The diffusion coefficient of oxygen in the mixed conducting oxide $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0.2, 0.5, 0.8$) has been measured by an electrochemical technique which allows the simultaneous measurement of coulometric titration data, such that the ionic transport properties can also be calculated. At $850^\circ\text{C}$, the chemical diffusion coefficient was measured to be of the order of $10^{-7} - 10^{-6} \text{ cm}^2/\text{s}$, and the ionic conductivity was found to lie in the range $10^{-3} - 10^{-2} \text{ S/cm}$, with the highest and lowest values in both cases exhibited by SrCo$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ and SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$, respectively. The activation energy for the transport of oxygen varied in the range 30 to 50 kcal/mol with increasing Co/Fe ratio. Increasing Co/Fe ratio appeared to cause, moreover, a decreasing chemical stability of the compound in reducing environments and an increasing affinity for forming reaction products with the zirconia electrolyte. These results lead to the conclusion that the compounds with high Co/Fe contents are not suitable as cathodes in solid oxide fuel cells.

**INTRODUCTION**

Mixed electronic and ionic conduction in the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ series of perovskites has received wide attention for a number of possible industrial applications of these materials (1), e.g., in oxidation catalysis, as electrodes in solid oxide fuel cells, oxygen sensors, and gas separation membranes. In addition to a high electronic conductivity, Teroaka et al. (1,2) have shown that these materials exhibit significant oxygen ion conductivity at elevated temperatures. The capability for oxygen conduction was attributed to a vacancy transport mechanism with reference to the data for the compounds $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ (3), which exhibit a high degree of nonstoichiometry in the form of oxygen vacancies (4,5).

The results of Teroaka et al. indicate, moreover, that the oxygen conductivity in the compound $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ increases with increasing $x$ (A site substitution) and decreasing $y$ (B site substitution). The highest oxygen permeation is exhibited by SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (2). These results were obtained by using multicrystalline specimens sintered from powder materials.
The present interest in this type of materials is related to possible applications as air cathodes in solid oxide fuel cells utilizing zirconia-base electrolytes and as membranes for separating oxygen from gas mixtures. In this respect, oxygen permeability measurements are not deemed conclusive due to possible porosity and other macroscopic defects in the sintered material. Four point conductivity measurements may be affected by surface diffusion and other interfacial phenomena. The purpose of this work is, therefore, to investigate the rate of oxygen transport in \( \text{SrCo}_{1-x}\text{Fe}_x\text{O}_3 \) by use of a solid state electrochemical technique (6), which guarantees that the measured properties are related to the transport of oxygen in the crystal bodies in the bulk of the material. The applications and advantages of electrochemical techniques for studying mass transfer and reaction kinetics in solid state ionics have been reviewed in detail (7,8).

**THEORY**

The system for diffusion experiments consists of a pellet of thickness \( L \) sandwiched between a current collector and the electron blocking yttria-stabilized zirconia (YSZ) electrolyte as sketched in figure 1. The pellet acts as one of the electrodes in the electrochemical cell. All surfaces of the pellet except the one adjacent to the electrolyte are sealed against oxygen. The opposite surface of the YSZ electrolyte is coated with porous Pt film as the electrode with the opposite polarity. Application of a constant potential across the cell maintains a fixed and well defined oxygen activity at the YSZ-specimen interface. Since YSZ does not have an appreciable electronic conductivity, the charge crossing the interface is ionic in nature. While the concentration of oxygen ions in the specimen relaxes in response to the potential step by passage of charge across the interface, it is assumed that the oxygen ion concentration at the specimen surface remains constant, as is commonly done in transient diffusion experiments of this nature. The relaxation process is therefore expressed by the one-dimensional form of Fick's second law, which can be solved to give the following relationship between the cell current and time at large times, in response to a potential step:

\[
I = \frac{2QD}{L^2} \exp \left( -\frac{\pi^2 D t}{4L^2} \right) \quad (t \gg L^2/D) \tag{1}
\]

where \( Q \) is the total charge passed during the potential step \( (Q = \int_0^t Idt) \). Since the current and charge are readily measurable, the diffusion coefficient \( D \) can be determined from equation 1 for a given cell potential \( E \).

