Lattice Relaxation and Electrochemical Performances of Cobalt-Doped Sr$_{0.9}$Ce$_{0.1}$MnO$_{3+δ}$ Composite Cathodes for Intermediate-Temperature Solid Oxide Fuel Cells

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The relaxation mechanism of the octahedral distortion in Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_3$ (SCMCo) as a function of the cobalt content and temperature, and the electrochemical properties of the SCMCo-SDC composite cathodes were investigated. Substituted cobalt ions and manganese ions for Sr, Mn in a mixed valence state consisting of Co$^{3+}$/Co$^{2+}$ and Mn$^{4+}$/Mn$^{3+}$, respectively. The Co K-edges were shifted toward low energy by an increase in the Co content, which indicates that Co$^{3+}$ (0.55 Å) is reduced to Co$^{2+}$ (0.65 Å). The decrease in the difference in ionic radii between B-site elements relieved the octahedral distortion as confirmed by a decrease in the peak intensity in the Fourier transformed EXAFS of the Co K-edge. The lattice volume increased up to 1.4 and 1.9 vol. % with Co content and temperature, respectively. The Co-O bond angle was closer to 180° with an increase in Co content thereby leading to an increase in the oxygen ion conductivity. Therefore, the relaxation of the distortion by substitution of cobalt ions should affect the improvement in the oxygen mobility. The polarization resistances of the SCMCo-SDC composite cathodes at 650 °C were decreased up to four times with an increase in the cobalt content, and the power densities of the single cells (Ni-SDC/SDC/SCMCo-SDC) were also enhanced up to 177% with increasing cobalt content.

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Cerium doped strontium manganite (Sr$_{1-x}$Ce$_x$MnO$_3$, SCM) perovskite oxides have received attention as a cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs) due to its high electrical conductivity and interfacial stability with CeO$_2$-based electrolytes.$^{1,2}$ However, the polarization resistance ($R_p$) can be increased through doping of cerium oxide for structural stability and enhancement of the electrical conductivity.$^4$ The increase in $R_p$ is associated with a decrease in oxygen vacancy concentration and mobility, due to the strong hybridization between the Ce 4f/5d and oxygen 2p orbitals and an increase in the MnO$_6$ structural distortion, respectively.$^5,6$ We have investigated Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_3$ (SCMCo) to enhance the oxygen vacancy concentration and have identified the lower $R_p$ because of the increase in oxygen vacancy, which is a result of the mixed valence state of cobalt ions.$^7$

It is reported that BO$_6$ octahedral distortion can occur in most perovskite oxides (expressed as ABO$_3$) because of formation of oxygen vacancy and difference in ionic radii, which is occurred by temperature and mixed valence state changes of the transition metals.$^{3,8,9}$ Lattice changes attributed by the oxygen vacancy with elevated temperature can affect the conduction path for oxygen vacancies as a geometrical factor.$^{10}$ The difference in the ionic radii induced by the valence change of transition metals in the B-site is also another factor contributing to BO$_6$ distortion. We hypothesize that the difference in the ionic radius between cobalt ions and Mn ion in SCMCo has an effect on the octahedral change of BO$_6$ because cobalt ion has a stronger self-reduction property from Co$^{3+}$ to Co$^{2+}$ relative to other transition metal ions at elevated temperature. Therefore, the conduction properties of oxygen vacancies are a result of Co doping, in terms of the carrier mobility, based on the investigation of the effects of temperature and the valence state of cobalt ions on BO$_6$ octahedral distortion as a main conduction path of oxygen vacancies in a SCMCo system.

In this work, we investigated the mechanism of BO$_6$ lattice changes using Co K-edge XANES and EXAFS data analysis and in-situ structural analysis over an intermediate temperature range for Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_{3+δ}$ (SCMCo, 0.1 ≤ x ≥ 0.3) cathodes and considered the oxygen mobility in terms of lattice changes. The electrochemical performances of Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_{3+δ}$-Sm$_{0.2}$Ce$_{0.8}$O$_2$ (SCMCo-SDC) (x = 0.1–0.3) composite cathodes were also characterized and compared to the conduction properties of the SCMCo cathode.

