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REMARKS

ELECTRICAL PROPERTIES AND DEFECT STRUCTURE IN THE Sr-Fe-Co-O SYSTEM

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ABSTRACT

The ceramic Sr-Fe-Co-O has potential use as a membrane in gas separation. This material exhibits high conductivity of both electrons and oxygen ions. It allows oxygen to penetrate at high flux rates without other gas components. Electrical properties are essential to understanding the oxygen transport mechanism and defect structure of this material. By using a gas-tight electrochemical cell with flowing air as the reference environment, we were able to achieve an oxygen partial pressure (p_{O_2}) as low as 10^{-16} atm. Total and ionic conductivities of Sr-Fe-Co-O have been studied as a function of p_{O_2} at elevated temperature. In air, both total and ionic conductivities increase with temperature, while the ionic transference number is almost independent of temperature, with a value of ≈ 0.4 . Experimental results show that ionic conductivity decreases with decreasing p_{O_2} at high p_{O_2} ($\geq 10^{-6}$ atm). This suggests that interstitial oxygen ions and electron holes are the dominant charge carriers. At 800°C in air, total conductivity and ionic conductivity are 17 and 7 S/cm, respectively. Defect dynamics in this system can be understood by means of the trivalence-to-divalence transition of Fe ions when p_{O_2} is reduced. By using the conductivity results, we estimated oxygen permeation through a ceramic membrane made of this material. The calculated oxygen permeability agrees with the experimental value obtained directly from an operating methane conversion reactor.

INTRODUCTION

Mixed-oxide conductors find wide application in high-temperature solid-state electrochemical devices such as solid-oxide fuel cells, batteries, and sensors. These materials also hold particular promise as ceramic membranes designed to separate oxygen from air, because they are impervious to other gases. High oxygen permeability, usually associated with high oxygen ionic conductivity, is desirable in the separation process. Materials of the $\text{Sr}(\text{Fe},\text{Co})\text{O}_x$ system are technologically important because of their combined high oxygen ionic and electronic conductivities at elevated temperature and their structural stability in both oxidizing and reducing atmospheres [1-4]. Ceramic membranes made of this material can be used for gas separation without the need for external electrical circuitry. One could use this material to produce syngas ($\text{CO}+\text{H}_2$) by direct conversion of methane and other basic hydrocarbon gases, such as coal gas. Air can be used as the oxidant in the conversion process because the ceramic membrane can successfully separate oxygen from air at a commercially feasible flux rate. Thus, these materials have potential uses in applications that could improve the economics of the methane conversion process [3, 5-7]. Recently, Balachandran et al. [5] reported that membrane tubes made of $\text{SrFeCo}_{0.5}\text{O}_x$ ceramic powder have been tested in an actual methane gas conversion reactor. Methane conversion efficiencies $> 98\%$ were obtained in reactor runs of more than 1000 h at 850°C .

A understanding of the electrical properties and the defect dynamics of this material is essential and will help us to find the optimal operating conditions for the conversion reactor. In the meantime, it may also give us some clues for developing better materials.

In this paper, we discuss the temperature- and p_{O_2} -dependent conductivities of the $\text{Sr}(\text{Fe},\text{Co})\text{O}_x$ system. Based on experimental results, a defect model is proposed to explain the electrical properties of this system. Oxygen permeability will be estimated by using conductivity data and will then be compared with the value obtained from methane conversion reactor.

EXPERIMENTAL

Sr(Fe,Co)O_x powder was made with appropriate amounts of SrCO₃, Co(NO₃)₂·6H₂O, and Fe₂O₃ by the conventional solid-state reaction method. The average particle size was ≈7 μm. Pellets of 21.5 mm diameter and ≈3 mm thickness were made with a hydraulic press at a 1.2×10³ MPa load, then sintered in air at ≈1200°C for 5 h. Bulk density of the samples was ≈95% of theoretical value. Bar samples for conductivity measurements were cut from the pellets.

Gas-tight electrochemical cells [8] were used to achieve a reduced-oxygen environment. pO₂ inside the cell was determined from the electromotive force generated across a disk of yttria-stabilized zirconia and the reference atmosphere pO₂' with following equation

$$EMF = \frac{RT}{4F} \ln \left(\frac{pO_2''}{pO_2'} \right) \quad (1)$$

where pO₂'' and pO₂' are the oxygen partial pressure inside and outside the gas-tight cell, respectively; R is the gas constant; F is the Faraday constant; and T is the absolute temperature.

Total conductivity was measured by the conventional the four-probe method. Ionic conductivity was measured with four-probe electron-blocking method [9].