The long-time solution is preferred in evaluating the experimental data in the present work because equation 1 is not strongly dependent on the geometry (smoothness) of the specimen-perovskite interface and the nature of initial conditions. Even if these conditions cannot be strictly satisfied, it can be shown that the current transient at large times is still directly proportional to \( \exp(-\pi^2 D t/4L^2) \), such that the diffusion coefficient can be determined from the slope of experimentally obtained \( \ln I - t \) relationship.

The measured diffusion coefficient \( \bar{D} \) is related to the component or ionic diffusion coefficient \( D_i \) by the expression (7,9)
\[ \bar{D} = D_t e \left( \frac{\partial \ln a^*}{\partial \ln c^*} \right) \]  

(2)

where \( a^* \) and \( c^* \) are the activity and concentration of neutral oxygen, respectively, and \( t_e \) is the electron transference number. The ionic diffusion coefficient is related to the tracer diffusion coefficient which can be measured directly by radiotracer techniques (8).

For a perovskite of type \( ABO_{y-\delta} \), the quantity within the parantheses, the so-called enhancement factor, can be expressed as (7,9)

\[ \frac{\partial \ln a^*}{\partial \ln c^*} = -\frac{zF(y-\delta)}{RT} \frac{\partial \bar{E}}{\partial \delta} \]  

(3)

where \( z \) is the valence of the diffusing species. The derivative on the right can be evaluated from the slope of the coulometric titration curve by using the equation

\[ \frac{\partial E}{\partial \delta} = -\frac{zFW}{M} \frac{\partial E}{\partial Q} \]  

(4)

where \( W \) and \( M \) are, respectively, the mass and the molecular weight of the specimen. The ionic conductivity can in turn be estimated from the Nernst-Einstein relationship

\[ \sigma_i = \frac{4F^2cD_i}{RT} \]  

(5)

\[ \sigma_i = \frac{\bar{D}}{Vt_e(\partial \bar{E}/\partial Q)} \]  

(6)

where \( V \) is the specimen volume. Equation 6 is obtained by combining equations 2 through 5.

Thus, the potential-step technique provides data for obtaining the chemical diffusion coefficient \( \bar{D} \), the ionic transport properties \( D_t \) and \( \sigma_i \), and a certain amount of information about the thermodynamic properties of the material (coulometric titration data). The absolute value of \( \delta \) and \( t_e \) have to be obtained from separate experiments. However, for the materials under consideration, \( t_e \) is close to unity. Neglecting \( \delta \) relative to \( y \) in equation 3 will probably lead to an error of 10% or less in estimating the enhancement factor and \( D_t \). Notice that \( \sigma_i \) is independent of the absolute value of \( \delta \) (see equation 6).

**EXPERIMENTAL**

Stoichiometric ratios of reagent grade \( Sr(NO)_3 \), \( Co(NO)_3 \cdot 6H_2O \), and \( Fe_2O_3 \) were ground and mixed to give the desired \( x \) value in \( SrCo_{1-x}Fe_xO_{3-\delta} \). The mixtures
were calcined, first in powder form, and subsequently twice in pelletized form at about 1000°C. X-ray powder diffraction analyses of the products indicated a perovskite structure with no discernable impurities. Sintering was performed at 1200°C after observing that the melting point of SrCo08Fe02O3_6 lies around 1300°C. The resulting densities of pellets were about 90% of the theoretical values determined by X-ray diffraction.

Single crystal slabs of 10 mole percent YSZ were used as the electrolyte. The pellets and the YSZ slabs were metallographically polished through 1 μm diamond paste on one surface and coated, respectively, with gold and porous platinum on the opposite surfaces. The polished surface of specimen was placed against the polished YSZ surface with a thin, porous Pt film in between to facilitate the interfacial transport of oxygen. A Pt foil was pressed on the gold coated surface of the pellet as the current collector. The space between the foil and the YSZ was filled with Pyrex (figure 1). The cell was finally pressed by a spring mechanism against a Pt-foil ring as the opposite current collector on the Pt coated face of the YSZ slab. The gold coating was intended, together with the Pyrex plug, as a diffusion barrier against oxygen. It also functioned as a barrier in preventing a possible chemical interaction between the Pyrex and the specimen. Additional details about the cell construction can be found in reference 6. The pellets were of the order of 1 mm in thickness and 20 mm² in exposed area.

