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Study of the Mixed-Conducting  $\text{SrFeCo}_{0.5}\text{O}_y$  System\*

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## STUDY OF THE MIXED-CONDUCTING SrFeCo<sub>0.5</sub>O<sub>y</sub> SYSTEM

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### ABSTRACT

Mixed-conducting Sr-Fe-Co oxides have potential applications in dense ceramic membranes for high-purity oxygen separation and/or methane conversion to produce syngas (CO + H<sub>2</sub>), because of their combined high electronic/ionic conductivity and significant oxygen permeability. SrFeCo<sub>0.5</sub>O<sub>y</sub> has been synthesized by the solid-state reaction method. Conductivities were measured at elevated temperatures in various gas environments and rose with increasing temperature and increasing oxygen partial pressure (pO<sub>2</sub>) in the surrounding environment. Neutron powder diffraction experiments revealed that in a high pO<sub>2</sub> environment the SrFeCo<sub>0.5</sub>O<sub>y</sub> material consists of three different phases. The relative concentration of each component phase is dependent on temperature and pO<sub>2</sub> in the surrounding environment. In air, Sr<sub>2</sub>(Fe,Co)<sub>3</sub>O<sub>y</sub> (236 phase) is the majority phase and consists of >75wt.% of the total, while the perovskite and rocksalt phases account for ≈20wt.% and <5wt.%, respectively. However, in a reducing environment, the 236 phase decomposes and converts to perovskite and rocksalt phase at high temperature. In an environment of pO<sub>2</sub> < 10<sup>-12.2</sup> atm, the 236 phase is completely converted into perovskite (brownmillerite) and rocksalt phases.

Keywords: Neutron diffraction, Mixed conductor, Ceramic membrane, Oxygen permeation, Sr-Fe-Co oxide.

### INTRODUCTION

Oxides with mixed electronic and oxygen ionic conductivities have been widely studied for use as components in high-temperature electrochemical devices such as solid-oxide fuel cells, oxygen sensors, oxygen pumps, batteries, and catalysts for oxygen-permeable membranes [1-5]. The SrFeCo<sub>0.5</sub>O<sub>y</sub> not only has high combined electronic and oxygen ionic conductivities but also appreciable oxygen permeability [6-8]. It holds particular promise for use in ceramic membranes designed to separate oxygen from air, being impervious to other gaseous constituents. SrFeCo<sub>0.5</sub>O<sub>y</sub> can be used to produce syngas (CO + H<sub>2</sub>) by direct conversion of methane and other basic hydrocarbon gases, such as coal gas, without external electrical circuitry [6]. The oxygen permeation flux through this type of membrane could be considered commercially feasible [9-12].

The intense interest in developing materials with high oxygen ionic conductivity has recently focused on perovskite and/or perovskite-related oxygen-deficient structures, for example, the brownmillerite structure [13]. Although the idealized perovskite structure does not contain oxygen vacancies, its structure is extremely

versatile. Oxygen ionic conduction can be induced by incorporating oxygen vacancies into the structure. The brownmillerite structure is related to the perovskite structure but contains ordered oxygen vacancies that result in significant oxide ionic conduction (normally due to the existence of oxygen vacancies). In those materials, oxygen vacancies are the primary charge carriers for oxygen ionic conduction. Activation energies of these materials are normally greater than 1 eV, and the oxygen surface exchange rate is low. Unlike the brownmillerite and similar materials, SrFeCo<sub>0.5</sub>O<sub>y</sub> (SFC) utilizes interstitial oxide ions and holes as the predominant charge carriers in an oxygen-rich environment [7,14], and its oxygen surface exchange rate is sufficiently high that the oxygen transport is primarily bulk-controlled [15]. The oxygen ionic conductivity and oxygen permeability of SFC are superior to these of other mixed-conducting materials. These unique oxygen transport properties make the SFC a technologically important material.

In this paper, we focus on the relationships between structure and transport properties of the SFC materials. We report neutron powder diffraction results and temperature- and oxygen-partial-pressure (pO<sub>2</sub>)-dependent electrical conductivity. Based on our experimental results, we attempt to build a coherent picture to correlate the structure, oxygen transport properties, and thermodynamics of the SFC system.

## EXPERIMENTAL

SFC powder was made by the solid-state reaction method. Details were reported earlier in Ref. 7. Pellets were made by pressing uniaxially with a 120-MPa load, followed by sintering in air at  $\approx 1200^\circ\text{C}$  for 5 h. The true density of SFC, measured on powder by AccuPyc 1330 pycnometry, agrees with the theoretical density obtained from the X-ray diffraction pattern. Bulk density of the sintered pellets was measured by the Archimedes method and found to be  $\approx 95\%$  of the theoretical value. Scanning electron microscopy and electron-dispersive X-ray analysis revealed good homogeneity and phase integrity.

