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DEFECT STRUCTURE OF THE MIXED-CONDUCTING Sr-Fe-Co-O SYSTEM

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ABSTRACT

Electrical conductivity of the mixed-conducting Sr-Fe-Co-O system was investigated at elevated temperatures and various oxygen partial pressures (pO_2). The system exhibits not only high combined electrical and oxygen ionic conductivities but also structural stability in both oxidizing and reducing environments. The conductivity of $SrFeCo_{0.5}O_x$ increases with increasing temperature and increasing pO_2 , within our experimental pO_2 range ($1 \geq pO_2 \geq 10^{-18}$ atm). p-type conduction behavior was observed. The activation energy of which increases with decreasing pO_2 . A model of the defect chemistry in the Sr-Fe-Co-O system is proposed. The pO_2 -dependent conducting behavior can be understood by considering the trivalent-to-divalent transition of the transition metal ions in the system.

INTRODUCTION

Mixed-conducting ceramic oxides have potential uses in solid-oxide fuel cells, batteries, sensors, oxygen-permeable membranes and other electrochemical devices. The Sr-Fe-Co-O system exhibits not only high combined electrical and oxygen ionic conductivities but it is also structurally stable [1,2] in both oxidizing and reducing environments. Dense ceramic membranes made of this material can be used to separate oxygen from air without the need for external electrical circuitry. The oxygen permeation flux rate through dense membranes made of this material can be considered commercially feasible, and use of this material would greatly improve the economics of fuel production [3-8].

When used as a ceramic membrane in gas separation, $SrFeCo_{0.5}O_x$ is exposed to large oxygen chemical potential gradients. Oxygen transport from high to low oxygen partial pressure (pO_2) in the gas separation reactor will occur if the oxygen partial pressure difference, ΔpO_2 , can develop substantial oxygen flux. Therefore, an understanding of the oxygen permeation process, which is closely related to the electrical transport properties, is important to the search for better oxygen-permeable membrane materials.

In this paper, we discuss the temperature- and pO_2 -dependent conductivity of $SrFeCo_{0.5}O_x$. Activation energy, E_a , is obtained by fitting the conductivity data to the equation $\sigma \cdot T = A \exp(-E_a / kT)$. A defect chemistry model of this system is proposed and examined with the conductivity data.

EXPERIMENTAL

$SrFeCo_{0.5}O_x$ powder was made by the solid-state reaction method. Appropriate amounts of $SrCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, and Fe_2O_3 were mixed and then ground in isopropanol with zirconia medium for 15 h. After drying, the mixture was calcined in air at $850^\circ C$ for 16 h, with intermittent grinding. After the final calcination, the powder was ground with an agate mortar and pestle to an average particle size of $\approx 7 \mu m$. The resulting powder was pressed with a 1.2 GPa load into pellets 21.5 mm in diameter and ≈ 5 mm thick. The pellets were covered by powder of the same composition to eliminate contamination and then sintered at $\approx 1200^\circ C$ for 5 h. Subsequently, the pellets were cut into thin bars with a diamond saw for conductivity measurement.

X-ray powder diffraction results obtained for the $\text{SrFeCo}_{0.5}\text{O}_x$ show that the sintered sample contained a single phase [9]. The theoretical density of $\text{SrFeCo}_{0.5}\text{O}_x$ was measured on the powder with an AccuPyc 1330 pycnometer and confirmed by X-ray powder diffraction results. Bulk density of the sample used in our experiments was $\approx 95\%$ of theoretical value.

Conductivity of the specimen was measured by the DC four-probe method. Four platinum wires, of 0.2 mm in diameter, were wound around the specimen to serve as current and voltage leads. A Keithley 263 current source was used to supply the current, and the voltage was measured with a Keithley 196 system digital multimeter. Conductivity of the specimen was calculated by

$$\sigma = \frac{I \cdot d_{vv}}{V \cdot S} \quad (1)$$

where I is the applied current (in A), V is the voltage across the two voltage leads (in V), d_{vv} and S are the separation of the voltage probes (in cm) and the cross-sectional area of the specimen (in cm^2), respectively. Activation energy was calculated by fitting the temperature-dependent conductivity data to the equation

$$\sigma = \frac{A}{T} \exp\left(\frac{E_a}{kT}\right) \quad (2)$$

where A is a constant, E_a is the activation energy, k is the Boltzmann constant, and T is the absolute temperature. To measure the conductivity in various $p\text{O}_2$ environments, premixed gas cylinders were used.