The current transients and the amount of charge passed, Q, at the applied potential steps were obtained in the conventional manner by use of PAR Model 173 potentiostats equipped with Model 179 digital coulometers. Most of the data for establishing the temperature dependence of transport properties were obtained by applying ±20 mV steps to the cell with respect to the closed circuit potential (0 V). In measuring the potential dependence of the diffusion coefficient, larger steps than 20 mV (typically 50 and 100) were applied in the negative direction, such that oxygen was depleted from the sample. After a given specimen started decomposing, the experiment was continued in the galvanostatic mode for the purpose of speeding up the titration process in an effort to extract additional thermodynamic data.

RESULTS

General

Most current transients measured in response to an applied potential step, as shown in figure 2, were exponential in nature starting from a very early stage in the run, indicating that equation 2 is obeyed. These data were also characterized by a certain leakage current, as indicated by the steady-state portion of the curve in figure 2, resulting from oxygen diffusion through the glass seal. However, this amounted to a small fraction of the initial current level and did not affect the cell behavior significantly except at very low oxygen partial pressures. The measured coulometric data were corrected for the leak in the following manner by utilizing the exponential dependence of current on time:

\[ Q_{corr} = Q_{meas} - I_o t_f - \frac{I_o}{m} e^{mt_f} \]  

where \( I_o \) is the steady state value of the measured current (leakage current), \( t_f \) is the duration of run, and \( I_o \) and \( m \) are the parameters obtained by fitting the exponential part of the data to the equation

[7]
Equation 7 not only accounts for the contribution due to the leakage current (second term on the right) but also corrects for the possibility that the run is terminated before steady state is attained (third term on the right). In the latter case, $I_e$ is obtained also by curve fitting of the experimental data to equation 8.

Another problem associated with the present measurements was a certain decrease (about 100 and 30%, respectively) in the measured diffusion coefficient relative to that of a fresh specimen over a period of several days at a given temperature in the case of compounds $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$. At the end of this period, the diffusion coefficient measured at a given potential attained a steady-state value. The compound $SrCo_{0.2}Fe_{0.8}O_{3-\delta}$ was not affected. The cause of this observation has not been investigated. However, the formation of a third phase at the specimen - YSZ interface is considered as a good possibility.

Temperature Dependence

Figure 3 shows the Arrhenius plots for the chemical diffusion coefficients $D$ of the three compounds initially stabilized at 850°C. The data are limited to potentials in the vicinity of the closed circuit potential (0, 20, and -20 mV). The plot includes data for replicate $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ specimens, which have identical compositions and thermal history but somewhat different geometries as indicated on the figure. It can be seen that the diffusion coefficients for the replicate specimens lie within the same order of magnitude. The thinner specimen ($L = 0.79$ mm) with the lower diffusion coefficients underwent appreciable interaction with the glass seal (as indicated by color change) around the edges because the gold coat protection was not adequate. Therefore, only the data for the thicker specimen ($L = 1.04$ mm) is used in the remainder of the paper.

The data in figure 3 indicate that measured diffusion coefficient $D$ of oxygen in $SrCo_{1-x}Fe_xO_{3-\delta}$ is associated with high activation energies varying from about 50 kcal/mol for $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ to about 30 kcal/mol for $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$. The compound $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ exhibits the lowest diffusion coefficients, while $SrCo_{0.5}Fe_{0.5}O_{3-\delta}$ has the highest values.

The temperature dependence of the ionic diffusion coefficients and ionic conductivities, calculated from the measured diffusion coefficients and the enhancement factor data, are shown, respectively, in figures 4 and 5. The relative magnitudes of these properties for the three compounds and the activation energies calculated from their temperature dependence are not too different from those obtained from the chemical diffusion coefficient data (figure 3). This is explained by the fact that the enhancement factor does not vary significantly with temperature in the vicinity of the closed circuit potential. For some of the values plotted in figures 4 and 5, coulometric titration data were not available, and these values were calculated by using enhancement factors of about 80, a value indicated by measurements on the three types of materials over a wide range of temperatures. These points lie close to the lines obtained by regression analyses of the directly measured data.
Potential Dependence at 850°C

The applicability of these cobaltites as fuel cell cathodes and gas separation membranes was further investigated by measuring the effect of applied potential (or equivalently the effect of oxygen partial pressure) on the oxygen transport properties and the stability of the compounds at 850°C, a typical operating temperature. Figure 6 shows that the compounds undergo a significant increase in oxygen vacancy concentration with increasing potential in the negative direction (or decreasing oxygen partial pressure). The vacancy concentration is slightly higher with increasing Co/Fe ratio; however, this difference is discernable at potentials more negative than -100 mV.