Electrical conductivity of the sample was determined by the conventional four-probe method on bar specimens cut from the sintered pellets. Details of the experimental setup for high-temperature measurement were reported earlier [7]. Premixed gases (AGA Gas, Cleveland, OH) were used for the controlled-gas environments.

Neutron powder diffraction measurements were carried out on the General Purpose Powder Diffractometer (GPPD) at Argonne's Intense Pulsed Neutron Source (IPNS). Measurements of the variable-temperature and surrounding gas environment were performed in a "Miller" furnace with an yttrium-stabilized zirconia electrolyte oxygen sensor (Ceramic Oxide Fabricators SIRO2). Several gases were used in varying combinations to achieve the desired range of partial pressures of oxygen: air ( $<10$  ppm H<sub>2</sub>O), argon ( $>99.996\%$ ), 5.12% O<sub>2</sub>/bal. Ar, 1% CO/bal. Ar, and CO<sub>2</sub>. The furnace was heated/cooled at  $240^\circ\text{C}/\text{h}$  with a 20-min equilibration period at the testing temperature. Gas flows were controlled with Brooks Series 5820 mass flow controllers before they entered a mixing loop and were delivered to the furnace. Data were collected on the  $90^\circ$  bank, and Rietveld [16]

analysis was performed with GSAS [17]. Details of data analysis are reported in Ref. 18.

## RESULTS AND DISCUSSION

Using the conventional four-probe and electron-blocking four-probe methods, we measured the total and ionic conductivities of SFC. The ionic transference number can be determined from ionic conductivity divided by total conductivity. The total, electronic, and ionic conductivities and the ionic transference number of SFC in air are plotted in Fig. 1 as a function of temperature. Conductivities increase with increasing temperature, whereas the ionic transference number is almost independent of temperature. At 800°C in air, the total conductivity and oxygen ionic conductivity are  $\approx 17$  and  $7 \text{ S}\cdot\text{cm}^{-1}$ , respectively, which leads to an ionic transference number of  $\approx 0.4$ . This result indicates that the electronic and ionic conductivities of the SFC materials are comparable in value, i.e., their ratio is close to unity. This makes the SFC materials unique among other mixed conductors, in which electronic transference numbers are much greater than ionic transference numbers, or vice versa.

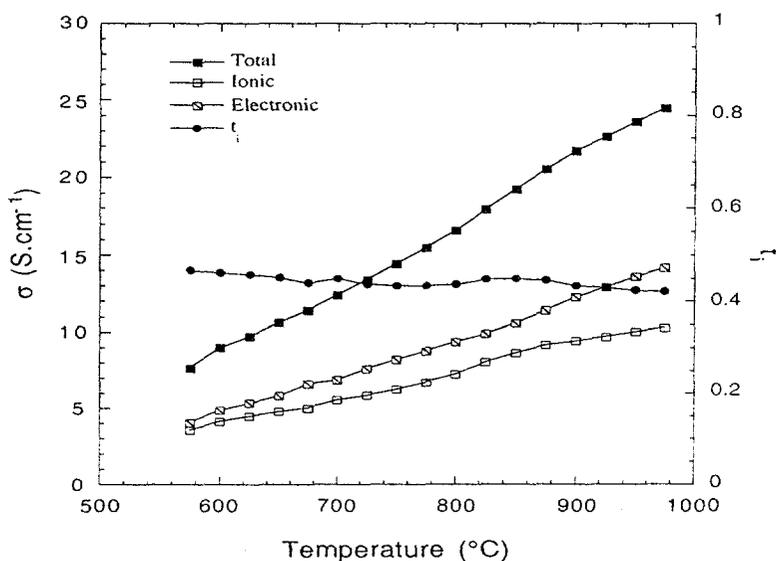


Fig. 1. Total, electronic, and ionic conductivities, and ionic transference number of  $\text{SrFeCo}_{0.5}\text{O}_y$  material as a function of temperature.

Figure 2 shows  $\log(T\cdot\sigma)$  as a function of reciprocal temperature for an SFC sample in various oxygen environments. The  $\log(T\cdot\sigma)$  vs. reciprocal temperature curves have good linear dependence; therefore, activation energy can be derived from slopes of these curves. Conductivity,  $\sigma$ , at 950°C and the activation energy,  $E_a$ , of SFC in various  $p\text{O}_2$  environments are listed in Table 1. Conductivity increases with increasing  $p\text{O}_2$ . In high- $p\text{O}_2$  environments, activation energy of SFC samples was low ( $\approx 0.35 \text{ eV}$ ). It increased with decreasing  $p\text{O}_2$  in a reducing environment.

