Effects of ZrO_2 addition on structure, oxygen permeation and stability of $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ oxides

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Introduction

Mixed-conducting oxides have received considerable attention as possible candidate materials for application in oxygen separation membranes and catalytic membrane reactors. Although the bright future of electronic conducting membrane reactor in the POM reaction, the commercial application of mixed-conductive membranes is often limited by specific disadvantages of the membrane materials known at the present time, for instance, the order-disorder phase transition in the oxygen sublattice. Such a transition is characteristic of most perovskites derived from the strontium cobalites $SrCoO_{3-\delta}$.[1] In addition, a high oxygen chemical potential gradient in the Sr(Co, Fe)$O_{3-\delta}$ type membranes results in a crystal lattice mismatch inside the ceramic, leading to the fracture of the membranes. [2] Thus, the disadvantages of $SrCoO_{3-\delta}$ based ceramics create a necessity to develop new materials and optimizing known materials for oxygen separation and catalytic membrane reactors.

Recently, a novel perovskite-related oxide membrane, which was prepared by addition of 9 wt% ZrO_2 into $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ (SCFZ), has been reported in our laboratory.[3] The oxygen nonstoichiometry, transport properties and structure stability of SCFZ have been investigated. [4] It showed that the stability of $SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ (SCF) was greatly improved with the addition of ZrO_2, while the oxygen permeability was slightly reduced. The aim of the present study was to investigate the effect of various amounts of ZrO_2 additions on structure, oxygen permeation and stability of SCF in an attempt to search for a suitable composition exhibiting high oxygen flux as well as structural stability in reducing atmosphere.

Experimental

ZrO_2-$SrCo_{0.4}Fe_{0.6}O_{3-\delta}$ (SCFZ) powders with the ZrO_2 additions of 0, 1, 3, 5, 7 and 9 wt% were prepared by conventional solid-state reaction. The required amounts of $SrCO_3$, Co_2O_3, Fe_2O_3 and monoclinic ZrO_2 were mixed and milled for 24 h followed by calcination in air at 1223 K for 4 h. The calcined powders were pressed into disks of 16 mm in diameter with an oil pressure of 200 MPa and then sintered in air at 1473 K for 5 h to form the dense membranes. X-ray diffraction (XRD) was collected on a Bruker D8 Advance diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis was performed using a JSM 6300 scanning microscope equipped with a Sigma energy dispersive X-ray microanalysis system. SEM images were recorded in back-scattered electron modes.

Oxygen permeation measurements were performed using a permeation apparatus reported previously. [2] The membrane samples were sealed by two gold rings. Before beginning of the oxygen permeation measurement, the assembly was heated to 1313 K and held for 4 h to form the bonding. One side of the membrane was exposed to air (P_h = 0.209 atm) at a flow rate of 200 ml min^{-1} while the other side was exposed to a lower oxygen partial pressure (Po_2) that was controlled by regulating the He flow rate by mass flow controllers (Models D07/ZM, Beijing Jianzhong Machine Factory, China). A gas chromatograph (GC, Model Shimabzu GC-7A) equipped with a 5 A molecule sieve column was connected to the exit of the sweep side. The amount of oxygen passing through the membrane was calculated from the measured outlet flow rate and the oxygen content.

Results and Discussion

Crystal structure characterization

XRD patterns of the as-synthesized powders with ZrO_2 additions of 1-9% showed the existence of SCF and $SrZrO_3$ phase. But for the sintered membrane (Figure 1), the second phase $SrZrO_3$ was reabsorbed into the perovskite for the compositions with ZrO_2 additions ≤ 7 wt%. Small amount of Co_3O_4 was also detected by XRD analysis. The formation of Co-rich phase may attribute to two parts: the segregation of Co at high temperature[5] and the precipitate of Co to maintain the stoichiometry because of Zr dissolution in SCF as will be discussed below. The presence of these phases in the samples was confirmed by SEM-EDX analysis for the sintered membranes. The results are shown in Figure 2 taking 1% and 9% ZrO_2 addition as examples. Besides, EDX analysis performed on the region corresponding to the SCF phase showed the presence of Zr, indicating the dissolution of Zr in SCF phase took place. The ratio between Sr, Co, Fe, and Zr in five membranes with ZrO_2 addition from 1% to 9% were1:0.48:0.84:0.027, 1:0.42:0.77:0.067, 1:0.38:0.75:0.099, 1:0.51:0.77:0.15, 1:0.38:0.76:0.19, respectively, indicating Zr content in SCF phase increased directly with amount of ZrO_2 additions.

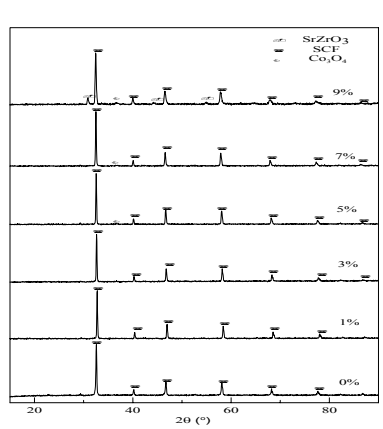
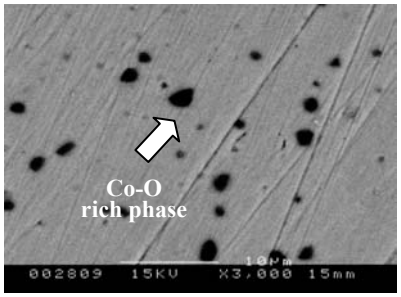


Figure 1. XRD patterns of sintered membranes.