RESULTS AND DISCUSSION

Conductivities in Air

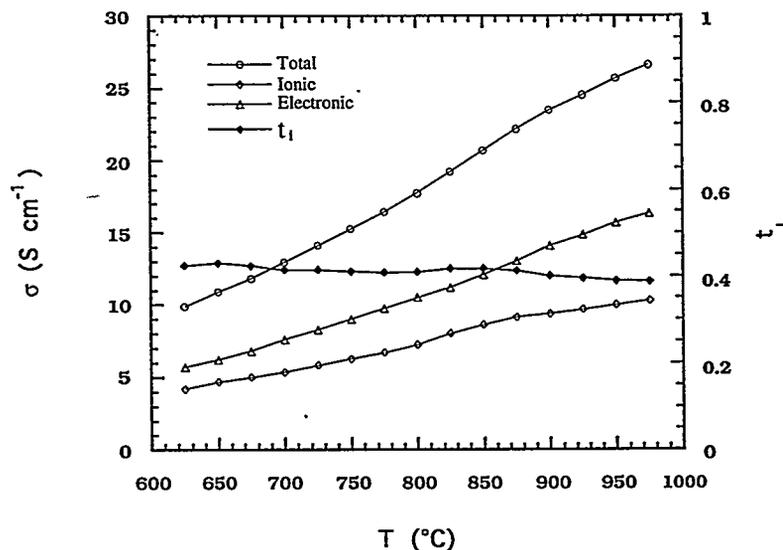


Fig. 1. Temperature dependence of conductivities, corresponding to left y-axis; and ionic transference number, corresponding to right y-axis, in air.

Conductivities and ionic transference number are plotted in Fig. 1 as a function of temperature. The total, electronic, and ionic conductivities all increase with increased temperature. The ionic transference number is almost independent of temperature. At 800°C, total and ionic conductivities are 17 and 7 S cm⁻¹, respectively. Within the experimental temperature region (625 to 975°C), the ionic transference number is almost independent of temperature with a value of ≈0.4. The ionic transference number describes the contribution from oxide ions to the total conductivity of the sample. Unlike other ceramic materials, Sr(Fe,Co)O_x has an ionic transference number neither much greater than nor much less than 1. This means that the contributions to total conductivity from both electronic and oxide ionic conducting species are relatively similar. We will see in the following discussion that this is a desirable characteristic for high oxygen permeation.

Conductivity as a Function of pO₂

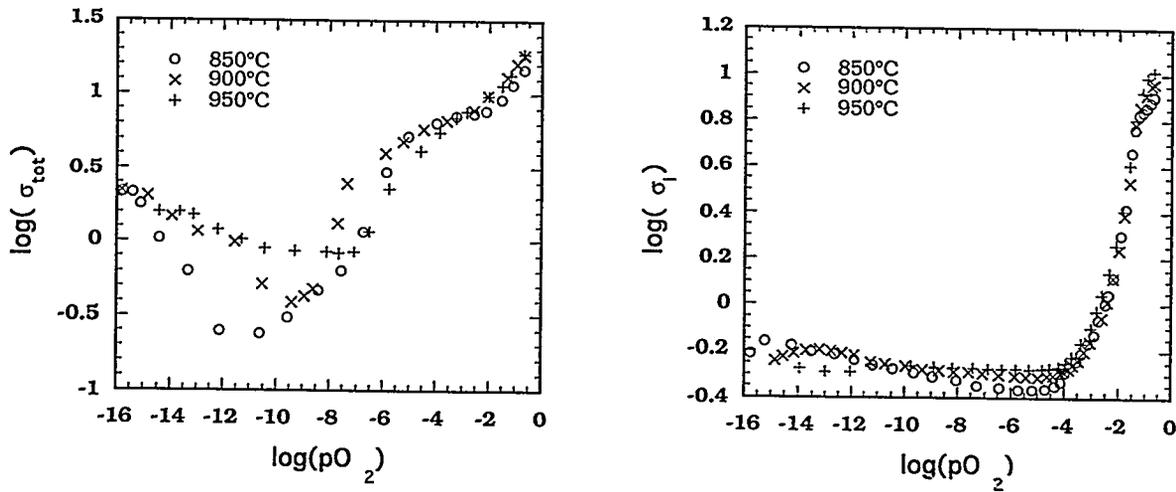


Fig. 2. Oxygen partial pressure dependence of total and ionic conductivities at three different temperatures.

The pO_2 dependence of total and ionic conductivities at three different temperatures is plotted in Fig. 2. Total conductivity in the high- pO_2 range decreases linearly as pO_2 decreases. The slope of the $\log(\sigma)$ vs. $\log(pO_2)$ curve is $\approx 1/5$ in this relatively high- pO_2 region. As pO_2 continues to decrease, the curve flattens and then enters another linear portion with a slope of $\approx 1/4$, then reaches its minimum, and finally increases linearly with a slope of $\approx 1/4$. Ionic conductivity decreases almost linearly with a slope of $\approx 1/2$ as pO_2 decreases. As pO_2 continues to decrease, ionic conductivity decreases much more slowly than before, then reaches its minimum, where it becomes independent of pO_2 . For the lowest temperature curve (850°C), a small bump appears in the low- pO_2 region.

