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Unsteady-state permeation and surface exchange of dual-phase membranes

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ABSTRACT

Unsteady-state permeation in the initial stage was investigated on ceria-based dual-phase membranes by coating $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) active porous layers onto the surface of membranes. It is found that the unsteady period is greatly influenced by the active porous layer. The membrane with LSC porous layers coated on both sides reaches a steady state immediately while starting the permeation testing. However, the membranes without LSC porous layers coated on one side or both sides need several to tens of hours to achieve the steady state. The active porous layer can improve the oxygen flux and decrease the permeation activation energy, and the membrane with coating on both sides had the highest flux and lowest E_a. In addition, the active porous layer can eliminate oxygen exchange limitations on the membrane surface. The changes of surface microstructures are suggested as the cause of unsteady-state permeation.

1. Introduction

Dense ceramic membrane reactors fabricated from mixed-oxide ionic and electronic conductors are used to separate oxygen from air, convert natural gas to syngas and catalytically oxidize light hydrocarbons [1–4]. Oxygen-permeable membranes can potentially reduce syngas generation costs by over 25% [5] and achieve zero CO_2 emission when integrated with oxyfuel technology in power plants [6]. Although the potential benefits of these membranes have attracted the attention of both scientists and companies, many difficulties still limit the commercial development of this technology. One problem is that few materials can meet commercial process requirements, although many perovskite membranes were successful in producing syngas in laboratories for hundreds or thousands of hours [7–18].

Dual-phase composite ceramic membranes were recently suggested for replacement of single-phase perovskite membranes [19–26]. Dual-phase composite membranes made of a noble metal and oxide ionic conductors were first used for oxygen separation [25,26], including Ag–Bi_2O_3 and Pd–yttria-stabilized zirconia (YSZ). Recently, ceramic dual-phase composite membranes such as $Ce_{0.8}Gd_{0.2}O_{1.9}$–$La_{0.7}Sr_{0.3}MnO_3$ (GDC–LSM) [19], $Ce_{0.8}Gd_{0.2}O_{1.9}$–$La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_3$ (GDC–LSCF) [20], $Ce_{0.8}Sm_{0.2}O_{1.9}$–$La_{0.8}Sr_{0.2}CrO_3$ (SDC–LSCr) [21], $Ce_{0.8}Gd_{0.2}O_{1.9}$–$Gd_{0.2}Sr_{0.8}FeO_3$ (GDC–GSF) and $Ce_{0.8}Sm_{0.15}O_{1.925}$–$Sm_{0.6}Sr_{0.4}FeO_3$ (SDC–SSF) [22–24] have been investigated. A significant increase in oxygen permeation flux in the initial stage was observed for the composite materials mentioned above except for GDC–LSM, and it usually took more than 50 h to reach steady-state oxygen permeation [21–24]. The oxygen permeation flux at steady state is often higher than the initial value. Similarly, unsteady permeation phenomena were reported on perovskite membranes. Xu and Thomson observed an irreversible increase in oxygen flux during their investigation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and attributed the increase to gradual facilitation and movement of an oxygen defect structure from the oxygen-lean side to the oxygen-rich side of the membrane [27]. Kharton et al. observed the unsteady increase of oxygen flux on $LaCoO_{3-\delta}$ perovskite membrane, and regarded that the long stabilization process (~100 h) is unlikely to be related to slow surface reactions [28]. That is to say, the unsteady permeation for perovskite membranes relates to bulk diffusion process.

In the case of ceria-based dual-phase composite membranes, the mechanism for the increase in oxygen permeation flux with time is still not clear. In the present study we investigated unsteady-state oxygen permeation in the initial stage by coating membrane surfaces with an LSC porous layer. A membrane of 75 wt.% $Ce_{0.85}Sm_{0.15}O_{1.925}$–25 wt.% $Sm_{0.6}Sr_{0.4}FeO_3$ (SDC–SSF) was used as a model ceria-based dual-phase composite membrane.

2. Experimental

2.1. Membrane preparation

The SDC–SSF composite powder was synthesized via a one-pot procedure as previously described [23]. The resulting powder was pressed into disks under pressure of ~200 MPa. The green disks were sintered at 1400 °C for 3 h. All dual-phase composite membrane samples used in oxygen permeation tests had a relative density of ≥95%. After being polished to 0.5 mm, the membranes were coated with a porous layer by brushing the LSC slurry on the surfaces of membranes to improve the oxygen surface exchange rate. The slurry was prepared by

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mixing terpineol and LSC powder at a weight ratio of 1:1. Porous layers were calcined in situ around 950 °C for several hours. The thickness of the porous layers was usually ~20 μm and the porosity was larger than 50%, as shown in Fig. 1. Table 1 lists details for SDC–SSF dual-phase membranes with or without LSC porous layers on each side.

2.2. Operation and characterization

All the membranes were sealed by silver rings at the melt point of silver. Oxygen permeation experiments were performed in a vertical high-temperature gas permeation cell. The effective inner surface area of the membrane discs was controlled at approximately 0.9 cm^2. Dried synthesized air (100 ml min^{-1}) was used as the feed and high-purity helium was used as purge gas on the other side of the membrane. The effluent was analyzed by gas chromatography on an Agilent 6890 instrument. The oxygen permeation flux through the membrane was calculated based on the flow rate and oxygen concentration of the effluent. The leakage for all permeation experiments was <1%.

The phase structure of the membrane materials was determined by X-ray diffraction (XRD, Rigaku D/Max-RB, Cu K_α radiation) in the 2θ range 20–80° with a step width of 0.02°. The morphology of as-prepared and used membranes was observed under a scanning electron microscope (SEM, Quanta 200F).

