**Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ CATHODE MATERIAL FOR SOFC OPERATING AT A REDUCED TEMPERATURE**

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**ABSTRACT**

We investigated the characteristics of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ as a cathode material for Solid Oxide Fuel Cells operating at a reduced temperature. Single phase Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ ($0 \leq x \leq 1.0$) was prepared in order to investigate the electrical conductivity, and thermal expansion. When $x$ is between 0 and 0.3, the thermal expansion coefficient of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ is less than $1.2 \times 10^{-5}$ K$^{-1}$, which is the value for Pr$_{0.8}$Sr$_{0.2}$MnO$_3$. The overpotential between Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ ($x=0.0, 0.5, 1.0$) cathodes and YSZ (8mol.% yttria) electrolyte (anode: Ni-YSZ cermet) was investigated from 850°C to 700°C by the AC impedance method. Although the exchange current density for cathodes containing Co is lower than those with Pr$_{0.8}$Sr$_{0.2}$MnO$_3$, their overpotential at a high current density is smaller than those with Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ because of their large charge transfer coefficients.

**INTRODUCTION**

Solid oxide fuel cells (SOFC) operating at about 1000°C have been frequently studied.[1,2] However, such high temperature operation causes material problems including electrode sintering and interfacial diffusion between electrolyte and electrode.[1] One possible way to overcome this problem is to reduce the SOFC operating temperature.[3] To achieve this, efforts have been made to reduce the ohmic loss of the electrolyte by fabricating a thin layer of YSZ or by finding new materials with high ionic conductivity.[1,4-5] In contrast, it is assumed that a decrease in the operating temperature leads to a large overpotential between the electrolyte and electrode because the electrochemical reaction rate decreases. This may be another crucial problem in terms of low temperature operation. Therefore it is important to investigate the electrochemical reaction mechanism at the electrolyte/electrode interface in the lower temperature range.

Perovskite type oxides (ABO$_3$) containing Co ions are known to have higher conductivity and electrocatalysis than those of the most commonly used cathode material La$_{1-x}$Sr$_x$MnO$_3$.[6,7] However, the thermal expansion coefficient of these materials is much larger ($2.2 \times 10^{-5}$ K$^{-1}$) than that of La$_{0.8}$Sr$_{0.2}$MnO$_3$ ($1.2 \times 10^{-5}$ K$^{-1}$). [1] It is interesting to investigate the possibility of using solid solution systems containing Mn and Co ions to improve the electrochemical properties without causing a thermal expansion mismatch with the electrolytes. In this study, we examine the properties of a solid solution of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ ($0 \leq x \leq 1.0$) as a cathode material in the 700°C to 850°C temperature range. We also discuss the mechanism of the electrochemical reaction at the interface between electrolyte and cathode.
EXPERIMENTAL

Thermal expansion coefficient and electrical conductivity measurements.

Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ samples were prepared from high purity Pr$_6$O$_{11}$, SrCO$_3$, MnO$_2$ and Co$_3$O$_4$ powders. They were mixed and then de-carbonated and pre-reacted by calcination in air at 1100°C for 24 hours. They were then ground and pressed into pellets at a pressure 3 ton/cm$^2$. The pellets were sintered in air between 1300°C and 1500°C. The phase purity of the fired products was examined by X-ray diffraction measurements using nickel-filtered Cu Kα radiation. All products were single phase (rhombohedral). The thermal expansion coefficient was measured from room temperature to 1100°C at a heating rate of 2°C/min. Four Pt leads were attached to the sintered samples for conductivity measurements by the DC four terminal method. The electrical conductivity was measured from 300°C to 1100°C in air at a heating rate of 2°C/min.

Single cell measurements.

The geometry of the cell we used is shown in Fig.1. We used Ni-YSZ, Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$, and porous Pt for the anode, cathode and reference electrode, respectively. First, NiO-YSZ powder with PVA was painted on a 0.3mm-thick YSZ (8mol%) plate and fired at 1400°C for 1 hour, then Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ (X= 0.0, 0.5, 1.0) powder mixed with ethylene glycol and Pt paste was painted on the plate and fired at 950°C in air for 1 hour. The Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ powder had a mean diameter of 3.0 μm. Pt mesh was used as the current collector. The typical area of the cathode and anode was about 1.6cm$^2$.