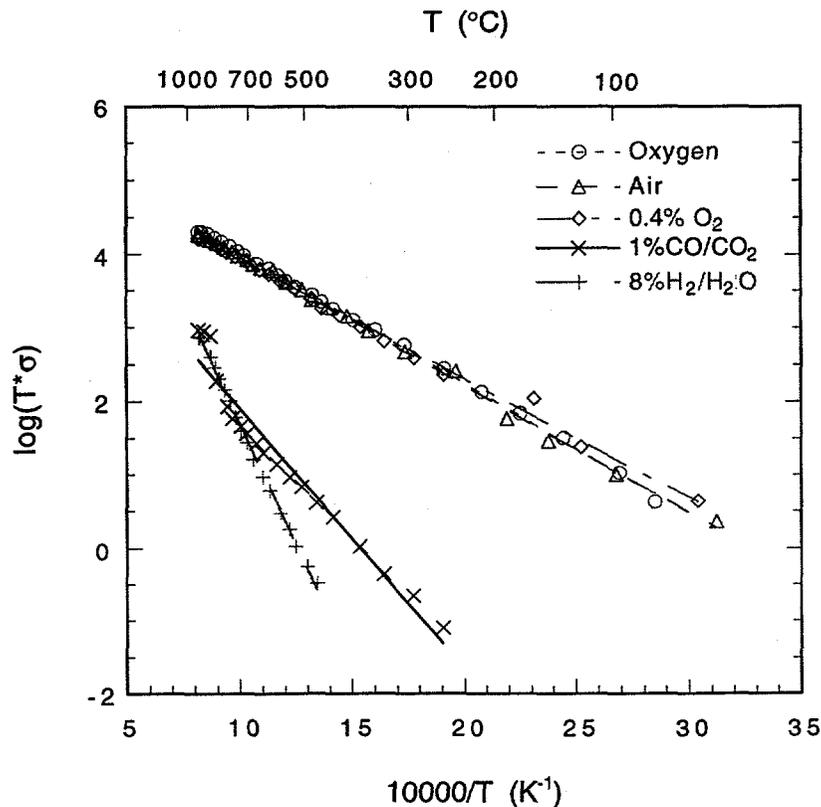


Fig. 1. $\text{Log}(T \cdot \sigma)$ of $\text{SrFeCo}_{0.5}\text{O}_x$ as a function of reciprocal temperature for various $p\text{O}_2$ levels.

RESULTS AND DISCUSSION

The conductivity of $\text{SrFeCo}_{0.5}\text{O}_x$ increases with increasing temperature and $p\text{O}_2$. Figure 1, a plot of $\log(T \cdot \sigma)$ as a function of reciprocal temperature in various oxygen environments, shows that $\log(T \cdot \sigma)$ has good linear dependence on reciprocal temperature. According to Eq. 2, the activation energy of $\text{SrFeCo}_{0.5}\text{O}_x$ can be calculated from the slopes of $\log(T \cdot \sigma)$ vs. $10000/T$ curves. The activation energy of $\text{SrFeCo}_{0.5}\text{O}_x$ thus obtained is plotted in Fig. 2 as a function of $p\text{O}_2$. The activation energy increases with decreasing $p\text{O}_2$ in the low- $p\text{O}_2$ range ($< 10^{-3}$ atm), whereas in the high- $p\text{O}_2$ range ($> 10^{-3}$ atm) activation energy is independent of $p\text{O}_2$ and has lower value (≈ 0.35 eV) compare to those of other $\text{Sr}(\text{Fe},\text{Co})\text{O}_x$ systems [10,11].