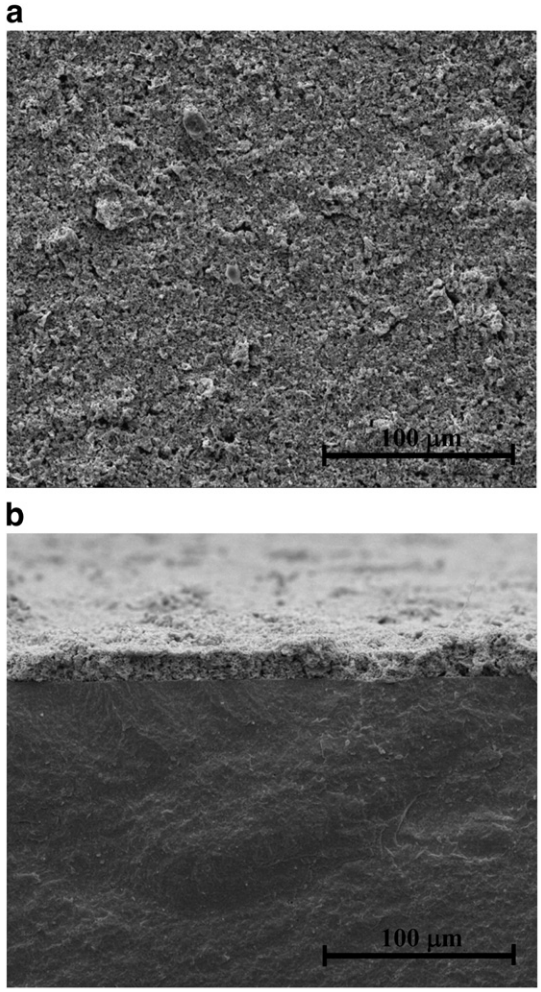

Fig. 1. SEM pictures of LSC porous layer on dual-phase membranes.

Table 1
Situations of SDC–SSF composite membrane with or without LSC porous layers, oxygen permeation energy (Ea) and permeation unsteady period. "+, −" Represent the membrane coated with or without LSC porous layers, respectively.

Samples	LSC porous layers		Unsteady period (h)	Ea (kJ/mol)
	He side	Air side		
SDC–SSF-I	−	−	40	117 ± 3
SDC–SSF-II	−	+	18	91.4 ± 0.9
SDC–SSF-III	+	−	8	106 ± 3
SDC–SSF-IV	+	+	0	62.1 ± 0.8

3. Results and discussion

3.1. Unsteady-state oxygen permeation in the initial stage

It has been reported that oxygen exchange rate can be effectively improved by coating the membrane surface with an LSC porous layer [29]. Fig. 2 shows the dependence of the oxygen permeation flux on time for SDC–SSF dual-phase composite membranes with or without an LSC layer on the membrane surface. The time to reach steady-state oxygen permeation is shown in Table 1. The membrane with LSC porous layers on both surfaces (SDC–SSF–IV) not only had the highest oxygen flux among the four samples, but also reached a steady state immediately. For the other three samples, the oxygen flux increased with time in the initial stage. The increase in oxygen flux was small for SDC–SSF–III with LSC only on the sweeping side, and large for SDC–SSF-I without any LSC. The increment in oxygen permeation flux decreased in the following order: SDC–SSF-I>SDC–SSF-II>SDC–SSF-III>SDC–SSF-IV, which is opposite to the order for the oxygen flux at steady state. In addition, it took longer for SDC–SSF-I to reach a steady state than the other three membranes (Fig. 2, Table 1). From the above results, we can find that the unsteady permeation relates to surface exchange process, and not relates to bulk diffusion. In our experiments, we found that the unsteady period occurred only once. When membranes reached steady-state permeation, helium was replaced by an air flow on the permeation side. After 50 h, the flow was switched back to helium. However, the oxygen flux remained at a steady value. This result differs from the phenomenon reported in the literature [21].

The influence of the operating temperature on the unsteady period is shown in Fig. 3 for membrane SDC–SSF-II. After the membrane was sealed at 963 °C the furnace temperature was decreased to 750 °C, then air and helium were introduced into the permeation cell. Fig. 3 shows the ratio of the oxygen flux at time t to that at time t_0 as the temperature was increased in a single continuous experiment. Thus t_0 for 850 and 940 °C corresponds to $t = 50$ h and $t = 100$ h, respectively. The initial permeation flux at each temperature is shown for comparison with the values obtained after reaching a steady state at

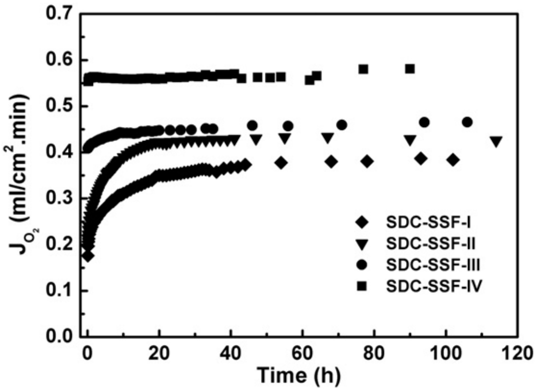

Fig. 2. Dependence of oxygen permeation fluxes on time at 940 °C of SDC–SSF dual-phase membranes with or without LSC porous layers on surfaces. Air flow rate: 100 ml min^{-1}; He flow rate: 30 ml min^{-1}.