Structural analysis and electrical conductivity of LapxSrMnxCu0.2O3–δ (0.1 ≤ x ≤ 0.4) for IT-SOFCs

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La1–xSr,Mn0.8Cu0.2O3–δ (LSMCu, 0.1 ≤ x ≤ 0.4) powders were prepared using the EDTA-citrate complexing process. The synthesized LSMCu powders were a pure perovskite phase, whereas the composition with x = 0.4 has two phases. The unit cell volumes decreased with increasing Sr2+ content because substituted Sr ions cause an increase in Mn4+ ions, which has a smaller ionic radius than Mn3+. The electrical conductivity also improved with increasing Sr addition in 0.1 ≤ x ≤ 0.3, revealing a small polaron hopping mechanism. The oxidation state of Mn ions increased with the addition of Sr ions in 0.1 ≤ x ≤ 0.3 but the oxidation state of Cu ions was unchanged in 0.1 ≤ x ≤ 0.3. The addition of Sr ions in the A-site of LSMCu can lead to a contraction of the lattice volume because of the decreased Mn–O bond length and increased Mn4+ ions, which can enhance the electrical conductivity.

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1. Introduction

Solid oxide fuel cells (SOFCs) are eco-friendly energy conversion devices that produce electricity directly from chemical energy via an oxidation reduction reaction (ORR) at high temperatures (T > 800°C). On the other hand, high operation temperatures cause degradation phenomena because of the unfavorable reaction of the adjacent cell components, which reduces the lifetime of the SOFCs. Therefore, the operating temperature needs to be reduced to improve the durability and commercialization of SOFCs. In the intermediate-temperature range between 600 and 800°C, however, lanthanum strontium manganite (La1–xSrMnO3, LSM), which is commonly used as the cathode in SOFCs, does not show satisfactory performance because of the poor kinetics of ORR.1–4)

The cathode performance in intermediate temperatures can be improved by substituting various transition metal ions in the B-site or changing the Sr content in the A-site of perovskite. Kuharuangrong et al. and Wandekar et al. studied manganite-based perovskites as potential cathodes for IT-SOFCs, including Fe, Co, and Ni-doped (La, Sr)MnO3.5–7) Berenov et al. investigated the variation in electrical conductivity of La0.8Sr0.2Cu1–xMnxO3 with the Cu content.5)

Yu and Fung investigated La1–x, Sr,CuO2.5–δ (LSCu) with x = 0.15, 0.2 and 0.3 as a possible cathode for IT-SOFCs. They reported that the LSCu showed excellent electrical properties with more than 20% Sr addition. Among them, a 30% Sr content resulted in the highest conductivity of 2400 S cm−1 in air at 800°C.6) Roosmalen et al. also examined the electrical conductivity depending on the temperature, density and Sr content in La1–x, Sr,MnO1.4–δ (x = 0, 0.15, 0.3, and 0.5), and reported an increase in conductivity with increasing Sr content.7)

Substitution of the A-site leads to a change in the valence state of the B-site, which affects the properties of perovskite-type materials, such as the electrical conductivity. Knowledge of the valence change in the B-site is important when selecting suitable cathode materials for IT-SOFCs. In lanthanum strontium manganese copper oxide (La1–x, Sr,Mn0.8Cu0.2O3–δ, LSMCu), which is a perovskite-type material, the valence change of Mn and Cu ions in the B-site will be affected by charge compensation by the addition of Sr ions to the A-site.

This study examined the effect of the valence change in Mn and Cu ions with various Sr contents on the crystal structure and electrical conductivity of LSMCu, which is a potential cathode material for IT-SOFCs. The EDTA-citrate complexing process (ECCP) was used to prepare the LSMCu at relatively low temperatures. The crystal structure and electrical conductivity at different Sr contents were investigated.