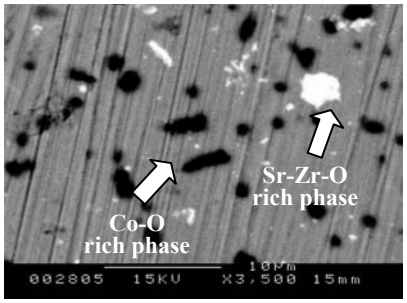
Unit cell dimensions for SCF phase calcined at 1473 K with various amount of ZrO_2 additions are shown in Figure 3. The expanded lattices of SCF phase were found for powders with the addition of ZrO_2 and the lattice parameters increased directly with amount of ZrO_2 addition. Increase of lattice parameter of SCF phase with increasing amount of ZrO_2 addition in these systems could be due to increasing amount of Zr dissolution in B site of SCF phase as indicated by the SEM-EDX analysis. The larger ionic radii of dopant ion Zr^{4+} (0.84 Å) in comparison to the host ions Fe^{3+} (0.65 Å) and Co^{3+} (0.61 Å) resulted in an expanded SCF lattice.

Effect of amount of ZrO_2 addition on phase stability

To study the phase behavior under reducing atmospheres, SCFZ membranes with various amount of ZrO_2 additions were crushed and annealed in helium at 1123 K for 3 h and then applied for XRD analysis. The results are shown in Figure 4. Comparing with the XRD patterns of the fresh powders shown in Figure 1, we could see that the crystal structure of SCF had changed from cubic phase to an oxygen-vacancy ordered, orthorhombic phase Sr_2CoFeO_5. Structure stability of the materials seemed improved with increasing amount of ZrO_2 addition due to increasing amount of Zr dissolution in SCF phase, and when ZrO_2 addition was ≥ 3%, samples could maintain their structure in reducing atmospheres.



(a)



(b)

Figure 2. Back-scattered electron SEM images of membranes for ZrO_2 additions with (a)1%, (b)9%.

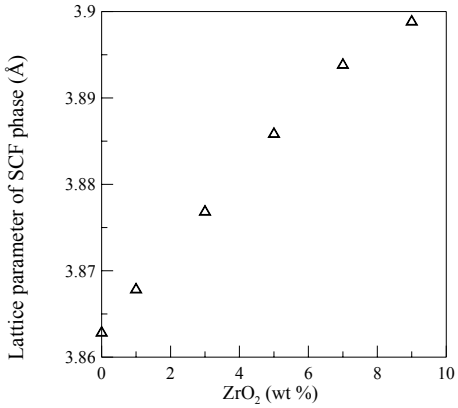


Figure 3. Unit cell dimensions for SCF phase calcined at 1473 K with various amount of ZrO_2 additions.

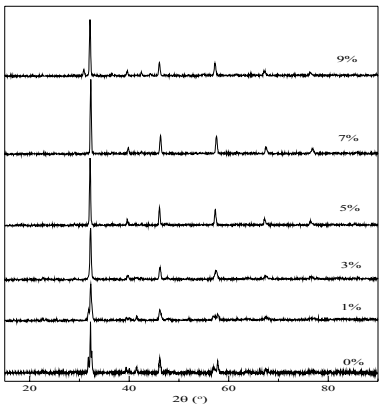


Figure 4. XRD patterns of SCFZ membranes annealed in helium at 1123 K for 3 h.

3.3. Effect of amount of ZrO_2 addition on oxygen permeation

The temperature dependence of oxygen flux through SCFZ membranes is shown in Figure 5 for the ZrO_2 additions of 0, 1, 3, 5, 7 and 9 wt%. The flow rate of He was controlled at 30 ml/min. The oxygen flux was found to decrease monotonically with the increasing amount of ZrO_2 addition due to the more amount of Zr dissolution in SCF phase. Solid solution of Zr in B sites of SCF increased the M-O bonding energy and reduced the concentration of oxide ion vacancies, both leading to a decrease in the oxygen permeability.

Another factor for evaluating the oxygen permeability of the membrane is the activation energy for oxygen permeation. As shown in Figure 5, two activation energies for oxygen permeation in the range of 973-1223K were observed for the compositions with ZrO_2 additions <3%, which was related to the order-disorder transition of oxygen vacancies.[1] In contrast, single activation for oxygen permeation was observed for samples with ZrO_2 addition >3%. The results were in accordance with the XRD analysis of the annealed samples shown in Figure 4. From the dependence of stability and oxygen permeability on the amount of ZrO_2 addition described above, the optimum ZrO_2 addition to greatly improve the structure stability without deleteriously affecting the oxygen permeability has been identified as 3 wt %.

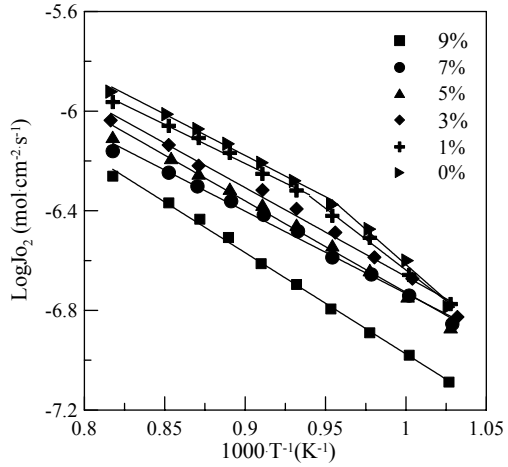


Figure 5. The Temperature dependence of oxygen permeation flux through SCFZ membranes with various ZrO_2 additions.

Acknowledgment

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