**Experimental**

**Powder preparation.**—Cathode powders of the Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_3$ compositions (SCMCo, x = 0.1, 0.2, and 0.3) were synthesized via the ethylenediaminetetraacetic (EDTA) citrate complexing process using nitrate solutions containing Sr, Ce, Co, and Mn acetate; the detailed procedure for the synthesis process is given in a preceding paper.$^3$ The synthesized SCMCo powders were mixed at a weight ratio of 1:1 with Sm$_{0.2}$Ce$_{0.8}$O$_2$ powder (SDC, Fuel Cell Materials, USA) and then ball-milled to obtain the composite cathode powder. Table I shows the denotations of the Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_3$ and their composite cathodes according to the Co content.

**Cell preparation.**—Symmetric cells were prepared to investigate the polarization resistance of the series of SCMCo-SDC composite cathodes supported on SDC electrolyte pellets. The SDC electrolyte pellets were sintered at 1400 °C for 10 h for densification. The ground and meshed SCMCo-SDC composite powders were ball-milled and mixed with a binder, prepared from α-terpineol and ethyl-cellulose, to form cathode pastes. The cathode pastes were screen-printed on both sides of the SDC pellets to form symmetric cathode structures with electrode areas of 0.28 cm$^2$. After drying, the symmetric cells were sintered at 1100 °C for 2 h in air to form a porous structure. Subsequently, a Pt current collector was attached to the electrode using Pt paste.

**Table I. Composition and abbreviations of Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_{3+δ}$ and their composite cathodes according to the Co content.**

| Co content | Cathode | Notation |
|------------|---------|----------|
| x          | Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_{3+δ}$ | SCMCo   |
| 10 mol%    | Sr$_{0.9}$Ce$_{0.1}$Mn$_{0.9}$Co$_{0.1}$O$_{3+δ}$ | SCMCo1  |
| 20 mol%    | Sr$_{0.9}$Ce$_{0.1}$Mn$_{0.8}$Co$_{0.2}$O$_{3+δ}$ | SCMCo2  |
| 30 mol%    | Sr$_{0.9}$Ce$_{0.1}$Mn$_{0.7}$Co$_{0.3}$O$_{3+δ}$ | SCMCo3  |
| x          | Sr$_{0.9}$Ce$_{0.1}$Mn$_{1-x}$Co$_x$O$_{3+δ}$ + Sm$_{0.2}$Ce$_{0.8}$O$_2$ | SCMCo-SDC |
| 10 mol%    | Sr$_{0.9}$Ce$_{0.1}$Mn$_{0.9}$Co$_{0.1}$O$_{3+δ}$ + Sm$_{0.2}$Ce$_{0.8}$O$_2$ | SCMCo1-SDC |
| 20 mol%    | Sr$_{0.9}$Ce$_{0.1}$Mn$_{0.8}$Co$_{0.2}$O$_{3+δ}$ + Sm$_{0.2}$Ce$_{0.8}$O$_2$ | SCMCo2-SDC |
| 30 mol%    | Sr$_{0.9}$Ce$_{0.1}$Mn$_{0.7}$Co$_{0.3}$O$_{3+δ}$ + Sm$_{0.2}$Ce$_{0.8}$O$_2$ | SCMCo3-SDC |

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The anode-supported SDC layer (Φ = 25 mm) was prepared using a dry-pressing method. The mixture of NiO-SDC (1:1 weight ratio) was pre-pressed at 200 MPa and was formed into an anode substrate. The SDC powder was uniformly distributed onto the anode substrate, co-pressed at 250 MPa, and subsequently co-sintered at 1400°C for 5 h to obtain an anode supported electrode/electrolyte. The SCMCo-SDC cathode paste was painted on the SDC electrolyte layer, which was then sintered at 1100°C for 2 h in air to form single cells of NiO–SDC/SDC/SCMCo-SDC.

**Characterization.**—A high-temperature X-ray diffraction (HT-XRD) analysis was performed to investigate the phase transition upon heating from 600 to 800°C with an interval of 50°C. The samples were heated at a rate of 10°C/min and were kept at various temperatures for 30 min until the temperature equilibrated. Then, the XRD-patterns were recorded using a step scan procedure (0.02°/20 step, 0.5 s time per step) in the 20 range of 10 to 90°. The Rietveld refinement result was subsequently calculated using the Fullprof software package.

