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# Improving oxygen permeation of MIEC membrane reactor by enhancing the electronic conductivity under intermediate-low oxygen partial pressures

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## ABSTRACT

Oxygen chemical potential decreases continuously across a mixed ionic-electronic conducting membrane as one side is fed with air and the other side is fed with methane for syngas production. At a certain position in the membrane bulk, the oxygen chemical potential is intermediate-low, i.e. corresponding to an oxygen partial pressure of  $10^{-10}$ – $10^{-15}$  atm. Insufficient electronic conductivity at an intermediate-low oxygen chemical potential may limit the oxygen transport across the membrane bulk under the syngas production condition. In this work, a new ceria based dual-phase membrane 75 wt%  $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925}$  – 25 wt%  $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$  (SDC–SSCF) was prepared as a membrane reactor for the syngas production. The conductivities of SDC–SSCF, 75 wt%  $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925}$  – 25 wt%  $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{Al}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$  (SDC–SSAF, as a control material) and related single-phase materials were investigated under various oxygen partial pressures. SDC–SSAF has enough high electronic conductivity under high and low oxygen partial pressures but limited electronic conductivity under the intermediate-low oxygen partial pressure, thus the low electronic conductivity limits the ambipolar diffusion in the membrane bulk. However, the electronic conductivity of SDC–SSCF is high enough in the whole range of oxygen partial pressure compared with the ionic conductivity. As a result, the oxygen permeation flux through a 0.5-mm-thick SDC–SSCF membrane is high up to  $7.6 \text{ mL cm}^{-2} \text{ min}^{-1}$  at  $950^\circ\text{C}$  for the syngas production, which is 1.8 times that of the SDC–SSAF membrane under the same condition. In addition, the SDC–SSCF membrane reactor was steadily operated for 220 h, and reached > 95% methane conversion and > 98% CO selectivity. The scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) analyses reveal the good stability of SDC–SSCF as a membrane reactor.

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## 1. Introduction

Mixed oxygen ionic-electronic conducting (MIEC) oxides have drawn considerable attention due to their versatile applications as catalysts [1,2], electrodes of solid oxide fuel cells (SOFCs) [3–5], oxygen-permeable membranes for pure oxygen production [6–11], or for the combination with oxy-fuel process for  $\text{CO}_2$  capture [12–16], and membrane reactors for the partial oxidation of light hydrocarbons [17–20] or water splitting for hydrogen production [21–23], or co-producing two types of syngas for ammonia and liquid-fuel synthesis [24]. The catalytic membrane reactor for the partial oxidation of methane (POM) to syngas ( $\text{H}_2 + \text{CO}$ ), the important feedstock for methanol production and Fischer–Tropsch (F–T) reaction, is energy- and cost-efficient in comparison with conventional technologies [25,26].

Many oxygen-permeable materials have been extensively investigated in recent years as membrane reactors for the POM reaction. Amongst them, dual-phase membrane materials are indicated as promising candidates with adjustable compositions according to practical requirements, owing to their good stability under strong reducing conditions [27–34]. The main challenges for dual-phase membranes lie in the chemical compatibility between the electronic conducting phase and ionic conducting phase, as well as the performance of oxygen permeation. Fluorite oxides such as zirconia- and ceria-based solid electrolytes are usually used as the oxygen ionic conducting phase for their high ionic conductivities. In the traditional dual-phase membranes, pure electronic conductors, such as  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  [27] and  $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$  [29], with extremely low ionic conductivity, block the transport of oxygen ions between the fluorite phase grains and thus leads to the low oxygen permeability of the dual-phase materials. Therefore, our group has developed some new dual-phase membranes that are made of ionic conducting oxides and MIEC