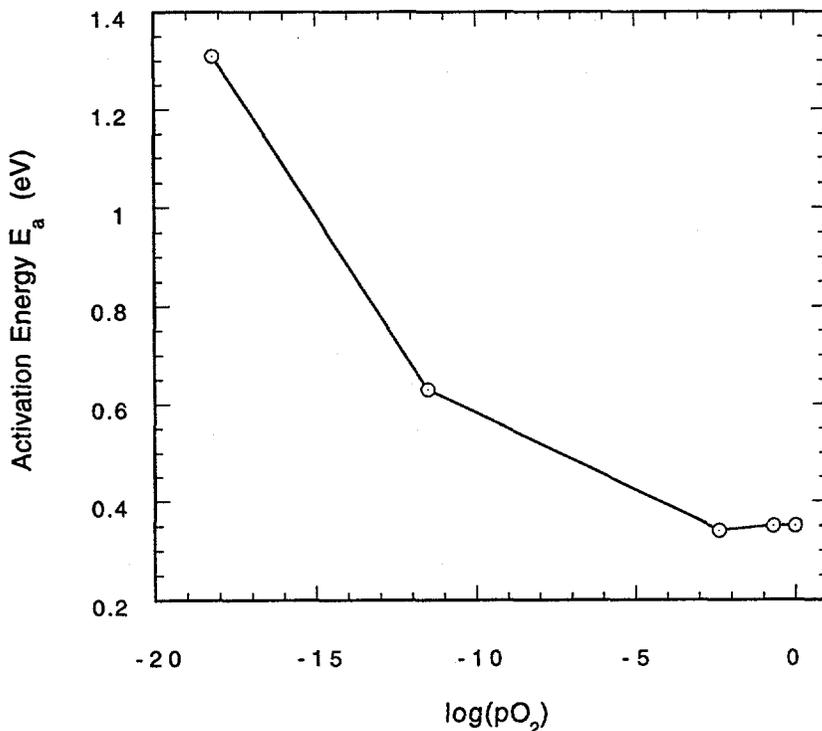


Fig. 2. Activation energy of $\text{SrFeCo}_{0.5}\text{O}_x$ as a function of $p\text{O}_2$.

The plot of $\log(\sigma)$ vs. $\log(p\text{O}_2)$ of $\text{SrFeCo}_{0.5}\text{O}_x$ at 950°C is shown in Fig. 3. This result is consistent with that we obtained earlier with a gas-tight electro-chemical cell [12]. In the intermediate- $p\text{O}_2$ range ($10^{-12} < p\text{O}_2 < 10^{-3}$ atm), the slope of $\log(\sigma)$ vs. $\log(p\text{O}_2)$ is $\approx 1/6$. This can be explained with the defect chemistry model described below. The interaction between transition metal ions and oxygen in the surrounding atmosphere can be represented as



