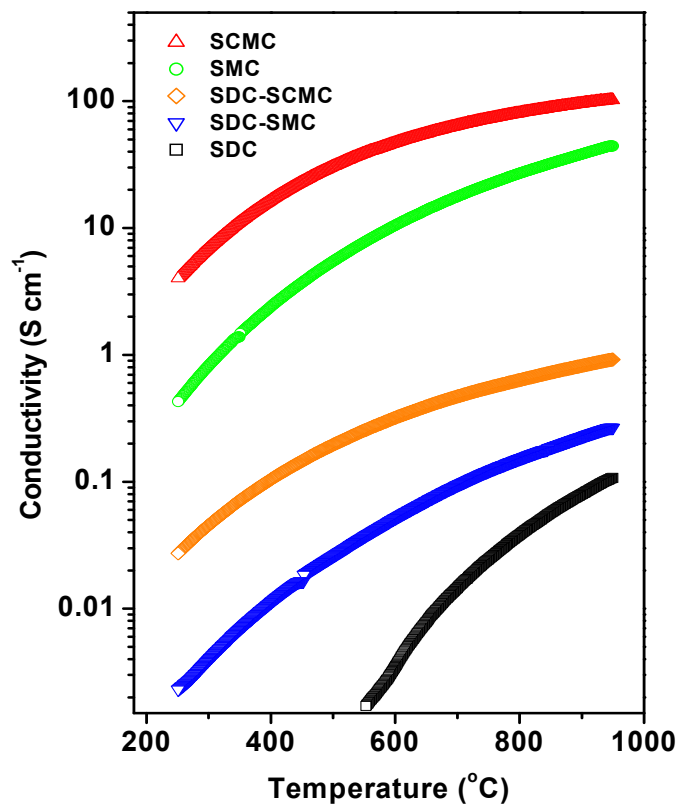
**Figures and Tables**



**Figure S1** XRD patterns of the as-prepared single-phase and dual-phase oxide powders. The samples are calcined at 1100 °C for SDC – SMC and SDC – SCMC powders, and at 900 °C for SDC, SMC and SCMC powders. \*

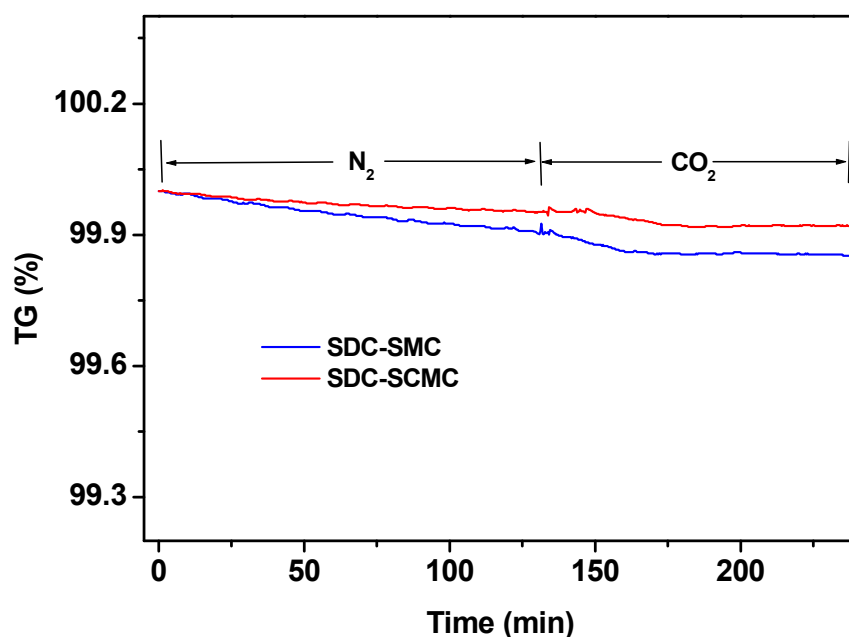
As shown in figure S1, all the diffraction of SDC-SMC and SDC-SCMC slightly shift to high angles. The cell parameters of the fluorite phase are 0.5448 nm for single-phase SDC, 0.5439 and 0.5434 nm for dual-phase SDC-SMC and SDC-SCMC, respectively. The shift of diffraction peaks to high angle of fluorite in the dual-phase system is because some Mn and Co ions transfer into the SDC lattice. Although  $\text{Ca}^{2+}$  (0.112 nm) has larger ionic radius than  $\text{Ce}^{4+}$  (0.097 nm) and  $\text{Sm}^{3+}$  (0.108 nm), constriction of the ceria lattice is always found because divalent  $\text{Ca}^{2+}$  introduces more oxygen vacancies and leads to the contraction of ceria lattice.<sup>2</sup> CaO and  $\text{CeO}_2$  can form solid solutions in a wide concentration range, so the migration of  $\text{Ca}^{2+}$  into ceria lattice cannot be avoided during the one-pot synthesis process. The smaller cell parameters of the fluorite phase in SDC-SCMC just reveals the transfer of  $\text{Ca}^{2+}$ . However, the change of cell parameters of