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oxides. Their oxygen fluxes are one order of magnitude higher than those of the traditional dual-phase membranes, and these membranes show high stability as membrane reactors for POM reaction [30,32,33]. For example, the dual-phase membranes based on strontium ferrite perovskites, 75 wt%  $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925} - 25 \text{ wt}\% \text{Sm}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$  (SDC-SSF) [32] and 75 wt%  $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925} - 25 \text{ wt}\% \text{Sm}_{0.6}\text{Sr}_{0.4}\text{Al}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$  (SDC-SSAF) [33] exhibit excellent stabilities under the syngas production condition and good oxygen permeation fluxes up to 4.2 and 4.3  $\text{mL cm}^{-2} \text{min}^{-1}$  at 950 °C, respectively. We found that Al doping indeed improves the stability under the syngas production conditions, but does not improve the oxygen permeation flux for POM reaction.

The oxygen permeation fluxes through MIEC membranes are mainly influenced by the conductivity (including electronic and ionic conductivities) and the oxygen partial pressure gradient when bulk diffusion is the rate-determining step. The dependences of the total conductivities on oxygen partial pressure for  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  [35–37] and  $\text{La}_{1-x}\text{Sr}_x\text{M}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$  (M = Al, Ti, Cr etc.) [35,38–42] were analyzed in detail in literatures. The total conductivities of these perovskite materials are predominantly p-type electronic conduction in a high oxygen partial pressure regime ( $> 10^{-10}$  atm), and n-type electronic in a very low oxygen partial pressure regime ( $< 10^{-15}$  atm). In the intermediate-low oxygen partial pressure range, usually  $10^{-10}$ – $10^{-15}$  atm, at elevated temperatures, a minimum value appears. At the point, oxygen ionic conduction dominates and the contributions of p-type and n-type electronic transport are low and comparable. In a POM membrane reactor, the oxygen partial pressure gradient across the membrane is very large. The membrane must withstand oxidizing atmosphere (air) on one side and highly reducing atmosphere ( $\text{CH}_4$ , CO and  $\text{H}_2$ ) with oxygen partial pressure down to  $10^{-21}$  atm on the other side at high temperatures. Fig. 1 shows the decrease of oxygen chemical potential across an MIEC membrane. According to the dependence of electronic conductivities on oxygen partial pressure for  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$  and  $\text{La}_{1-x}\text{Sr}_x\text{M}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ , the electronic conductivity of an MIEC membrane should decrease with oxygen chemical potential in zone I, reach a minimum value in zone II and then gradually increase in zone III. In zone II, the electronic conductivity is even lower than its ionic conductivity. Therefore, although an MIEC membrane has high electronic conductivities under both oxidizing and strong reducing atmospheres, its oxygen permeation may be still limited by the low electronic conductivity in zone II. For the ceria-based dual-phase membranes, the ceria is the main phase.

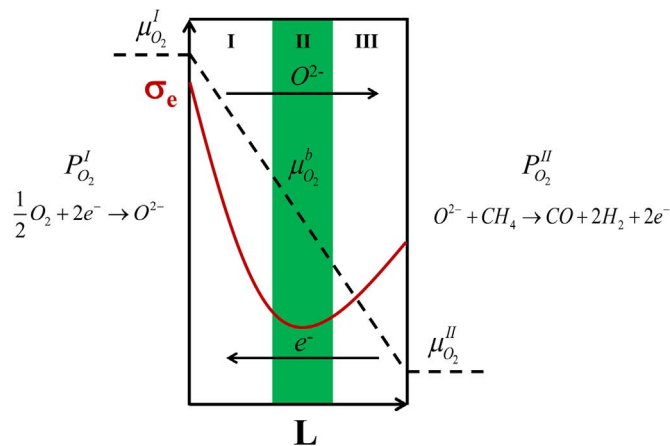


Fig. 1. Schematic illustration of oxygen chemical potential drop and conductivity change across an MIEC membrane in the POM reactor, where L represents the thickness of membrane, and  $\sigma_e$  is the electronic conductivity including p-type and n-type.