Increasing negative potential causes significant drops in the transport properties $D$, $D_i$, and $\sigma_i$ as shown for the chemical diffusion coefficient and ionic conductivity, respectively, in figures 7 and 8. No transport property data could be measured for the compounds $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $SrCo_{0.9}Fe_{0.1}O_{3-\delta}$ at potentials more negative than -350 mV because of onset of decomposition as will be discussed further below. For the more stable compound $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, however, these properties, especially the calculated $D_i$ and $\sigma_i$, attain relatively constant values at potentials more negative than -300 mV.

Stability

The potentiostatic current transients did not decay to the usual steady state values of a few microamps at -350 mV for $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and at -400 mV for $SrCo_{0.9}Fe_{0.1}O_{3-\delta}$. After going through minima, the currents stabilized at levels about an order of magnitude larger than the expected steady-state values, indicating the onset of decomposition. The data for compound $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, however, did not show any signs of decomposition at potentials more positive than -700 mV. The coulometric data for lower oxygen partial pressures, although of qualitative value due to gas leakage, suggested 4-phase plateaus for all three compounds at about -750 mV.

DISCUSSION AND CONCLUSIONS

The present results for the transport properties of oxygen in $SrCo_{1-x}Fe_xO_{3-\delta}$, even if corrected for possible formation of phases at the cobaltite - YSZ interface, are significantly lower than the values reported by Teroaka et al., based on oxygen permeability (2) and 4-point ionic conductivity (1) measurements. At the same time, the activation energies measured presently are much higher than those reported by Teroaka et al. (1). These authors argue that the diffusion coefficients calculated from their results agree well with the data of Fueki and coworkers for single crystal $La_{1-x}Sr_xCoO_{3-\delta}$ specimens.

Fueki and coworkers report chemical diffusion coefficients obtained by the gravimetric method (1) and ionic diffusion coefficients measured by radiotracer techniques (3). The latter data agree well with the present $D_i$ values and the related activation energies obtained for $SrCo_{1-x}Fe_xO_{3-\delta}$. However, it is not clear to the present authors how the chemical and ionic diffusion coefficients, with significantly different activation energies as reported by the Japanese workers, can be correlated in the light of the transport theory summarized earlier in this work. The activation energies calculated from the
chemical and ionic diffusion coefficients should not be different as long as the enhancement factor is independent of temperature as indicated both by the present data and the results of Fueki et al. (see figure 4 in reference 5).

The present results suggest that high Co/Fe concentrations are detrimental in reducing the oxygen ionic conductivity and decreasing the chemical stability of $SrCo_{1-x}Fe_xO_3$ series compounds. In addition, high Co/Fe ratios appear to induce chemical interaction with the YSZ electrolyte. These factors rule out the use of cobaltites with high Co contents as cathodes in solid oxide fuel cells. Furthermore, increasing Co/Fe ratio increases the activation energy for oxygen transport. This property limits the applicability of the material as an oxygen separation membrane to high temperatures (12).

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Figure 1. The electrochemical system for diffusion measurements.

Figure 2. Typical current response to a -20 mV potential step.

Figure 3. Arrhenius plot for the chemical diffusion coefficient.

Figure 4. Arrhenius plot for the ionic diffusion coefficient. Closed symbols: Calculated from measured chemical diffusion coefficient and enhancement factor data. Open symbols: Calculated from measured chemical diffusion data and an estimated enhancement factor of 80.
Figure 5. Arrhenius plot for the ionic conductivity. Closed and open symbols: See figure 4 caption.

Figure 6. Change of nonstoichiometry relative to the closed circuit conditions ($\delta_0$) as a function of applied potential at 850°C.

Figure 7. Effect of potential on the chemical diffusion coefficient at 850°C.

Figure 8. Effect of potential on the ionic conductivity at 850°C.