perovskite phase is difficult to be found. Three probable reasons should be considered. One is that the doping amount of  $\text{Ca}^{2+}$  is small, so the reduction of  $\text{Ca}^{2+}$  has little effects on the cell parameters; another is that only few  $\text{Ca}^{2+}$  ions migrate into ceria lattice; the third is that the strong diffraction peaks of perovskite phase always overlap with those of fluorite phase, as a result it is difficult to accurately get the cell parameters of perovskite phase. The XRD analysis reveals that reactions (or inter-diffusion of metal elements) between SDC and SMC/SCMC could not be avoided if the membranes were prepared via the one-pot procedure, but in the previous investigation it was found that the inter-diffusion has little influence on oxygen permeation.<sup>3</sup>



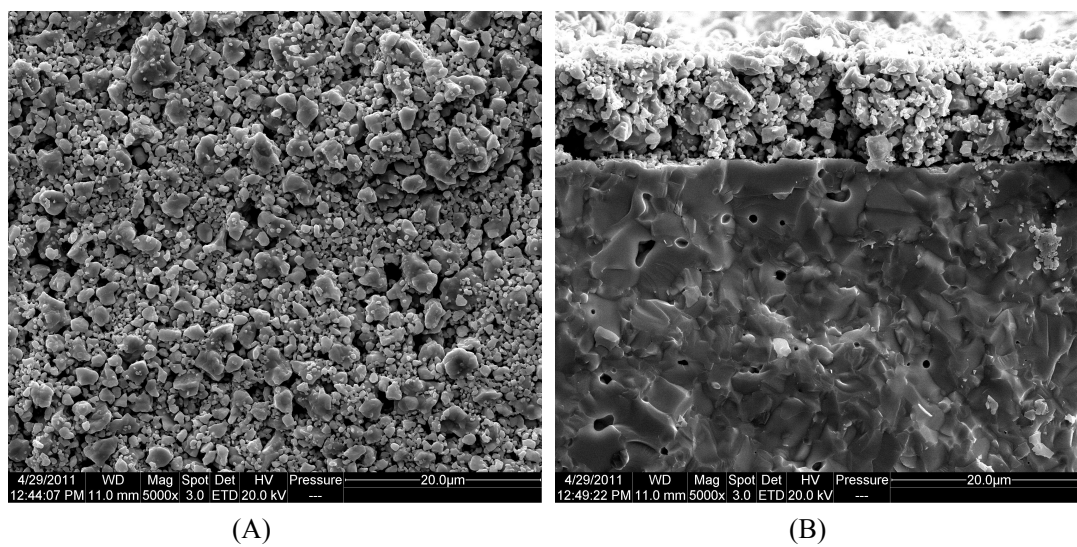
**Figure S2** Temperature dependence of total electric conductivities of the dual-phase and single-phase materials.\*

