Mn valence state and electrode performance of perovskite-type cathode $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ ($x = 0, 0.2$) for intermediate-temperature solid oxide fuel cells

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Abstract. Cu-free and Cu-doped LSM system, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_{3-\delta}$ ($x = 0, 0.2$), with perovskite structure were prepared using an EDTA combined citrate process and the effects of Cu ion at B-site were investigated. Electrical conductivity and polarization resistance of the Cu-doped LSM were $210 \text{ S}\cdot\text{cm}^{-1}$ at 750°C , and $2.54 \text{ }\Omega\cdot\text{cm}^2$ at 800°C , respectively which were better than those of the Cu-free LSM. This indicated that the electrode performance of LSM was improved by the addition of Cu. The oxidation state of Mn ions increased with addition of Cu. The increase in the oxidation state of Mn ions was due to the formation of Mn^{4+} ions and oxygen vacancies. The addition of Cu ions to LSM systems could lead to enhanced electrode performance for oxygen reduction reactions originating from the change in valence of Mn ions.

Keywords. Cu-doped LSM; electrical conductivity; polarization resistance; valence state; oxygen reduction reaction.

1. Introduction

Lanthanum strontium manganite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ (LSM), is a well known cathode material for solid oxide fuel cells (SOFCs) owing to its thermal and chemical stability and to its high electro-catalytic activity for oxygen reduction reactions (ORR) at high temperatures. When a La^{3+} ion is replaced by a Sr^{2+} ion at an A-site, it leads to a compensating charge transition of Mn^{3+} – Mn^{4+} which can enhance its electrical conductivity (Minh 1993; Roosmalen *et al* 1993; Lee *et al* 1995; Richter *et al* 2009; Sun *et al* 2009; Zhi *et al* 2011). It can be expressed in the Kröger–Vink notation as:

At lower and intermediate temperatures (IT-SOFCs, 600–800 °C), however, LSM does not provide satisfactory performance due to the poor kinetics of electrode reactions.

To improve the intermediate temperature performance of LSM cathodes, doping transition-metal ions into B-site of LSM which can promote the formation of oxygen vacancies has been investigated. Certain doped perovskite oxides with oxygen ionic, electronic or mixed-oxygen ionic and electronic conductivity can be obtained using the strategy of

substitution (Chen *et al* 2003; Kuharungrong *et al* 2004; Wandekar *et al* 2005; Berenov *et al* 2007; Zheng *et al* 2009).

The catalytic activity of perovskite materials is mainly determined by the transition metals at B-site. Therefore, valence and vacancy of the transition metal ions at B-site is important to enhance the catalytic activity. A combination of two different ions at B-site brings about synergistic effects and can also improve the performance of LSM cathode. In particular, a partial substitution of Mn^{3+} by a di- or tri-valent ion at B-site changes the average Mn valence, which is strongly related to the electrical conductivity of LSM cathodes (Tanaka and Misono 2001; Kuharungrong *et al* 2004; Zheng *et al* 2009; Zhang *et al* 2009).

In this study, we investigated doping effect at B-site of a commonly used composition of LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$) with a view to its possible use in IT-SOFCs. Copper ion was selected as a doping element because it has several oxidation states. The most stable Cu ion is Cu^{2+} , but there is also Cu^{3+} state in some perovskite oxides (Berenov *et al* 2007; Kim *et al* 2008). The radius of Cu^{2+} ion is similar to that of Mn^{3+} ion and Mn site can be occupied by Cu. The lattice parameters and crystal structure will be affected due to mismatch in the ionic radii of Mn and Cu ions. Hence, the combination of Mn and Cu ions at B-site will have an effect on the performance of LSM cathode.

In the previous study (Ryu *et al* 2012), we examined effect of the valence change of Cu-doped LSM system with varying

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Sr contents on the crystal structure and electrical conductivity. In this work, we have focused on Cu-doping effect at Mn site in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$. Cu-free ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$, LSM) and Cu-doped LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$, LSMCu) powders were synthesized using an ethylenediamine-tetraacetic acid (EDTA)-combined citrate process (ECCP). The crystal structure, electrical conductivity and polarization resistance were studied. The synergistic effects between Cu and Mn at B-site were also discussed in terms of defect formation.