In order to estimate the electrode resistance and overpotential at the cathode/electrolyte interface, we performed spectroscopic AC impedance measurements using a Schlumberger 1260 impedancemeter and a 1286 electrochemical interface. AC current with a small amplitude was superposed on DC bias current and applied through the anode to the cathode in the oxygen reduction direction. The AC voltage signal between the cathode and the reference electrode was detected and analyzed by the analyzer. The frequency of the AC signal was swept typically from 0.1Hz to 200kHz for each DC bias current. The amplitude of the AC current was selected so that the amplitude of the AC voltage signal was smaller than 5mV in each sweep. The DC bias current was varied from 0 to 1950mA in the measurements of each temperature.

RESULTS AND DISCUSSIONS

1. Thermal Expansion Coefficient

The compositional dependence on thermal expansion coefficient (TEC) is shown in Fig.3. The thermal expansion coefficient represents values averaged from room temperature up to 800°C or 1000°C. When the value of x in the Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ system is less than 0.2, the TEC is very close to that of YSZ. With increases in x, the TEC increases gradually and passes the value for La$_{0.8}$Sr$_{0.2}$MnO$_3$ at x=0.4. This result
suggests that Pr$_{0.8}$Sr$_{0.2}$MnO$_3$ is a good candidate as a base material for use in forming a cobaltate-manganite solid solution cathode material.

2. Electrical Conductivity

Figure 4 shows the temperature dependence of the electrical conductivity, $\sigma$. When $x$ is between 0 and 0.5, the ln($\sigma$T) vs. 1/T plots are on a straight line for each $x$ value and exhibit a semiconductor-like temperature dependence. This behavior is probably due to hopping conduction.[8] When $x$ exceeds 0.5, a conductivity jump is observed and the temperature dependence becomes saturated. Pr$_{0.8}$Sr$_{0.2}$CoO$_3$ is known to be a metallic conductor. This rapid increase in conductivity at $x$=0.6 may correspond to a transition from semiconductor-like to metallic conduction.

Conductivity at high temperature is important for an SOFC cathode material. The compositional dependence of the conductivity at 800°C is shown in Fig.5. An increase in $x$ causes a decrease in conductivity between $x$=0 and $x$=0.5. However, the conductivity at $x$=0.5 still remains at a high value.

3. Electrode Characteristics

The dependence of current density, $i$, on overpotential, $\eta$, and on temperature, $T$, can be described by the Butler-Volmer formula as follows.

$$i = i_{ex} \left[ \exp \left( \frac{\alpha n F}{R T} \eta \right) - \exp \left( -\frac{(1-\alpha) n F}{R T} \eta \right) \right]$$

Where $i_{ex}$ is the exchange current density and $\alpha$ is the charge transfer coefficient. $R$, $F$ and $n$ indicate the gas constant, Faraday constant and number of electrons transferred in the reaction, respectively.[9,10] The analysis of the impedance measurement results are based on this equation.

3.1 Compositional Dependence of the Interface Resistance. Cole-Cole plots of cells with Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ cathodes at 10mA (about 5.4mA/cm$^2$, near open circuit condition) and 800°C are shown in Fig. 6. Plots at the high frequency limit do not converge with the horizontal axes. This is mainly due to the existence of an inductive factor along the circuit of our setup. The interface resistance, $R_{ct}$, which corresponds to the intercept of a capacitive loop (imaginary part of impedance is negative) increases when $x$ increases from 0 to 1.0. The resistance of the interface normalized by the electrode area, $R_{ct}/S$ is reciprocally proportional to the exchange current density, $i_{ex}$, which is thought to be proportional to the length of the triple phase boundary (TPB) and the oxygen reduction activity. [11,12]

$$i_{ex} = \left( \frac{S}{R_{ct}} \right) \frac{RT}{nF}$$

Values of $i_{ex}$ estimated using this relation are listed in Table I. The oxygen catalytic activity of the cathodes seems to decrease with increases in Co in the Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ system, because the mean diameters of the powder are almost the same, so are the TPBs.
3.2 DC Bias Current Dependence of the Interface Resistance. Figure 8 shows Cole-Cole plots of cells with Pr$_{0.8}$Sr$_{0.2}$Mn$_{0.5}$Co$_{0.5}$O$_3$ cathodes at 800°C. The DC bias current ranges from 0mA to 1900mA. While the capacitive loop shrinks with increases in current, the inductive loop develops and becomes almost the same size as the corresponding capacitive loop. The interface resistance is reduced by the inductive loop.