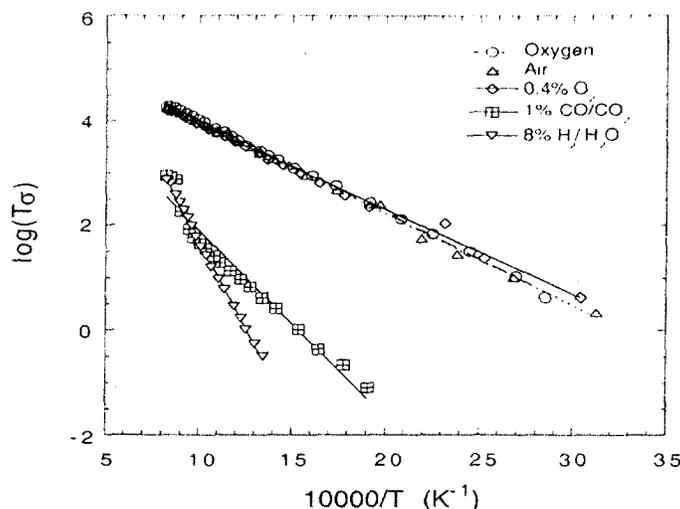


Fig. 2. Arrhenius plot of conductivity of  $\text{SrFeCo}_{0.5}\text{O}_y$  in various surrounding environments.

Table 1. Conductivity at  $950^\circ\text{C}$  and activation energy of SFC in various oxygen atmospheres.

Atmosphere	$\log(p\text{O}_2)$	$\sigma$ ( $\text{S}\cdot\text{cm}^{-1}$ )	$E_a$ (eV)
100% $\text{O}_2$	0	23.21	0.35
Air	-0.678	20.91	0.35
0.4% $\text{O}_2/\text{Ar}$	-2.373	18.68	0.34
1% $\text{CO}/\text{CO}_2$	-11.5	1.05	0.63
8% $\text{H}_2/\text{H}_2\text{O}$	-18.2	0.86	1.31

The structure of  $\text{Sr}_3\text{Fe}_6\text{O}_{13}$  (cobalt-free 236 phase) as described by Yoshiasa et al. [19] is not correct in detail. Nor is the structure of the cobalt-doped 236 phase completely correct as described in recent reports [20-23], although the imperfections are less dramatic. Until the correct cell and space groups are correctly determined, the Iba2 space group remains sufficient for studying the multiphase SFC material, as demonstrated by Fjellvag et al. [21] and Mitchell et al. [22]. In our study, we used the Yoshiasa structure as the model to fit the 236 phase in SFC material.

Figure 3 shows neutron powder diffraction patterns obtained for the SFC material at  $900^\circ\text{C}$  under reducing partial pressure, from bottom to top. In air (shown in the bottom pattern in Fig. 3), three phases (236, perovskite, and rocksalt) are easily identified in the material. Figure 4 shows a three-phase Rietveld profile fitting to the neutron powder diffraction data of the SFC sample obtained at  $900^\circ\text{C}$  in air. The refinement is acceptably good. Refinement results show that SFC is composed of >75% 236 phase,  $\approx 20\%$  perovskite phase, and <5% rocksalt phase at  $900^\circ\text{C}$  in air.