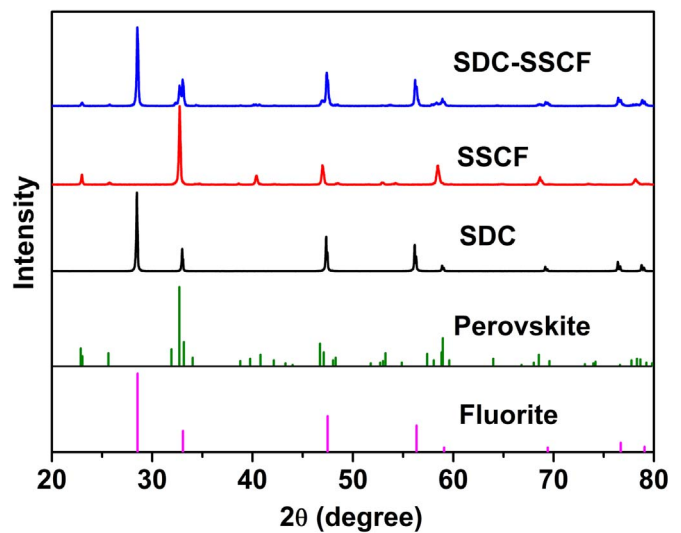


Fig. 2. XRD patterns of single phase oxides and dual-phase membrane. The standard JCPDS files for perovskite ( $\text{SmFeO}_3$ , PDF#39-1490) and fluorite ( $\text{CeO}_2$ , PDF#43-1002) oxides are also listed in this figure.

Ionic conductivity of ceria is marginally affected by oxygen partial pressure [43]; thus, the low electronic conductivity in zone II may significantly affect the oxygen permeation flux because ceria is still not reduced to produce remarkable n-type electronic conduction in the intermediate-low oxygen partial pressure range. It is possible to improve the electronic conductivity in the zone II by changing the chemical composition of the MIEC phase in ceria-based dual-phase membranes. Cr-based perovskite oxides exhibit high electronic conductivity in the oxygen partial pressure range of  $0.21$ – $10^{-21}$  atm [44]. Therefore, a combination of transition metal Cr and Fe on the B-site of perovskites may produce considerable ionic conductivity and high electronic conductivity at intermediate-low oxygen partial pressures.

Herein, we design a ceria based new dual-phase membrane of 75 wt%  $\text{Ce}_{0.85}\text{Sm}_{0.15}\text{O}_{1.925} - 25 \text{ wt}\% \text{Sm}_{0.6}\text{Sr}_{0.4}\text{Cr}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$  (SDC-SSCF). Its conductivity is higher than SDC-SSAF under various oxygen partial pressures, especially in the oxygen partial pressure range of  $10^{-2}$ – $10^{-15}$  atm. Its oxygen permeation flux reaches to 7.6  $\text{mL cm}^{-2} \text{min}^{-1}$  in the POM reactor at 950 °C, and the flux is about 1.8 times that of SDC-SSAF under the same condition. This result indicates that the improvement of electronic conductivity in the intermediate-low oxygen partial pressure range is effective to improve the oxygen permeation flux of dual-phase membranes for POM reaction.

## 2. Experimental

### 2.1. Preparation of membranes and catalysts

The SDC-SSCF powder was prepared by a simple one-pot solid state reaction method (SSR). The required amounts of  $\text{CeO}_2$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SrCO}_3$  and  $\text{Cr}_2\text{O}_3$  were mixed and ball-milled in ethanol for 5 h and then calcined at 1100 and 1200 °C for 10 h, respectively. The particle size of the resultant powder is 100–600 nm. The MIEC and fluorite phases cannot be distinguished as they are ball-milled together. The resultant powder was pressed into green disks under a pressure of  $\sim 200$  MPa and then sintered at 1450 °C for 5 h in stagnant air with heating and cooling rates of  $2$  °C  $\text{min}^{-1}$ . All membranes used for oxygen permeation tests and membrane reactors were polished to 0.5 mm in thickness by 500-mesh waterproof sandpaper. One or both sides of the membrane were coated with a  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC, prepared via a sol-gel

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