The ionic conductivity of SDC almost equals to its total conductivity under air atmosphere. Since both dual-phase membranes contain 75wt% of SDC, their ionic conductivities are close to that of SDC. Therefore, the electronic conductivities of the two dual-phase materials can be approximately calculated by subtracting the ionic conductivity of SDC from the total conductivities of dual-phase materials. The calculated electronic conductivities are about 0.15 and 0.8 S cm<sup>-1</sup> for SDC-SMC and SDC-SCMC, respectively at 950 °C. Therefore, the electronic conductivity of SDC-SCMC is enough high compared with the ionic conductivity, but the electronic conductivity of SDC-SMC is insufficient. As a result, the oxygen permeation through SDC-SMC is limited by electronic transport, and that is why the permeation flux of SDC-SMC is smaller than that of SDC-SCMC.

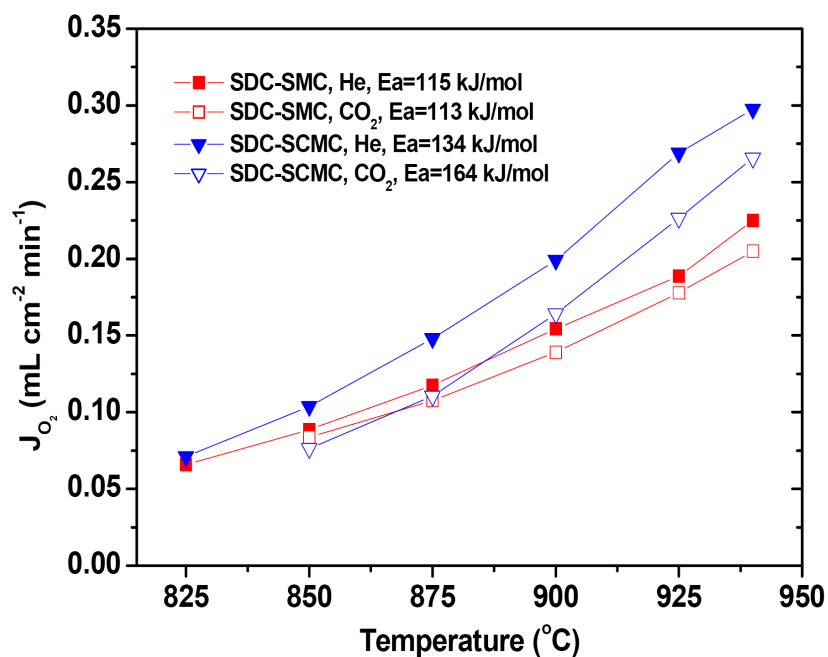


**Figure S3** TG plots of the two dual-phase materials under N<sub>2</sub> or CO<sub>2</sub> atmosphere at 850 °C.\*

TG experiments were to test the absorption of CO<sub>2</sub> by the two dual-phase materials. The materials were heated up to 850 °C under N<sub>2</sub> and then held at the temperature for 2 h, then the N<sub>2</sub> atmosphere was switched to CO<sub>2</sub> and held at the same temperature for another 2 h. If the materials can absorb CO<sub>2</sub>, the weight of the samples would increase; if not, the weight of the samples would decrease as those in N<sub>2</sub>. As shown in the TG figure, the weight of the two samples gradually decrease under N<sub>2</sub>; when the atmosphere was switched to CO<sub>2</sub>, the weight of the two samples still decrease in first one hour and then keep constant. There is no weight increase step, so one can conclude that the two materials cannot absorb CO<sub>2</sub> at 850 °C. In other words, the two materials are CO<sub>2</sub>-stable at 850 °C.



**Figure S4** SEM pictures of the porous SDC-SMC coatings on dual-phase membranes. The porous layers were calcined at 1100 °C for 3 h.