The potential of the reference electrode can be affected by DC bias current and so can be modulated by the current signal in the low frequency region. This modulation could cause the inductive loop. However such a possibility was ruled out, because inductive loops of the same size appear not only in the reference-cathode measurements but also in the anode-cathode measurements, while they do not appear in the reference-anode measurements shown in Figs. 9 (a), (b).

In Fig.10, the interface resistances are plotted as a function of the DC bias current density of the electrodes at 800°C. The interface resistance should equal the discrepancy between the low and high frequency limits in the real part. However the impedance plots did not completely converge to a point even at very low frequency. Therefore we use the value at 0.1Hz as the steady state (DC) value. The interface resistance order of the three cells changes at about 50mA/cm$^2$. This result suggests that catalytic activity of the cathode containing Co increases with the current density. The interface resistances of the three electrodes have different bias current dependencies. On the basis of the Butler-Volmer formula, this difference can be attributed to the difference in the charge transfer coefficient, α. When η is large, Following Tafel’s relation can approximate the Butler-Volmer formula.[9,11]

$$\ln(i) - \ln(i_{ex}) = \frac{\alpha nF}{RT} \eta$$

We estimated the values of α from Tafel plots. Overpotential, η(i) in Tafel’s equation was obtained by the integration (trapezoidal approximation) of $R_{ct}$ with DC bias current from 0 to the corresponding values. Tafel plots, based on the values of $R_{ct}$ in Fig.10, are shown in Fig.11. We calculated the α values from the gradients of the plots at 150mV. They are listed in Table I. The electrodes containing Co tend to have large values. This could be caused by an electrochemical reaction at the interface between the cathode and the O$_2$ gas as well as at the TPB.[13] The exchange current density, $i_{ex}$, can be obtained by extrapolating formula [3] (ln(i) vs. η ) from 150mV to 0mV(i axes) in Fig.11. These values are also listed in Table I, and agree with the $i_{ex}$ values, obtained from $R_{ct}$ in Fig.6.

3.3 Temperature Dependence of the Interface Resistance. Figure 12 shows the temperature dependence of the Tafel plots of cells with Pr$_{0.8}$Sr$_{0.2}$Mn$_{0.5}$Co$_{0.5}$O$_3$ cathodes tested from 700°C to 850°C. The solid lines indicate the overpotential calculated as in Fig.10. The broken lines represent the overpotential calculated by the same procedure but based on the resistance values corresponding to the intercepts of the capacitive loops. The
difference between the solid and broken lines shows the development of the inductive loops. The increase in the inductive loops begins at almost the same overpotential (around 50mV) from 700°C to 850°C. Arrhenius plots of the current density for Pr0.8Sr0.2Mn1-xCoxO3 cathodes are shown in Fig. 13. Here we used the current densities corresponding to 150mV in the Tafel plots. The activation energy for each cell is calculated from the slope of the plots and is listed in Table I. In spite of the dispersion of the plots, the cathodes containing Co tend to have a lower activation energy and are preferable for reduced temperature operation. The lowest value in our work is 1.4eV, which is still higher than the values of zirconia based electrolytes of about 1eV.[14] This means that loss at the electrode/electrolyte interface becomes crucial for the operation of the SOFC at a reduced temperature of 800°C or below.

3.4 Origin of the Inductive Loop. The inductive loop which appeared in the low frequency region implies that there is another electrode reaction process with a long time constant. Mass transport processes usually appear in the low frequency region. However, the process exhibits a linear increase in the real and imaginary part with a frequency decrease in the capacitive quadrant.[15] Therefore, in the present experiments, the inductive loops can not be explained by the mass transport process. Some processes have been proposed as the origin of the inductive loops in the low frequency region.[13,16] These cases involve intermediate processes on the electrode. In these processes, electrons are transferred to atoms that are adsorbed on the electrode. The overpotential change can cause a change in the fraction of atom coverage on the electrode, and this change in coverage influences the current density with some delay. Because such a step-wise charge transfer model requires fast ion conduction in or on the electrode in order to supply ions (oxygen ions) to the TPB. The ion conduction in LaCoO3 is reported to be much faster than in LaMnO3, and so the step-wise charge transfer model is feasible in our case. The charge transfer coefficient, \( \alpha \), of the Butler-Volmer formula should have a larger value, if the electrode reaction occurs not only at TPB but also on the electrode surface.[13] The electrodes which contain Co have a larger \( \alpha \) value. This fact also agrees with the model which requires a charge transfer reaction on the surface of the electrode as well as at the TPB. With this model the onset of the inductive loop process at a current density or overpotential may be explained as follows; the increase in current or overpotential increases the vacancy concentration of the electrode and enhances the step-wise charge transfer process which exhibits an inductive response to the AC signal.