2. Experimental procedure

All the LSMCu (La1–x, Sr,Mn0.8Cu0.2O3–δ, 0.1 ≤ x ≤ 0.4) powders were synthesized using an EDTA-citrate complexing process (ECCP). La(NO3)3·6H2O (Alfa Aesar, ≥99.9%), Sr(NO3)2 (Sigma-Aldrich, ≥99.0%), Mn(CH3COO)2·4H2O (Sigma-Aldrich, ≥99.0%) and Cu(NO3)2·2H2O (Alfa Aesar, ≥98%) precursors were dissolved in deionized water according to the stoichiometry of the composition to prepare a homogeneous mixed metal solution. Subsequently, ethylene-diaminetetraacetic acid (EDTA) powder (Alfa Aesar) was added to a 1N NH4OH solution to prepare a NH3·EDTA buffer solution. The NH3·EDTA and citric acid for chelation were applied to the mixed metal solution, which was called a sol state, in sequence at a total metal ion: EDTA: citric acid mole ratio of 1:1:2. The sol was heated with stirring at 85°C and the pH was adjusted to approximately 6 by adding a 1N NH4OH solution. An opaque viscous gel obtained by continuous stirring and heating was baked to solidify in an oven at 250°C for 4 h. The solidified precursors were then calcined in air at 750°C for 8 h. Figure 1 summarizes the entire synthesis procedures in a flow chart. The calcined powders were pressed into a pellet and bar type sample
under a cold-isostatic pressure (CIP) of 150 MPa after uniaxial pressure. The formed samples were sintered in air at 1250°C to densify the ceramic body.

X-ray diffraction (XRD) of the calcined and sintered powders was performed at room temperature using a step scan procedure (0.005°/2θ step) in the 2θ range from 20 to 80° (X’Pert-Pro MPD PW3040/60, PANalytical). The lattice parameters were refined by Rietveld analysis using the entire pattern refinement module of PANalytical X’Pert HighScore Plus software. The XRD peak shape was fitted to a pseudo-Voight function, and the background was fitted to a fifth-degree polynomial. The morphology of the sintered samples was observed by field emission-scanning electron microscopy/energy dispersive X-ray spectroscopy (FE-SEM/EDS, Hitachi S-4800). The electrical conductivity was measured from a 4-probe DC measurement between 500 and 900°C in air using the bar type samples with Pt wires. The samples that were applied to the 4-probe DC measurements with dimensions of 5 × 3 × 30 mm³ were ground with a cutting tool prior to the electrical measurements. The current supplied by a Keithley 2400 current source was 20 mA and the voltages were measured using an Agilent 34401A digital multimeter. X-ray photoemission spectroscopy (XPS) was carried out using an ESCALAB 250 XPS system (Thermo Fisher Scientific) with an AlKα source (hv = 1486.6 eV).

3. Results and discussion

Figure 2 presents the XRD patterns of the LSM and LSMCu powders (a) calcined at 750°C and (b) sintered at 1250°C for 4h. The XRD patterns after calcination at 750°C [Fig. 2(a)] showed no impurities and only a pure perovskite phase. The LSMCu powders sintered at 1250°C showed single perovskite, but the sample with a composition of x = 0.4 contained a second phase with peaks observed at 32 and 42° 2θ. The limit of the Sr content in the LSM system was reported to be 0.5 mol, but a second phase was observed in the La₁₋ₓSrₓMn₀.₈Cu₀.₂O₃₋₄ system for the sample with x = 0.4. They were identified as strontium copper oxide (SrCuO₂) and copper oxide (Cu₂O).

Table 1 lists the crystal structures and lattice parameters of the sintered powders. All the patterns of the sintered samples were fitted to the R-3c rhombohedral space-group. The lattice volumes decreased with increasing Sr content after sintering at 1250°C for 4h. The perovskite structure has two volume contraction factors of the lattice. One is a size factor. The lattice contraction occurred by the substitution of A-site ions, which have a smaller ionic radius than the ions in the lattice.
The other factor is charge compensation. If the substitution of ions with a similar or larger ionic radius occurs, the lattice volume can decrease due to a decrease in the radius of the B-site ions by oxidation. When Sr\(^{2+}\)(1.18 Å) ions, which have a larger ionic radius than La\(^{3+}\)(1.032 Å) ions, substitute in the LSM system, the oxidation of Mn ions can occur from Mn\(^{3+}\)(0.645 Å) to Mn\(^{4+}\)(0.53 Å). With increasing Sr addition, the lattice contraction occurs over a 0.2 mol Sr content because some of Mn\(^{3+}\) ions located at B-site will change to Mn\(^{4+}\) ions due to the maintenance of charge neutrality.\(^{11}\) Similarly, in the LSMCu system, the charge compensation effect of the transition metal in the B-site could also affect the lattice contraction due to the decreased Mn–O bond length. On the other hand, the lattice contraction at x = 0.4 does not appear to be the only Sr content. The lattice parameters of SrCu\(_2\)O\(_4\) and Cu\(_2\)O are smaller than those of LSMCu.\(^{12}\) Therefore, lattice contraction was affected by Sr addition in 0.1 < x < 0.3, and the decrease in lattice volume at x = 0.4 was affected not only by the Sr content but also by the effect of a second phase.

