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PHASE STABILITY OF THE MIXED-CONDUCTING Sr-Fe-Co-O SYSTEM

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ABSTRACT

Mixed-conducting ceramic oxides have potential uses in high-temperature electrochemical applications such as solid oxide fuel cells, batteries, sensors, and oxygen-permeable membranes. The Sr-Fe-Co-O system combines high electronic/ionic conductivity with appreciable oxygen permeability at elevated temperatures. Dense ceramic membranes made of this material can be used to separate high-purity oxygen from air without the need for external electrical circuitry, or to partially oxidize methane to produce syngas. Samples of $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ (with $x = 0, 0.6, 1.0$, and 1.4) were prepared by solid-state reaction method in atmospheres with various oxygen partial pressures ($p\text{O}_2$) and were characterized by X-ray diffraction, scanning electron microscopy, and electrical conductivity testing. Phase components of the sample are dependent on cobalt concentration and $p\text{O}_2$. Electrical conductivity increases with increasing temperature and cobalt content in the material.

INTRODUCTION

Recently, oxides with mixed electronic and ionic conductivities have begun to attract attention because of their applications in high-temperature electrochemical processes [1-5]. For example, they are used as electrodes in solid oxide fuel cells, and if their oxygen permeability is high enough, they can be used as oxygen-separation membranes. Sr-Fe-Co-O has not only high combined electronic and oxygen ionic conductivity but also oxygen permeability that is superior to that of other reported ceramic oxides [6-11]. It is a good candidate material as a dense membrane for separation of high-purity oxygen. In an oxygen separation reactor, oxygen can be transported from the high oxygen partial pressure ($p\text{O}_2$) side to the low- $p\text{O}_2$ side under the driving force of the $p\text{O}_2$ difference, $\Delta\log(p\text{O}_2)$, without the need for external electric circuitry. Balachandran et al. [7] demonstrated that extruded membrane tubes made of Sr-Fe-Co oxide can be used for partial oxidation of methane to produce syngas ($\text{CO} + \text{H}_2$) in a methane conversion reactor that operates at $\approx 850^\circ\text{C}$. In this type of reactor, oxygen on one side of the membrane was separated from air on the other side of the membrane. Methane conversion efficiencies of $>98\%$ were observed and the reactor tubes have operated for >1000 h. Moreover, the oxygen flux obtained from the separation of air in this type of conversion reactor is considered commercially feasible. The use of this technology can significantly reduce the cost of oxygen separation [12].

To obtain sufficient oxygen flux, the gas separation reactor must be operated at high temperatures and substantial $p\text{O}_2$ differences. Therefore, stability of the ceramic membranes is an important issue. Certain compounds of $\text{SrFe}_{1-x}\text{Co}_x\text{O}_{3-\delta}$ were found unsuitable for use in gas separation because they lack stability in highly reducing environments [13]. Thermodynamic calculations can normally give us accurate data on the stability of a system. However, certain

examples of discrepancies between the calculated thermodynamic stability and the actual results indicate the importance of obtaining supporting data from real systems [14].

In this paper, we report our studies on the structural and phase stability of $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ materials in air and reducing argon environments. In-situ electrical conductivity and ex-situ room-temperature X-ray diffraction (XRD) and scanning electron microscopy (SEM) experiments were used to characterize the material.

EXPERIMENTAL

The $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ (with $x = 0, 0.6, 1.0$, and 1.4) powders were made by a solid-state reaction method, with appropriate amounts of SrCO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and Fe_2O_3 ; mixing and grinding were conducted in isopropanol with zirconia media for 10 h. After drying, the mixture was calcined in air at 850°C for 16 h, with intermittent grinding. After final calcination, the powder was ground with an agate mortar and pestle to an average particle size of $\approx 7\text{ }\mu\text{m}$. The resulting powder was pressed uniaxially with a 1200-MPa load into bars 7.5 mm wide, 44 mm long, and $\approx 5\text{ mm}$ thick. The bars were then sintered in air at $\approx 1200^\circ\text{C}$ for 5 h. The true density was measured on powder with an AccuPyc 1330 pycnometer. Bulk density was determined by the Archimedeian method, with isopropanol as the liquid medium. Calculated relative density of air-sintered $\text{SrFeCo}_{0.5}\text{O}_x$ samples was $\approx 95\%$ of theoretical value. Thin bars $\approx 1 \times 5 \times 20\text{ mm}^3$ were cut from the samples and subjected to postannealing heat treatment in various low- $p\text{O}_2$ environments at $900\text{--}1100^\circ\text{C}$.