**Figure S5** Temperature dependence of dual-phase membranes swept by helium or CO<sub>2</sub>. Only the air side of the membranes coated with SDC-SMC porous layers. The difference of oxygen partial pressure across membranes was controlled at 21 kPa / 0.5 kPa by adjusting the flow rate of the sweeping gases.\*

As the XRD patterns revealed, the diffusion of Mn, Co and Ca ions from the perovskite phase to fluorite phase will change the activation energy and ionic conductivity of oxygen ionic diffusion in fluorite phase. Here, the fluorite phase is the main phase in the dual-phase system and the surface exchange limitation can be ignored after both sides of the membranes coated with oxygen activation catalyst. Therefore, the permeation activation energy is largely dependent on the activation energy of oxygen ionic diffusion through fluorite phases. Compared with SDC-SMC, the higher permeation activation of SDC-SCMC is related to the diffusion of Ca<sup>2+</sup> into the fluorite lattice in this dual-phase system.



**Table S1** Surface exchange resistance constants of the two dual-phase membranes at different temperatures swept by helium and CO<sub>2</sub>, respectively.\*

Temperature (°C)	Surface exchange resistance constant ( $r_0''$ ) ( $\Omega \text{ cm}^2$ )			
	SDC-SMC		SDC-SCMC	
	He	CO <sub>2</sub>	He	CO <sub>2</sub>
940	0.00543	0.0106	0.00702	0.00924
900	0.00858	0.0137	0.0104	0.0150
850	0.0169	0.0224	0.0224	0.0303

A general transport equation derived by the authors recently,<sup>3,4</sup> gives:

$$j_{O_2} = -\frac{1}{4^2 F^2} \frac{1}{r' + r^b + r''} \Delta\mu_{O_2}^{tot} = -\frac{\Delta\mu_{O_2}^{tot}}{4^2 F^2} \frac{1}{r^{tot}} \quad (2)$$

where  $r'$ ,  $r''$  and  $r^b$  are permeation resistances of interface region of feed side, interface region of permeation side and membrane bulk, respectively;  $-\Delta\mu_{O_2}^{tot}/4^2 F^2$  is the total driving force across the membrane.  $r^{tot} = r' + r^b + r''$  is the total permeation resistance, and can be calculated from the following equations:

$$r^{tot} = -\frac{\Delta\mu_{O_2}^{tot}}{4^2 F^2 j_{O_2}} = -\frac{RT}{4^2 F^2 j_{O_2}} \ln \frac{P_{O_2}^{II}}{P_{O_2}^I} \quad (3)$$

In general, the specific resistances of the interfacial regions are functions of oxygen partial pressure. Usually, a simply power function can be used to describe the relationship between interface specific resistance and the oxygen partial pressure; therefore we can obtain the following relationship:

$$r' = r_0' (P_{O_2}^I / P_0)^{-\frac{1}{n}} \quad (4)$$

and

$$r'' = r_0'' (P_{O_2}^{II} / P_0)^{-\frac{1}{n}} \quad (5)$$

where  $P_0$ ,  $r_0'$  and  $r_0''$  are the oxygen partial pressure of 1 bar, area specific resistances of the feed side and permeation side at oxygen partial pressure of 1 bar, respectively.  $n$  is a positive number, typically an integer. Usually it equals to 2 basing on many experimental data. Therefore, one can get the following two relationships:

$$r^{tot} = r'_0(P_{O_2}^I / P_0)^{\frac{1}{2}} + (r^b + r'') \quad (6)$$

and

$$r^{tot} = r''_0(P_{O_2}^{II} / P_0)^{\frac{1}{2}} + (r^b + r') \quad (7)$$

The total specific resistance can be calculated from equation (3), and if the oxygen pressure on the permeation side is fixed and on the feed side is varied, one can obtain  $r'_0$  and  $r^b + r''$  through linear regression. Similarly,  $r''_0$  and  $r^b + r'$  can be obtained through linear regression of Eq. (7).

Here, only the area specific resistances of the permeation side were especially concerned, and the results were listed in Table S1.

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