The electroneutrality equation for the intermediate range can be written as

$$2[\text{O}_i''] = p \quad (4)$$

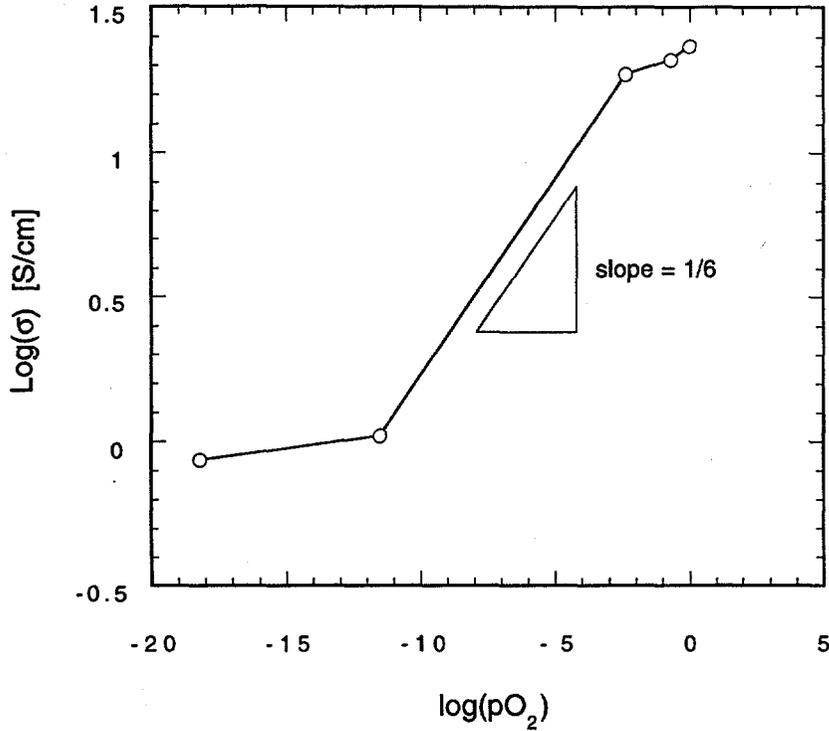


Fig. 3. Conductivity of SrFeCo_{0.5}O_x as a function of pO₂ at 950°C.

where $p = [\text{Fe}_{\text{Fe}}^{\bullet}]$ is the concentration of holes. Thus, the mass-balance relationship of the transition metal ion is

$$[\text{Fe}_{\text{Fe}}^{\bullet}] + [\text{Fe}_{\text{Fe}}^{\times}] = 1 \quad (5)$$

Here, we use Fe to represent both Fe and Co transition metal ions. Equation 3 leads to the mass reaction relationship

$$K = \frac{[\text{Fe}_{\text{Fe}}^{\bullet}]^2 \cdot [\text{O}_i^{\prime\prime}]}{[\text{Fe}_{\text{Fe}}^{\times}]^2 \cdot (p\text{O}_2)^{1/2}} \quad (6)$$

where K is the temperature-dependent reaction constant. If we let $x = [\text{Fe}_{\text{Fe}}^{\bullet}]$, and use Eqs. 4 and 5, we obtain

$$[\text{O}_i^{\prime\prime}] = \frac{x}{2} \quad (7)$$

and

$$[\text{Fe}_{\text{Fe}}^{\times}] = 1 - x \quad (8)$$

Substituting Eqs. 7 and 8 into Eq. 6, we obtain

$$K = \frac{x^3}{2(1-x)^2 \cdot (pO_2)^{1/2}} \quad (9)$$

Under the condition $x \ll 1$, i.e., the concentration of trivalent transition metal ions is much lower than the concentration of divalent transition metal ions, Eq. 9 gives us

$$p = x \propto (pO_2)^{1/6} \quad (10)$$

and

$$[O_i''] = \frac{x}{2} \propto (pO_2)^{1/6} \quad (11)$$

Because the conductivity is proportional to the concentrations of charge carriers, it leads to

$$\sigma \propto (pO_2)^{1/6} \quad (12)$$

The 1/6 dependence of the slope in Fig. 3 indicates that the trivalent-to-divalent transition of the transition metal ions plays an important role in the interaction between the $SrFeCo_{0.5}O_x$ sample and oxygen in the surrounding atmosphere.

CONCLUSIONS

$SrFeCo_{0.5}O_x$ exhibits not only high electronic and oxygen ionic conductivities but it is also structurally stable in both oxidizing and reducing atmospheres. It is a technologically important material for use in high-temperature electrochemical applications and holds particular promise as a dense ceramic membrane for separation of oxygen from air. The conductivity of $SrFeCo_{0.5}O_x$ increases with increasing temperature and pO_2 . It is a p-type conductor and its $\log(T \cdot \sigma)$ vs. $1/T$ curve exhibits good linear dependence. The activation energy of $SrFeCo_{0.5}O_x$, which decreases with increasing pO_2 , is ≈ 0.35 eV in air. The pO_2 -dependent conductivity behavior can be understood by considering the divalent-to-trivalent transition of the transition metal ions in the sample.

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