Figure 3 shows the microstructures of the sintered samples for La\(_{1-x}\)Sr\(_x\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\)(0.1 ≤ x ≤ 0.4) powders sintered at 1250°C. The normal grain growth was observed on the surface of all compositions but the second phases identified at x = 0.4 were formed at the grain boundary. Kuhanangrong reported that the grain size affects the electrical conductivity.\(^{13}\) Therefore, the grain growth affected by an increase in Sr content (up to x = 0.3) has an advantageous effect on the conductivity of LSMCu.

Figures 3(e) and 3(f) show the EDS results of the A and B areas at x = 0.4, respectively. The A area is the part of a grain and the B area is a second phase in the grain boundary. The composition of the second phase according to EDS in Fig. 3(f) was strontium, copper and oxygen, which concur with the XRD data. Figure 4 shows the electrical conductivity (S·cm\(^{-1}\)) of the sample (0.1 ≤ x ≤ 0.4) sintered at 1250°C as a function of the reciprocal absolute temperature. All samples exhibited a linear dependence over a wide range of temperatures. The linear dependence is characteristic of a small polaron hopping mechanism.\(^{13,14}\) The mechanism of the electrical conductivity is polaron hopping by free electrons. Moreover, it was reported that an increase in free electrons contributes to an increase in electrical conductivity in the LSM and LaSrCuO\(_3\) system.\(^{9,10}\) The electrical conductivity depends on the Sr content for 0.1 ≤ x ≤ 0.3, and the composition with x = 0.3 exhibited the

Table 1. Lattice parameters and crystal structures of the La\(_{1-x}\)Sr\(_x\)Mn\(_{0.8}\)Cu\(_{0.2}\)O\(_3\)(0.1 ≤ x ≤ 0.4) powders sintered at 1250°C

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameters (Å)</th>
<th>Structure type</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(<em>{0.8})Sr(</em>{0.2})MnO(_3)</td>
<td>a: 5.5311, c: 13.3733, V: 354.31 Å</td>
<td>Rhombohedral (R-3c)</td>
</tr>
<tr>
<td>La(<em>{0.9})Sr(</em>{0.1})Mn(<em>{0.8})Cu(</em>{0.2})O(_3)</td>
<td>a: 5.5336, c: 13.3560, V: 354.18 Å</td>
<td>Rhombohedral (R-3c)</td>
</tr>
<tr>
<td>La(<em>{0.8})Sr(</em>{0.2})Mn(<em>{0.8})Cu(</em>{0.2})O(_3)</td>
<td>a: 5.5242, c: 13.3481, V: 352.77 Å</td>
<td>Rhombohedral (R-3c)</td>
</tr>
<tr>
<td>La(<em>{0.7})Sr(</em>{0.3})Mn(<em>{0.8})Cu(</em>{0.2})O(_3)</td>
<td>a: 5.4967, c: 13.3321, V: 348.85 Å</td>
<td>Rhombohedral (R-3c)</td>
</tr>
<tr>
<td>La(<em>{0.6})Sr(</em>{0.4})Mn(<em>{0.8})Cu(</em>{0.2})O(_3)</td>
<td>a: 5.4872, c: 13.3525, V: 348.17 Å</td>
<td>Rhombohedral (R-3c)</td>
</tr>
</tbody>
</table>
highest conductivity among the samples, showing a conductivity of 208.4 S·cm⁻¹ at 750°C. This is a suitable value (100 S·cm⁻¹) as a cathode for SOFCs. The electrical conductivity at x = 0.1, 0.2 and 0.4 showed lower conductivity than that of LSM, but the conductivity of all samples increased with increasing temperature. The increasing electrical conductivity with temperature can be explained by a charge compensation effect, which is an oxidation reaction from Mn⁺⁺⁺ to Mn⁺⁺⁺⁺.

