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Effect of CuO additive on the sintering and performance of niobium-doped strontium cobaltite as oxygen separation membranes

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ABSTRACT

In this work, the effects of CuO addition on sintering behavior, crystal structure and the oxygen permeation of $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCN) membranes have been investigated. XRD characterization demonstrated that copper could incorporate into the perovskite lattices with certain solubility dependent on temperature. Small amount of CuO (5 wt.%) successfully reduced the sintering temperature of the SCN membrane by 180 °C. A relative density of 95.4% was reached for the membrane with 5 wt.% CuO additive after sintering at 1000 °C. The promoting effect on sintering is likely associated with liquid assisted sintering. The incorporation of copper into the SCN lattice has minimal effect on the membrane sintering but a significant effect on the membrane integrity. As compared to the single-phase SCN membranes, the introduction of CuO as a sintering aid does not affect the electronic conductivity of the membrane between 700 and 900 °C, but the oxygen permeability is slightly reduced. Permeation study of the membranes of 0.9 mm thickness demonstrated oxygen fluxes of 1.5, 1.4, 1.3 and 1.2 ml cm^{-2} min^{-1} [STP] at 800 °C for the membranes containing 0 (pure SCN), 1, 3 and 5 wt.% CuO, respectively. The results suggest that the introduction of CuO as a sintering aid had a more significant effect on the oxygen surface exchange kinetics than on the oxygen bulk diffusion rate.

1. Introduction

Since the pioneering systematic demonstration of high oxygen permeation flux through some dense ion-transport ceramic membranes with the perovskite composition of $SrCo_{1-y}Fe_yO_{3-\delta}$ and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ by Teraoka et al. in 1980s [1,2], there has been considerable interests from both academic and industrial communities in such membranes as an alternative method for oxygen separation from air [3–9]. The enthusiasm for this new technology was triggered by its intrinsic advantages over the traditional industrial scale oxygen production method of cryogenic distillation of air. These advantages include the capability for continuous oxygen production, more size flexibility, and potential reduction in capital cost both for plant construction and oxygen production.

The oxygen semipermeability of ion-transport membranes is related to their mixed oxygen-ionic and electronic conductivity at elevated temperatures. When there is an oxygen potential difference between the two membrane surfaces, the oxygen in the oxygen-rich side atmosphere adsorbs onto the membrane surface, where it dissociates into oxygen ions via a series of complicated surface reactions. The oxygen ions then migrate through the membrane bulk to the oxygen-lean side membrane surface with the simultaneous diffusion of electrons in a reverse direction to maintain local electric neutrality. The oxygen ions then re-combine to form oxygen molecule, which finally releases into the oxygen-lean side atmosphere [10,11]. Macroscopically, it appears as if oxygen molecule can permeate through the membrane. Oxygen-ion conduction is realized by the diffusion of oxygen ions through oxygen vacancies, while the electron conduction is created via the electron hopping between B-site cations and the oxygen ions via a mechanism similar to the Zener double exchange [12,13]. Because of the ion-diffusion mechanism for oxygen permeation, infinite oxygen permeation selectivity is expected if the membrane can be fabricated without any penetrating pinholes.

Dense ion-transport membranes are typically fabricated by powder synthesis-shape forming-sintering process. Oxide powder is first prepared by a standard ceramic process or a more advanced wet chemical method, and is then formed into flat or tubular shape membranes by extrusion, dry pressing, tape casting or other advanced techniques, these green membranes are finally sintered at elevated temperatures to allow densification [14–16]. In order to achieve a high sintering density, ultrahigh sintering temperatures

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are typically required, which can result in the loss of some easily vaporized membrane components, such as Ba and Sr, and make it difficult to precisely control the material composition, causing a significant effect on the stability and oxygen permeability of the membranes. However, sometimes the membranes fail to be totally densified even by sintering near the melting point. Nowadays the application of sintering aids to reduce the temperatures for densification of the electrolyte membranes has been well exploited [17–21]. Various sintering aids have been described in literature, including Fe_2O_3, Co_3O_4, NiO, CuO, Al_2O_3 and Bi_2O_3 [17–20]. The densification temperatures of some electrolyte membranes were significantly reduced through adopting proper sintering aids, and recently several authors also used sintering aids for the fabrication of ion-transport membranes [22–24].

Previously we have investigated perovskite-type $SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCN) as an ion-transport membrane for the oxygen separation [25]. Very high oxygen permeation fluxes at elevated temperatures were demonstrated for the thick SCN membrane by us and also by other research group [25–27]. In this study, CuO was applied as a sintering aid for the purpose of reducing the sintering temperature of the SCN membranes. The performance of ion-transport membranes is closely related with their elemental composition, phase structure and microstructure. Besides reducing the sintering temperature, the sintering aid could also result in a change of microstructure and local composition of the membranes, which may have a significant impact on the membrane performance. Herein, the effect of CuO and its concentration on the sintering, phase structure, microstructure, and oxygen permeability of the SCN membrane was systematically studied. The possible mechanism for reducing sintering temperature and slightly decreased oxygen permeation flux is discussed.