Room-temperature X-ray powder diffraction analysis was carried out with a Scintag XDS-2000 diffractometer. Data were taken with $\text{Cu K}\alpha$ radiation. A high-purity intrinsic Ge energy-dispersive detector was used to minimize background due to sample fluorescence. A continuous scan with a 2θ scanning rate of $1^\circ/\text{min}$ and chopping step of 0.03° was used to collect data. SEM observations were conducted with a JEOL JSM-5400 scanning microscope at an accelerating voltage of 20 KeV.

Conductivity of the sample was determined by the four-probe method. Platinum wires were attached to the specimen bar to serve as current and voltage leads. Resistance of the specimen was measured with an HP 4192A LF impedance analyzer at 23 Hz. Details of the experimental configuration for measuring conductivity were reported earlier [10]. A K-type thermocouple was attached to an yttria-stabilized zirconia (YSZ) plate on which the sample bars were placed for the heat treatments. The thermocouple was used for both controlling and detecting the temperature of the programmable electric furnace. Temperature tolerance within the uniform hot zone of the furnace is $\pm 1^\circ\text{C}$. Desirable gaseous environments were obtained by flowing premixed gases through the system during the experiments.

RESULTS AND DISCUSSIONS

Room-temperature XRD patterns of air-sintered $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ are plotted in Fig. 1 for different x values. The powder XRD pattern of the $x = 0$ composition (Fig. 1a) agrees with the result reported for a single crystal $\text{Sr}_4\text{Fe}_6\text{O}_{13}$ sample [15]. For comparison, the XRD pattern of the perovskite phase $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_x$ is plotted in Fig. 1e. Air-sintered $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ ($x = 1$, Fig. 1c) is a multiple phase material, with $\approx 40\%$ perovskite phase, as obtained from Rietveld analysis [16]. Air-sintered $\text{Sr}_2\text{Fe}_{2.4}\text{Co}_{0.6}\text{O}_y$ ($x = 0.6$, Fig. 1b) contains less than 3% perovskite phase, while air-sintered $\text{Sr}_2\text{Fe}_{1.6}\text{Co}_{1.4}\text{O}_y$ ($x = 1.4$, Fig. 1d) has more than 90% perovskite phase. Traces of cobalt

Fig. 1. Room-temperature X-ray diffraction patterns of air-sintered samples: (a) $\text{Sr}_2\text{Fe}_3\text{O}_y$, (b) $\text{Sr}_2\text{Fe}_{2.4}\text{Co}_{0.6}\text{O}_y$, (c) $\text{Sr}_2\text{Fe}_2\text{CoO}_y$, (d) $\text{Sr}_2\text{Fe}_{1.6}\text{Co}_{1.4}\text{O}_y$, and (e) $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_y$.

Fig. 2. Room-temperature X-ray diffraction patterns of argon-annealed samples: (a) $\text{Sr}_2\text{Fe}_3\text{O}_y$, (b) $\text{Sr}_2\text{Fe}_{2.4}\text{Co}_{0.6}\text{O}_y$, (c) $\text{Sr}_2\text{Fe}_2\text{CoO}_y$, (d) $\text{Sr}_2\text{Fe}_{1.6}\text{Co}_{1.4}\text{O}_y$, and (e) $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_y$.

Fig. 3. SEM morphology of $\text{Sr}_2\text{Fe}_2\text{CoO}_x$ sample: (a) original surface of air-sintered sample, (b) polished surface of air-sintered sample, (c) original surface of argon-annealed sample, (d) polished surface of argon-annealed sample.