XAS measurements, including the X-ray absorption near edge spectra (XANES) and extended X-ray absorption fine structure (EXAFS), were performed on the 1D beam line in the Pohang Accelerator Laboratory (PLS-II, 3.0 GeV, Korea) using a Si (111) double crystal monochromator. The spectra were measured at room temperature in transmission mode for the Co K-edge under ambient conditions. Energy calibration was performed using a standard cobalt metal foil. To accurately retrieve the XANES spectra, the data were recorded with a step size of 0.2 eV in the edge region. X-ray photoelectron spectroscopy (XPS) was also carried out using an ESCALAB 250 XPS system (Thermo Fisher Scientific) with an Al Kα source (hv = 1486.6 eV).

Impedance measurements were conducted using an IViumStat (IVium, Netherlands) instrument over the frequency range from 10⁶ to 0.01 Hz with a 10 mV excitation voltage at operating temperatures of 600, 700, and 800°C under open circuit conditions in air. The electrochemical impedance spectroscopy (EIS) results were multiplied by 0.5 to account for the two electrodes. The measured impedance data were plotted on the complex plane and fitted to an equivalent circuit using Zview software.

Button cells were tested with humidified hydrogen (∼3% H₂O) as the fuel and air as the oxidant. The flow rates of the fuel and air were controlled at 40 ml/min using a precision flowmeter (APEX). The voltage–current curves were recorded by direct current load (IViumstat, Netherlands) at a scanning rate of 10 mV s⁻¹.

**Results and Discussion**

**Crystal structure.**—Figure 1 shows the XRD patterns of the SCMCo1, SCMCo2, and SCMCo3 powders and their main diffraction patterns.
Table II. Structural parameters of SCMCo sintered at 1350°C after Rietveld refinements as a function of temperature.

| Parameters | SCMCo10 | Room temp. | 600°C | 650°C | 700°C | 750°C | 800°C |
|------------|---------|------------|-------|-------|-------|-------|-------|
| a = b [Å] | 5.402   | 5.448      | 5.452 | 5.466 | 5.469 | 5.477 |
| c [Å]     | 7.639   | 7.704      | 7.712 | 7.734 | 7.734 | 7.718 |
| Volume [Å³] | 223.064 | 228.66     | 229.234 | 230.214 | 231.324 | 231.521 |
| Structure | I4/mmm | I4/mmm | I4/mmm | I4/mmm | I4/mmm | I4/mmm |
| Rwp [%]   | 5.937   | 5.914      | 6.005 | 6.123 | 5.396 | 5.353 |
| Rexp [%]  | 5.224   | 5.609      | 5.094 | 5.088 | 5.085 | 4.141 |
| χ²        | 1.291   | 1.561      | 1.389 | 1.447 | 1.726 | 2.109 |

| Parameters | SCMCo20 | Room temp. | 600°C | 650°C | 700°C | 750°C | 800°C |
|------------|---------|------------|-------|-------|-------|-------|-------|
| a = b [Å] | 5.412   | 5.458      | 5.461 | 5.462 | 5.468 | 5.475 |
| c [Å]     | 7.656   | 7.715      | 7.737 | 7.726 | 7.734 | 7.743 |
| Volume [Å³] | 224.242 | 229.828    | 230.737 | 231.415 | 232.524 | 232.124 |
| Structure | I4/mmm | I4/mmm | I4/mmm | I4/mmm | I4/mmm | I4/mmm |
| Rwp [%]   | 5.874   | 5.961      | 6.707 | 6.616 | 7.942 | 6.874 |
| Rexp [%]  | 6.046   | 5.971      | 5.940 | 5.715 | 7.541 | 6.874 |
| χ²        | 0.943   | 0.996      | 1.274 | 1.765 | 1.840 | 2.415 |

| Parameters | SCMCo30 | Room temp. | 600°C | 650°C | 700°C | 750°C | 800°C |
|------------|---------|------------|-------|-------|-------|-------|-------|
| a = b [Å] | 5.403   | 5.461      | 5.467 | 5.472 | 5.487 | 5.495 |
| c [Å]     | 7.721   | 7.724      | 7.732 | 7.741 | 7.776 | 7.781 |
| Volume [Å³] | 225.395 | 230.349    | 231.094 | 231.787 | 234.113 | 234.947 |
| Structure | I4/mmm | I4/mmm | I4/mmm | I4/mmm | I4/mmm | I4/mmm |
| Rwp [%]   | 6.539   | 5.872      | 6.543 | 6.751 | 7.154 | 6.755 |
| Rexp [%]  | 5.673   | 5.603      | 5.851 | 5.712 | 6.548 | 6.548 |
| χ²        | 1.328   | 1.098      | 1.374 | 1.561 | 1.984 | 2.145 |