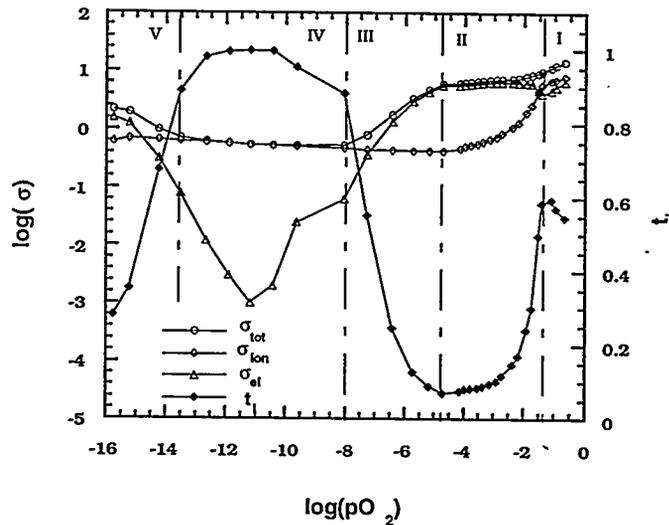


Fig. 3. Oxygen partial pressure dependence of total, ionic, and electronic conductivities, corresponding to left y-axis; and ionic transference number, corresponding to right y-axis, at 850°C.

Figure 3 shows the pO_2 dependence of total, ionic, and electronic conductivities and the ionic transference number at 850°C. Based on conductivity behavior, the entire experimental pO_2 range

can be divided into five regions, within each of which electronic and ionic conductivities behave differently. These behaviors can be understood with a Frenkel disorder in the oxygen sublattice. In the sample, ionic thermal disorder can be written in the notation of Kroger [10] as



where O_o^x , O_i'' , and V_o^{**} indicate normal oxygen on the oxygen site, interstitial oxygen ion with two electron charges, and doubly ionized oxygen vacancy, respectively. Equation 2 describes oxygen as it leaves a normal lattice site vacant by moving into an interstitial position. The intrinsic thermal electron-hole generation is described in a similar manner by

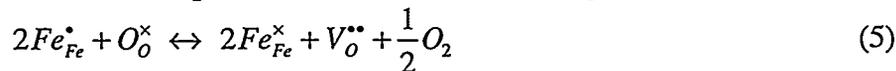


while equilibrium with the gas phase,



occurs by exchange of oxygen between the crystal lattice and the gas.

In our sample, we have two variable-valence metal ions, Fe and Co. In the temperature and pO_2 range of our experiment, Co ions are most likely in the divalent state, and Fe ions can have a trivalent-to-divalent transition when pO_2 is reduced. The Fe^{3+} to Fe^{2+} transition under the reduced oxygen environment can be represented in the notation of Kroger:



or in a simple way as



where Fe_{Fe}^{\bullet} and Fe_{Fe}^x correspond to trivalent and divalent Fe ions, respectively. The electroneutrality relationship should now be written as

$$n + 2[O_i''] = p + 2[V_o^{**}] + [Fe_{Fe}^{\bullet}] \quad (7)$$

Solving the above equations (2-7) with the Brouwer approach [11], we can get the defect concentration as a function of pO_2 for the five different limitations [12].

Based on our defect model, the trivalence-to-divalence transition should occur near the boundary of region II and region III. At high pO_2 , the concentrations of oxide ions (O_i'') and holes ($Fe_{Fe}^{\bullet} = h^*$) are much higher than those of oxygen vacancies (V_o^{**}) and electrons (e'); the conductivity behaviors are dominated by O_i'' and h^* . In region I, $[O_i'']$ and p decrease while $[V_o^{**}]$ and n increase with decreased pO_2 . Although the slopes for $[O_i'']$ and p are the same (both $\approx 1/6$, because the mobility of holes is greater than that of interstitial oxygen ions), electronic conductivity changes more rapidly than ionic conductivity. This is why we see an increase in the ionic transference number with decreased pO_2 in this region.

In region II, the concentrations of h^* and e' do not change, and the concentrations of O_i'' and V_o^{**} change more rapidly, with slopes of $1/2$ and $-1/2$, respectively. This leads to a more rapid change in ionic conductivity than in electronic conductivity. Hence, the ionic transference number decreases with decreased pO_2 and reaches its minimum at the boundary of regions II and III.

In region III, similar to the case in region I, $[O_i'']$ and p have the same slope, as do $[V_o^{**}]$ and n ; unlike the case in region I, we have $[O_i''] \geq [V_o^{**}]$ and $p \geq n$. Again, because the mobilities of electrons and holes are greater than those of oxygen ions and vacancies, electronic conductivity (which should equal the sum of electron and hole conductivities under this circumstance) decreases more rapidly than ionic conductivity with decreasing pO_2 . Thus, we observed an increase in ionic transference number.