oxide impurity phase were also observed in the $\text{Sr}_2\text{Fe}_{1.6}\text{Co}_{1.4}\text{O}_y$ sample. XRD patterns of the argon-annealed samples are shown in Fig. 2. At high temperatures, the perovskite phase can be reduced to the brownmillerite structure [17] in the reducing argon environment ($p\text{O}_2 \approx 10^{-6}$ atm). The argon-annealed $\text{Sr}_2\text{Fe}_3\text{O}_y$ ($x = 0$, Fig. 2a) has the same structure as that of the air-sintered sample and contains no brownmillerite phase, although other argon-annealed cobalt-containing samples all consist of brownmillerite phase. Content of the brownmillerite phase in annealed $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ increases with increasing x , as shown in Fig. 2b, 2c, and 2d. The cobalt oxide phase can be seen clearly in the cobalt-content samples. XRD of a pure brownmillerite phase of the argon-annealed $\text{SrFe}_{0.8}\text{Co}_{0.2}\text{O}_x$ sample is shown in Fig. 2e for comparison. Details on crystal structure of the $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ samples will be reported elsewhere [18]. The lattice parameters of air-sintered $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ samples are listed in Table 1.

Table 1. Lattice Parameters of the Air -Sintered $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ samples

Cobalt Content x	Phases Components	Lattice Parameters: a, b, c (Å)
0.0	O (>99%)	11.126, 18.978, 5.5864
0.3	O (>95%) + P (<5%)	11.081, 19.008, 5.5649
0.6	O (>90%) + P (<10%)	11.065, 19.008, 5.5618
1.0	O (>75%) + P (<25%)	11.017, 19.030, 5.5463

SEM images of the air-sintered and argon-annealed $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ sample are shown in Fig. 3; they reveal a dense homogeneous structure for both samples. Energy-dispersive X-ray (EDX) elemental analysis showed that the overall atomic ratio of the metal elements is consistent with that given in the chemical formula. The polished-surface SEM images showed that the argon-annealed sample is denser and contains fewer pores than the air-sintered sample. Spherical cobalt-rich phase was identified in the argon-annealed sample. By correlating SEM observation with XRD results, we identified the spherical phase as cobalt oxide (CoO , JCPD No. 9-402).

Fig. 4. Temperature dependence of $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ samples.

The total conductivity of $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ sample is shown in Fig. 4 as a function of temperature. Conductivity increases as temperature and cobalt content increase. At 900°C , the conductivity of $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ is ≈ 20 and $\approx 6 \text{ S}\cdot\text{cm}^{-1}$ in flowing air and argon environments, respectively. Conductivities of $\text{Sr}_2\text{Fe}_{2.4}\text{Co}_{0.6}\text{O}_y$ and $\text{Sr}_2\text{Fe}_3\text{O}_y$ are ≈ 10 and $\approx 0.6 \text{ S}\cdot\text{cm}^{-1}$, respectively, at 900°C in air. Figure 5 shows the transient conductivity of the $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ sample at 950°C after its surrounding atmosphere was changed. The conductivity recovered to its original value after the surrounding atmosphere was switched back to air from the reducing argon environment. This indicates that a phase transition in $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ is reversible after the surrounding atmosphere is changed.

Fig. 5. Conductivity transient behavior of $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ sample at 950°C .

CONCLUSIONS

Phase components of $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ are strongly dependent on the cobalt content in the sample. The $\text{Sr}_2\text{Fe}_3\text{O}_y$ sample is single-phase material, while the high-cobalt-content samples ($x > 0.6$) contain multiple phases. Perovskite phase in the high-cobalt-content samples increases with increasing cobalt content. In a reducing argon environment, the single-phase $\text{Sr}_2\text{Fe}_3\text{O}_y$ sample has the same crystal structure as the air-sintered sample, while the brownmillerite phase was observed in the cobalt-containing samples. Cobalt oxide has also been found in the argon-annealed cobalt containing samples.

Total conductivity of $\text{Sr}_2\text{Fe}_{3-x}\text{Co}_x\text{O}_y$ increases with increasing temperature and cobalt content in the sample. At 900°C , the conductivity of $\text{Sr}_2\text{Fe}_2\text{CoO}_y$ is ≈ 20 and $\approx 6 \text{ S}\cdot\text{cm}^{-1}$ in flowing air and argon environments, respectively. The conductivities of $\text{Sr}_2\text{Fe}_{2.4}\text{Co}_{0.6}\text{O}_y$ and $\text{Sr}_2\text{Fe}_3\text{O}_y$ are ≈ 10 and $\approx 0.6 \text{ S}\cdot\text{cm}^{-1}$, respectively, at 900°C in air. Transient conductivity behavior of the sample, after surrounding atmosphere is switched back and forth, indicates that the phase transition in the materials is reversible.

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