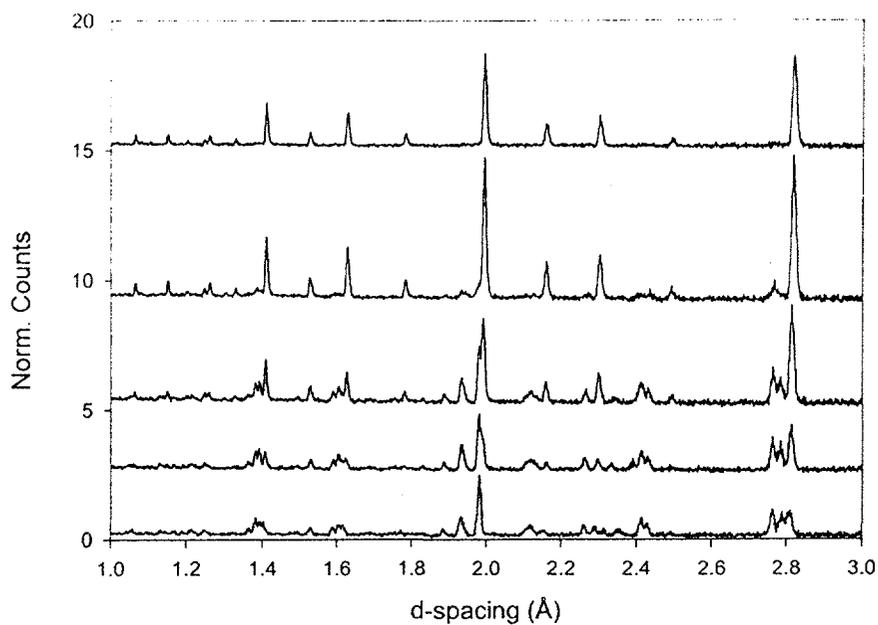


Fig. 3. Neutron powder diffraction patterns obtained on  $\text{SrFeCo}_{0.5}\text{O}_y$  material at  $900^\circ\text{C}$  under decreasing oxygen partial pressure, from bottom to top.

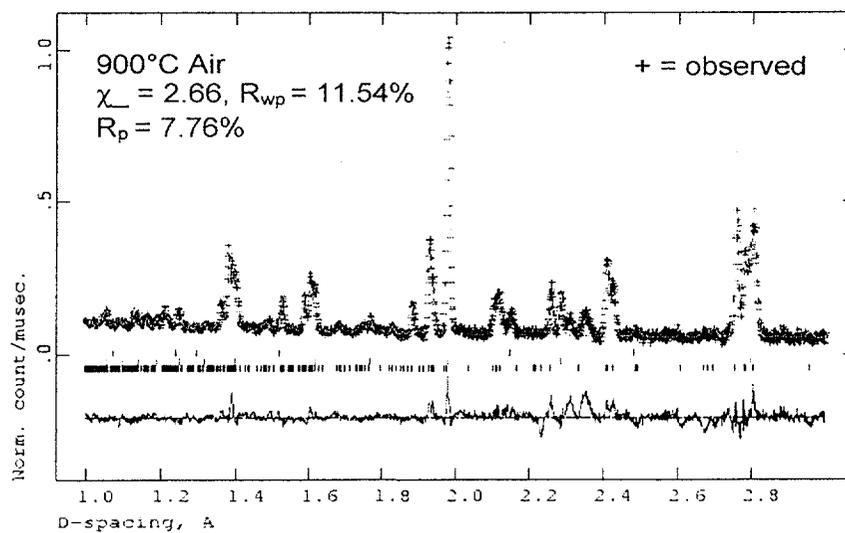


Fig. 4. Rietveld profile fit to neutron powder diffraction data of  $\text{SrFeCo}_{0.5}\text{O}_y$  sample at  $900^\circ\text{C}$  in air. Reflection markers represent rocksalt, perovskite, and 236 phases from top to bottom, respectively.

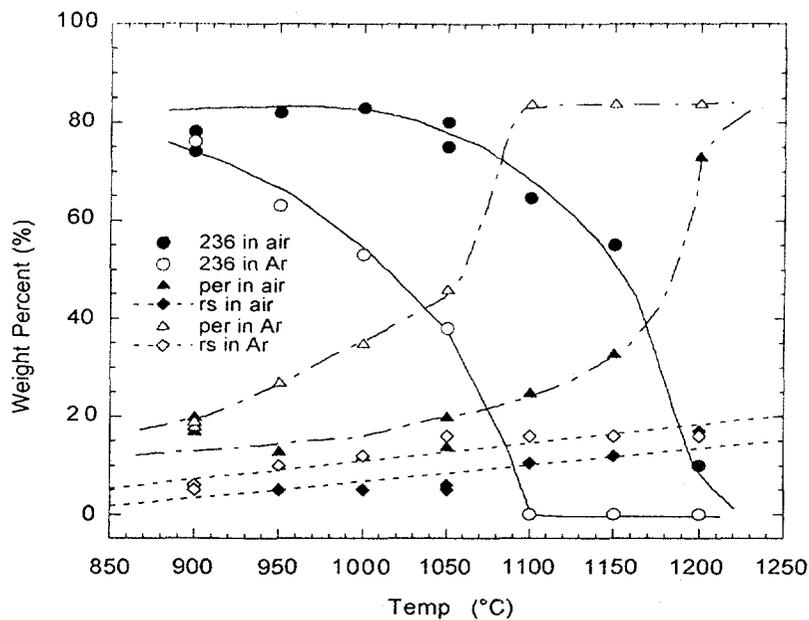


Fig. 5. Calculated weight fractions for phases presented in  $\text{SrFeCo}_{0.5}\text{O}_x$  at various  $p\text{O}_2$  values.