In region IV, the so-called mixed-conduction zone, $[O_i'']$ and $[V_o^{**}]$ are independent of pO_2 , p decreases while n increases with the decreasing in pO_2 , and ionic conductivity does not change while the electronic conductivity first decreases, reaches its minimum, and then increases. Thus, we observed the maximum in ionic transference number, corresponding to the minimum in

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 electronic conductivity, which happened at the point where concentrations of electrons and holes are equal.

In region V, $[V_{O}^{**}] \gg [O_i^-]$ and $n \gg p$, where the oxygen vacancies and electrons are the dominant charge carriers. Although the slopes of $[V_{O}^{**}]$ and n are the same because the mobility of electrons is greater than that of oxygen vacancies, electronic conductivity increases more rapidly than ionic conductivity, and the ionic transference number decreases with decreased pO_2 . Finally, the ionic transference number reaches a value of ≈ 0.3 at $\log(pO_2) = -16$.

Oxygen Permeation

Using the results of total and ionic conductivities as functions of pO_2 , we can calculate the flux rate of oxygen permeating through a membrane of thickness L with the following equation [13]:

$$jO_2 = \frac{1}{4F} jO^{2-} = -\frac{RT}{16F^2 L} \int_{pO_2(0)}^{pO_2(x)} \sigma_{tot} t_{ion} t_{el} d \ln(pO_2) \quad (8)$$

Considering a membrane of $L = 0.75$ mm thickness, the calculated oxygen flux rate and the experimental results obtained in an operating methane conversion reactor is plotted in Fig. 4.

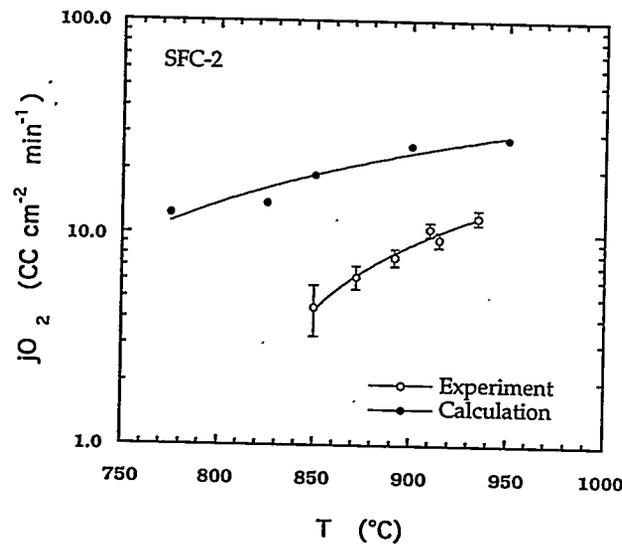


Fig. 4. Temperature dependence of oxygen permeation flux rate.

The permeability we calculated from the electrical conductivity results is close to that measured at the methane conversion reactor. This indicates that the bulk properties, rather than surface properties, are chiefly responsible for oxygen transport in $Sr(Fe,Co)O_x$. The oxygen permeation flux rate of $Sr(Fe,Co)O_x$ we obtained is two orders higher than that of the $(La,Sr)(Fe,Co)O_x$ system [14].

CONCLUSIONS

By using a gas-tight electrochemical cell with flowing air as the reference environment, we produced an oxygen partial pressure (pO_2) as low as 10^{-16} atm in the cell. Total and ionic conductivities were measured with conventional four-probe and electron-blocking four-probe methods at reduced pO_2 and elevated temperatures. At $800^\circ C$ in air, the total and ionic

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conductivities of Sr(Fe,Co)O_x are 17 and 7 S/cm respectively, and the ionic transference number is ≈ 0.4 . The $p\text{O}_2$ dependence of the electrical conductivity is quite complicated; conductivities, and thus the ionic transference number, behave differently in five regions when $p\text{O}_2$ is reduced from that of ambient air to 10^{-16} atm. However, with the defect model we proposed, in which the trivalence-to-divalence transition of Fe ions is taken into consideration, we can understand this system quite well. In the high- $p\text{O}_2$ range, interstitial oxygen ions and holes are the dominant charge carriers, while in the low- $p\text{O}_2$ range, oxygen vacancies and electrons are the dominant charge carriers. Due to the change of charge carrier concentration, the ionic transference number varies as a function of $p\text{O}_2$. Oxygen permeation flux has been calculated by using conductivity data; the calculated value and that obtained from an operating methane conversion reactor agree with each other within a factor of 2 to 3. This suggests that bulk properties of the sample play a main role in oxygen permeation.

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