Table III. Oxygen atomic position of SCMCo and bonding length/angle of Co-O bond.

| Parameters | SCMCo1 | Room temp. | 700°C | | SCMCo3 | Room temp. | 700°C |
|------------|--------|------------|-------| |        |------------|-------|
| O1 x       | 0      | 0.0014(3)  | 0     | | 0      | 0.0010(4)  | 0     |
| y          | 0      | 0.052(4)   | 0     | | 0      | 0.0078(5)  | 0     |
| z          | 0.26485(2) | 0.25616(2) | 0.25614(3) | | 0.25614(3) | 0.25614(3) | 0.25614(3) |
| O2 x       | 0.27314(2) | 0.26841(5) | 0.27251(6) | | 0.26841(5) | 0.27251(6) | 0.26841(5) |
| y          | 0.7451(1)  | 0.7481(3)  | 0.7515(7)  | | 0.7481(3)  | 0.7515(7)  | 0.7481(3)  |
| z          | 0.0180(1)  | 0.0087(3)  | 0.0074(2)  | | 0.0074(2)  | 0.0074(2)  | 0.0074(2)  |
| Co-O1 (Å)  | 1.4481(1)  | 1.4724(6)  | 1.4494(7)  | | 1.4494(7)  | 1.4794(7)  | 1.4494(7)  |
| Co-O2 (Å)  | 1.4382(4)  | 1.4681(2)  | 1.4414(2)  | | 1.4414(2)  | 1.4721(6)  | 1.4414(2)  |
| Co-O1-Co (°) | 176.1(4)  | 178.9(3)  | 178.1(2)  | | 178.1(2)  | 179.4(8)  | 179.1(7)  |
| Co-O2-Co (°) | 175.4(2)  | 177.4(2)  | 176.7(1)  | | 176.7(1)  | 179.4(8)  | 179.1(7)  |
Figure 2. Normalized (a) X-ray absorption near edge structure (XANES) spectra of Co K-edge and (b) X-ray photoemission spectra (XPS) of Mn L₃-edge for SCMCo and their standard powders.

corresponded that the energy shift toward low energy occurred along with the reduction of cobalt. We confirmed that the low-valence-state cobalt (Co⁺³) concentration was increased by the reduction of cobalt with a high valence state (Co³⁺) in the SCMCo system.

Figure 2b presents Mn L₃-edge X-ray photoemission spectra of SCMCo system with different Co content. Mn ions in this system existed as mixed valence state of Mn⁺⁴ and Mn⁺³. The reduction of Mn⁺⁴ was increased by an increase in Co substitution because a charge neutrality of SCMCo system should be maintained. We, therefore, hypothesize that a distortion of the octahedral structure in the SCMCo system is relieved by decreasing the difference in the ionic radii between Mn ions and Co ions having 6-coordinate Co³⁺ (0.55 Å) and Co⁺³ (0.65 Å) in the B-site.

The relaxation of the distortion could be confirmed by the Co K-edge EXAFS data according to an increase in Co content from Fig. 3. Local atomic structures of Co ions in SCMCo system were similar bond length between cobalt and nearest neighbor atoms. The Co-O, Co-Sr/Ce, and Co-Mn/Co distances were ~1.41 Å, ~2.76 Å, and ~3.25 Å, respectively. No peak shift was associated with the Co content, but a difference in the peak intensity can be clearly seen. Bindu et al. and Shin et al. reported that the peak intensity of the Fourier transfer was decreased by having severe MnO₆ octahedral distortion. Therefore, the increase in the intensity in Fig. 3 suggests the relaxation of the distortion octahedral distortion, which affects the decrease in polarization resistance by increasing the oxygen mobility.

**Chemical stability of SCMCo-SDC composite cathode.**—To achieve higher cathode performance, composite cathodes of SCMCo mixed with Sm-doped CeO₂ (SDC) were prepared, and the XRD patterns of the SCMCo3 and SDC powders and that of the SCMCo3-SDC composite cathode powder heated at 850°C for 100 h are shown in Fig. 4. The diffraction peaks of both SCMCo and SDC are visible in the composite phase, and no evidence of a reaction between the SCMCo and the SDC could be detected in the XRD pattern of the composite. This result suggests good chemical compatibility between SCMCo and the SDC electrolyte, which ensures a larger and more active triple phase boundary (TPB) region where the oxygen reduction reaction can occur without chemical intervention.