The increase in charged carriers affected by a valence change in the transition metal in the B-site can also contribute to the electrical conductivity in the LSMCu system. The activation energy (Eₐ) for hopping in 0.1 x 0.3/Sr was also dependent on the Sr composition with 0.1 x 0.4 warped second phase. Therefore, the high binding energy shift of Cu 2p peak, they did not show a clear binding energy shift for 0.1 x 0.3, and the unit cell volume decreased with the addition of Sr content. The Cu 2p peak, they did not show a clear binding energy shift for 0.1 x 0.3, and the unit cell volume decreased with the addition of Sr content. Consequently, the decreased lattice volume and increased electrical conductivity are linked to the increase in Mn⁺⁺⁺ in the composition, 0.1 x 0.3.

The electrical conductivity increases in proportional to the Sr content because the polaron hopping mechanism occurs easily between the Mn–O–Mn combinations due to an increase in the valence of the transition metal located in the B-site. The Mn 2p core level spectra of La₁₋ₓSrₓMn₀.8Cu₀.2O₃₋₀.₄. All spectra displayed Mn 2p₁/₂ and 2p₃/₂ spin-orbit doublet peaks located at approximately 642 and 653.5 eV, respectively. The oxidation state of Mn could be estimated from the full-width-half-maximum (FWHM) of the Mn 3s peak, but this estimation is difficult to apply to manganese compounds with more than three oxidation states of Mn because the peak intensity of Mn 3s is weaker than that of Mn 2p according to Murray et al. The Mn 2p₁/₂ peak is generally used to determine the mixed oxidation state of Mn with Mn²⁺, Mn³⁺ and Mn⁴⁺. The core level energy of the Mn 2p peak at x = 0.1 was 641.5 eV, which means a mixed valence state of Mn²⁺ and Mn³⁺. Figure 5(a) shows a slightly high binding energy shift in the Mn 2p peak for 0.1 x 0.3. The decrease in the core-level binding energy normally indicates a decrease in the positive charge of the transition metal. Therefore, the high binding energy shift of the Mn 2p peak for 0.1 x 0.3 appears as an increase in Mn⁴⁺ ions. In the composition with x = 0.4, the Mn 2p binding energy shifted to a lower energy, which means a decrease in the concentration of Mn⁴⁺ ions. The reduction of the charge compensation effect by Sr precipitation as a second phase was attributed to the decrease in Mn⁴⁺.

Figure 5(b) shows the Cu 2p peak positions with the Sr content. The Cu 2p₁/₂ peak main peak was observed at approximately 933.8 and 932.6 eV in the sample with 0.1 x 0.3 and x = 0.4, respectively. In addition, a strong satellite peak was observed at approximately 943.6 ± 0.2 eV. Copper oxide containing Cu²⁺ and/or Cu³⁺ has a strong satellite, whereas the oxide with Cu⁺ has no satellite. No change in the Cu 2p binding energy was observed between x = 0.1 and x = 0.3. The low energy binding shift of Cu 2p₁/₂ at x = 0.4 was affected by the second phase because of the increase in Cu⁺ ions in the second phase.

From the XP spectra, the valence change in Mn ions was influenced more by the Sr content than the Cu content. Consequently, the decreased lattice volume and increased electrical conductivity are linked to the increase in Mn⁴⁺ in the composition, 0.1 x 0.3.

4. Conclusion

La₁₋ₓSrₓMn₀.8Cu₀.2O₃₋₀.₄ (0.1 ≤ x ≤ 0.4) powders with a perovskite structure were prepared using an EDTA-citrate complexing process. A perovskite structure was identified with 0.1 ≤ x ≤ 0.3, and the unit cell volume decreased with the addition of Sr ions due to the increase in Mn⁴⁺ ions. The electrical conductivity was also dependent on the Sr composition with 0.1 ≤ x ≤ 0.3 with the composition at x = 0.3 exhibiting the highest value. On the other hand, the change in lattice volume and the decrease in electrical conductivity at x = 0.4 were affected by the second phases in the grain boundary. The Mn 2p peak with 0.1 ≤ x ≤ 0.3 moved to a high binding energy depending on the increase in Sr content, which indicates an increase in Mn⁴⁺ ions. In the case of the Cu 2p peak, they did not show a clear binding energy shift according to the Sr content at 0.1 ≤ x ≤ 0.3. A change in the valence state of Mn ions from Mn²⁺ to Mn⁴⁺ in the range 0.1–0.3 Sr leads to a change in the lattice volume and an increase in electrical conductivity.
The understanding of performance improvement with respect to the oxygen reduction reaction is also important for SOFC cathode application. Further experiments by impedance analysis will be progressed to determine the oxide ionic conductivity for oxygen reduction reaction according to different Sr content.

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