2. Experimental

2.1. Synthesis and preparation

SCN powder was prepared by a solid state reaction process, using $BaCO_3$, $SrCO_3$, Nb_2O_5 and Co_2O_3 (all in analytical grades) as reagents. The starting materials were ball-milled in acetone at the rotation speed of 400 rpm for 3 h. The mixtures were dried and calcined at 1100 °C in air for 5 h. The calcined powders were re-grinded with different amounts of CuO (1–5 wt.%) for 3 h in acetone. Oxides with the nominal composition of $SrCo_{0.782}Nb_{0.087}Cu_{0.131}O_{3-\delta}$ (SCNCu–5 wt.% CuO), $SrCo_{0.833}Nb_{0.0923}Cu_{0.077}O_{3-\delta}$ (SCNCu–3 wt.% CuO) and $SrCo_{0.8775}Nb_{0.0975}Cu_{0.025}O_{3-\delta}$ (SCNCu–1 wt.% CuO), which contain similar copper contents to SCN + CuO composites, were also synthesized. The synthesized powders were then pressed into disk-shape membranes in a stainless steel mold (15 mm in diameter) under a hydraulic pressure of 1.5×10^8 Pa. These green membranes were further sintered at 1000–1200 °C in air for 5 h.

2.2. Characterization

The crystal structures of the as-prepared powders were determined by an X-ray Diffractometer using Bruker D8 Advance with Cu Kα radiation at room temperature. The morphological features of the prepared membranes were examined using Environmental Scanning Electron Microscopy (ESEM, QUANTA-2000). The relative density of sintered membranes was measured by the Archimedes liquid displacement technique applying pure water as the medium. The electrical conductivity was measured in air by the four-probe *dc* method using Keithley 2420 Sourcemeter on sintered bars. The measurements were performed in air from 900 to 300 °C at a cooling rate 5 °C min^{-1}, with an interval 10 °C for two measurements.

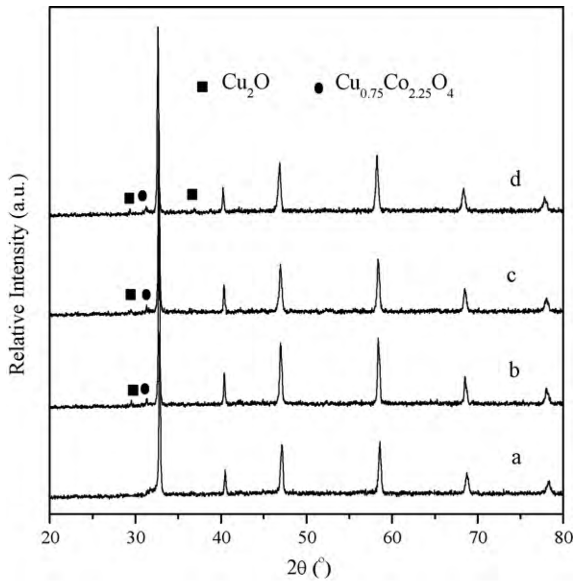

Fig. 1. Room-temperature XRD patterns of SCN + CuO obtained immediately after the calcinations, (a) pure SCN calcined at 1100 °C, (b) SCN + 1 wt.% CuO calcined at 1100 °C, (c) SCN + 3 wt.% CuO calcined at 1050 °C, and (d) SCN + 5 wt.% CuO calcined at 1000 °C (the non-marked signals in the figure are attributed to the perovskite phase of SCN).

2.3. Oxygen permeation measurement

The oxygen permeation flux measurements were performed with gas chromatograph method. The membrane disk was sealed to a quartz tube. The membrane sidewall was also sealed to avoid radial contribution to the oxygen flux. Ambient air was used as the feed gas and helium as the sweeping gas at a flow rate of 100 ml min^{-1} [STP]. The outlet gas was analyzed by Varian 3800 gas chromatography (GC) equipped with a 5 Å molecular sieve capillary column. The oxygen permeation flux was calculated by:

$$J_{O_2}\ (\text{mol/cm}^2\,\text{s}, \text{STP}) = \left[C_O - \frac{C_N \times 0.21}{0.79} \times \left(\frac{28}{32}\right)^{1/2}\right] \times \frac{F}{S} \qquad (1)$$

where C_O and C_N are the measured concentrations of oxygen and nitrogen in the gas on the sweep side, respectively, *F* is the flow rate of the exit gas on the sweep side, and *S* is the membrane geometric surface area of the sweep side.

3. Results and discussion

3.1. Phase structure and stability

The possible phase reaction between CuO additive and SCN during the sintering process was first examined by powder reaction. SCN in powder form was mixed with an amount of CuO similar to that being used as the sintering aid to facilitate the densification of the SCN membranes in subsequent investigation. The mixtures were then calcined at 1100 °C (1 wt.% CuO), 1050 °C (3 wt.% CuO) and 1000 °C (5 wt.% CuO) for 5 h. The specific calcination temperatures were selected based on the densification temperatures of the respective membranes, which will also be discussed in detail later. Fig. 1 shows the X-ray diffraction patterns of the various powders obtained immediately after the calcination. It should be noted that the non-marked signals in Fig. 1 are attributed to the perovskite SCN. As can be seen, pure SCN calcined at 1100 °C shows a perovskite structure with all its diffraction peaks indexed well based on cubic lattice symmetry, agreeing well with our previous observation [25]. The main perovskite structure was also observed