**Electrochemical characterization.**—Figure 5 shows the impedance spectra for the SCMCo-SDC cathode sintered at 1100°C for 2 h as a function of temperature. The spectra of SCMCo–SDC composite cathodes were fitted by a nonlinear least squares fitting...
Figure 5. Impedance spectra of the SCMCo-SDC symmetric cell on the SDC electrolyte in air: (a) 650, (b) 750, and (c) 800 °C.

program (Zplot) using the equivalent circuit which consisted of the resistance in series with the inductance (L) and two parallel resistance/constant phase elements (R/Q). R\(_1\), R\(_2\), and R\(_p\) refer to the ohmic, high-frequency and low-frequency resistances, respectively. Table IV presents the detailed resistance values. All samples presented a twofold lower R\(_p\) value than that of the single-phase SCMCo at same temperature. The SCMCo3-SDC composite cathode had the lowest R\(_p\) value among the samples, which was 0.48 Ω cm\(^2\) at 800 °C. The enhanced oxygen ion conductivity of the composite cathodes is attributed to the increase in the TPB region, which is provided by the ion conducting phase.

The decrease in R\(_p\) was mainly attributed to the R\(_2\) value related to the oxygen diffusion at the gas/cathode interface, and surface diffusion of oxygen species. An oxygen diffusion process in the SCMCo system could be enhanced by not only the formation of oxygen vacancy but also the relaxation of lattice distortion discussed above.

Figure 6 shows the Arrhenius plot of the polarization resistance of the SCMCo-SDC composite cathodes as a function of temperature. The activation energy (E\(_a\)) of R\(_p\) was 0.98 eV for the SCMCo1-SDC cathode. For the SCMCo2-SDC and SCMCo3-SDC composite cathodes, the activation energy was 0.73–0.75 eV, which is slightly lower than that of the SCMCo1-SDC cathode. The activation energies were presented as a single slope, which indicates that the same electrode reaction occurred across the measured temperature range for each cathode. The lower E\(_a\) of the composite cathodes relative to that of the SCMCo single cathodes (1.27–1.79 eV) indicates that the oxygen ion conductivity occurs more easily due to an expansion of the TPB region.

**Power density.**—To further evaluate the performance of the SCMCo-SDC as a cathode material, anode-supported fuel cells consisting Ni-SDC and SDC electrolyte were characterized. Fig. 7 shows
the current–voltage curves with different Co content at 650 °C. The
open circuit voltages of all samples were found to be approxi-
mately 0.83 eV. The maximum power densities (P\text{max}) of SCMCo1-
SDC, SCMCo2-SDC, and SCMCo3-SDC were 78.8 mW cm\text{−2},
106.7 mW cm\text{−2}, and 140.1 mW cm\text{−2}, respectively. In the se-
ries, SCMCo3–SDC has the highest values, which corresponds to
the result of Rp. The values are relatively low to compare with current
IT-SOFCs, but better performance can be achieved through further
optimization.

**Conclusions**

Cobalt ions in Sr\textsubscript{0.9}Co\textsubscript{0.1}Mn\textsubscript{1-x}Co\textsubscript{x}O\textsubscript{3-δ} (SCMCo) were in a mixed
valence state consisting of Co\textsuperscript{3+} and Co\textsuperscript{2+}, according to the XANES
analysis of Co K-edge. The Co K-edges and Mn L\textsubscript{3}-edges were shifted
toward low energy with an increase in the Co content, which indicates
that the Co and Mn ion are reduced from Co\textsuperscript{3+} to Co\textsuperscript{2+}. The decrease
in the average ionic radii between B-site elements relieved the oc-
tahedral distortion, as confirmed by a decrease in the peak intensity
in the Fourier transformed EXAFS of Co K-edge. After the Rietveld
refinement for in situ XRD at 600–800 °C, all samples had a perv-
ovskite structure in the I4/mmm space group and the lattice volume
expanded at elevated temperatures due to the oxygen vacancy. The
polarization resistances of the SCMCo-SDC composite cathodes on
the symmetric cell were decreased up to four times with an increase
in the cobalt content at 650 °C, and the power densities of the single
cells (Ni-SDC/SDC/SCMCo-SDC) were also enhanced up to 177%
with increased cobalt content.

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