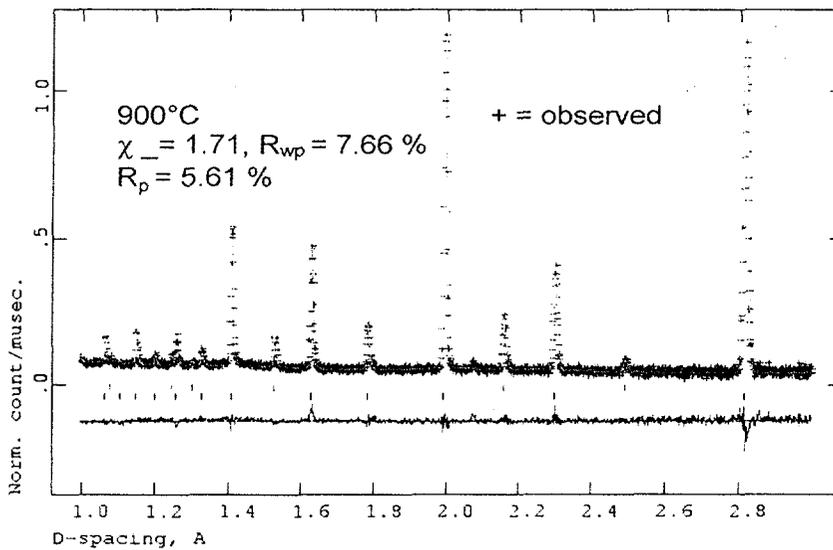


Fig. 6. Rietveld profile fit to neutron powder diffraction data from  $\text{SrFeCo}_{0.5}\text{O}_y$  sample at  $900^\circ\text{C}$  in reducing environment ( $p\text{O}_2 = 10^{-15}$  atm). Reflection markers represent rocksalt and perovskite phases from top to bottom, respectively.

Plotted in Fig. 5 are the weight fractions obtained from the Rietveld refinements performed on the SFC for the entire experiment in two different  $pO_2$  environment, air ( $pO_2 = 10^{-0.7}$  atm) and argon ( $pO_2 = 10^{-5.3}$  atm). Weight fraction of the perovskite phase increases with increasing temperature. In air, the 236 phase is stable below 1050°C. Above this temperature, it begins to convert into perovskite and rocksalt phases. At 900°C, in argon, the material consists of >75wt.% 236 phase, ≈20wt.% perovskite phase and <5wt.% rocksalt phase. This finding agrees with the phase transition of SFC that we reported earlier [14]. The 236 phase is completely converted into perovskite (brownmillerite) and rocksalt phases in highly reducing environments. Figure 6 shows a two-phase Rietveld fitting to the neutron powder diffraction data at 900°C with  $pO_2 = 10^{-15}$  atm. At 900°C with  $pO_2 = 10^{-15}$  atm, SFC consists of >80wt.% perovskite phase (primarily  $SrFeO_{2.5}$ ) and <20wt.% rocksalt phase (CoO), with no 236 phase observed. Rietveld analysis showed no indication of oxygen content dropping below 2.5 in the perovskite phase at 900°C.

## CONCLUSIONS

$SrFeCo_{0.5}O_v$  material (SFC) was synthesized by the solid-state reaction method. Conductivity of SFC was measured at elevated temperature in gas environments of various  $pO_2$  levels. Total, electronic, and ionic conductivities all increase with increasing temperature and increasing  $pO_2$ , while the ionic transference number is nearly independent of temperature with a value of ≈0.4. At 800°C in air, the total conductivity of SFC is ≈17 S·cm<sup>-1</sup>. Activation energy increases with decreasing  $pO_2$  in a reducing environment, while in a high  $pO_2$  environment, activation energy is independent of  $pO_2$  and has a value of ≈0.35 eV. Neutron powder diffraction experiments were conducted on the SFC at high temperature in various  $pO_2$  environments. In oxygen-rich environments, 236 phase is predominant in SFC. At 900°C in air, SFC consists of >75% 236 phase, ≈20% perovskite phase, and <5% rocksalt phase. However, in a reducing environment, the 236 phase decomposes and converts to perovskite and rocksalt phase at high temperature. In an environment of  $pO_2 < 10^{-12.2}$  atm, 236 phase is completely converted into perovskite (brownmillerite) and rocksalt phases. At 900°C with  $pO_2 = 10^{-15}$  atm, SFC consists of >80wt.% perovskite phase (primarily  $SrFeO_{2.5}$ ) and <20wt.% rocksalt phase (CoO), with no 236 phase observed.

## ACKNOWLEDGMENTS

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