CONCLUSIONS

The thermal expansion coefficient is not sensitive to the Co content of the Pr0.8Sr0.2Mn1-xCoxO3 system, when x is less than 0.4. The electrical conductivity of the Pr0.8Sr0.2Mn1-xCoxO3 system decreases gradually as x is increased and exhibits a jump at x=0.5. This is the critical point separating semiconductor-like and metallic regions of composition. An increase in Co content in the Pr0.8Sr0.2Mn1-xCoxO3 system causes a decrease in the exchange current density and an increase in the charge transfer coefficient. The lowest activation energy, 1.5eV, was obtained using a cell with a Pr0.8Sr0.2Mn0.5Co0.5O3 cathode. Inductive loops appear in Cole-Cole plots in the low frequency region, and develop with increases in current and x in the Pr0.8Sr0.2Mn1-xCoxO3 system.
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Table I Constants in the Butler-Volmer formula for the Pr_{0.8}Sr_{0.2}Mn_{1-x}Co_{x}O_{3} system at 800°C.

| cathode material         | i_{ex} (mA/cm²) | **i_{ex} (mA/cm²) | α  | ***E_{a} (eV) |
|--------------------------|-----------------|-------------------|----|--------------|
| Pr_{0.8}Sr_{0.2}MnO_{3}  | 42              | 60                | 0.48 | 2.4          |
| Pr_{0.8}Sr_{0.2}Mn_{0.5}Co_{0.5}O_{3} | 26 | 25                | 0.74 | 1.4          |
| Pr_{0.8}Sr_{0.2}Co_{0.5}O_{3} | 20 | 20                | 0.57 | 1.9          |

* i_{ex} calculated from the intercept of the Cole-Cole plots in Fig.6.
** i_{ex} calculated from an extrapolation of the Tafel plots in Fig.11.
*** Activation energies calculated from the Arrhenius plots in Fig.13.
Pt mesh (15mmØ) is used as a current corrector. Figure 1. Cell geometry.

Pr$_{0.8}$Sr$_{0.2}$Co$_x$Mn$_{1-x}$O$_3$

Pt mesh (15mmØ) is used as a current corrector.

Figure 2. Schematic structure of the fuel cell.

1-Electrolyte, 2-counter electrode (Ni-YSZ), 3-working electrode (Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$), 4-reference electrode (Pt), 5-Pt mesh, 6-Pt wire, 7-Pt tube, 8-Pt cap, 9-glass ring sealer, 10-thermocouple.

Figure 3. Compositional dependence on thermal expansion coefficient of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ at 800°C and 1000°C.
Figure 4. Temperature dependence of electrical conductivity of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$.

Figure 5. Compositional dependence of electrical conductivity of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ at 800 °C.
Pr0.8Sr0.2Mn1-xCoxO3 cathodes at 10mA (about 5.4mA/cm²) and 800°C.

Figure 6. Cole-Cole plots of cells with Pr0.8Sr0.2Mn1-xCoxO3 cathodes at 10mA (about 5.4mA/cm²) and 800°C.

Figure 7. Cole-Cole plots of cells with Pr0.8Sr0.2Mn1-xCoxO3 cathodes at 100 mA (about 54mA/cm²) and 800°C.

Figure 8. Cole-Cole plots of a cell with a Pr0.8Sr0.2Mn0.5Co0.5O3 cathode at 800°C. The DC bias current was varied from 0mA to 1900mA.

Figure 9. Cole-Cole plots of a cell with Pr0.8Sr0.2Mn0.5Co0.5O3 cathode at 100mA (about 54mA/cm²) and 800°C. (a) and (b) show anode-reference and cathode-anode responses, respectively. The cathode-reference response is shown in fig. 7 (x=0.5).
Figure 10. Interface resistances of Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ cathodes as a function of the DC bias current density of the electrodes at 800° C.

Figure 11. Tafel plots for the three cells with Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ cathodes. Overpotential values were calculated using the values in fig.10.

Figure 12. Temperature dependence of Tafel plots of a Pr$_{0.8}$Sr$_{0.2}$Mn$_{0.5}$Co$_{0.5}$O$_3$ cathode. For the broken lines the inductive loop contributions are not taken into account.

Figure 13. Arrhenius plots of current density for Pr$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Co$_x$O$_3$ cathodes.