2. Experimental

2.1 Synthesis of LSM and LSMCu powders

LSM and LSMCu powders were synthesized by an ECCP (Zheng *et al* 2009) using nitrate solution of La, Sr, Mn and Cu. A detailed description of the synthesis process is given in Ryu *et al* (2012). The chemical composition of the powders calcined at 750 °C for 12 h in air was analysed by inductively coupled plasma atomic emission spectrometry (ICP–AES, PERKIN–ELMER Optima 4300). The calcined powders were pressed uniaxially into green bars under a hydraulic pressure of 20 MPa. The green bars were then sintered at 1250 °C for 4 h and some of the sintered body was ground to obtain the sintered powders.

2.2 Characterization

Powder X-ray diffraction (XRD, PANalytical X'Pert-Pro MPD PW3040/60) of the sintered powders was performed at room temperature using a step scan procedure ($0.02^\circ/2\theta$ step, time per step 0.5 s) over a 2θ range of $10\text{--}90^\circ$. A Rietveld analysis program, MAUD (Lutterotti *et al* 1999) was applied for structural analysis using the full-profile fitting method. XRD peak shape was fitted to a pseudo-Voigt function and the background was fitted to a fourth-degree polynomial.

Electrical conductivity (σ) was measured using a 4-probe d.c. technique at temperatures between 400 and 900 °C in air using Pt wires. The sintered bars with approximate dimensions of $5 \times 3 \times 30 \text{ mm}^3$ were polished prior to electrical measurement. The current, 0.1–20 mA, was supplied by a Keithley 2400 current source and the voltages were measured using an Agilent 34401A digital multimeter.

The electrode polarization resistance (R_p) of the symmetrical cells of LSM and LSMCu cathodes was determined by a.c. impedance spectroscopy. For impedance analysis, dense discs of 8YSZ (8 mol% Y doped ZrO_2 , Fuelcell materials, 25 mm diameter and 300 μm thick) were used as an electrolyte. The cathode powder was mixed with a binder prepared from α -terpineol and ethylcellulose and the cathode with an area of 0.36 cm^2 was screen-printed on both sides of the YSZ disc. After drying, the cathodes were sintered at 1250 °C for 2 h in air. Pt meshes with Pt wires were attached to each electrode. Impedance measurements were carried

out using an IviumStat (Ivium) over the frequency range, $10^6\text{--}0.01 \text{ Hz}$, at an excitation voltage of 10 mV at 750–800 °C in air. R_p was determined from the difference between the high- and low-frequency intercept on the impedance spectra.

The near edge X-ray absorption fine structure (NEXAFS) was determined at 10D-XAS KIST beam line of PLS (Pohang light source), operating at 2.5 GeV with a maximum storage current of 200 mA. Prior to NEXAFS measurement, the powder samples were pelletized without any binder and positioned at the beam spot in the vacuum chamber holding at 5×10^{-6} torr. NEXAFS spectra were recorded at the oxygen K -edge (520–600 eV) and Mn $L_{2,3}$ -edges (520–600 eV), respectively.

3. Results and discussion

XRD patterns of LSM and LSMCu powders after the sintering process (1250 °C for 4 h) are shown in figure 1. After the powders were sintered, they had a single phase and all peak positions were indexed to $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (JCPDS 53-0058). All the observed patterns matched well with that of a rhombohedral space group (No. 167). The refined lattice parameters for the sintered powders are also shown in the inset of figure 1. The lattice parameters and the unit cell volumes decreased with the addition of Cu. Figures 2(a and b) indicates final Rietveld plots for LSM and LSMCu, respectively. The reliability factor indicated a good fit between experimental and calculated XRD patterns (goodness-of-fit 1.53 for LSM and 1.82 for LSMCu).

A difference in the ionic radius of Mn and doping ions can affect the lattice parameters and the crystal structure. Thus, Cu doping will change $\text{Mn}^{3+}\text{--Mn}^{4+}$ ratio and the exchange

Figure 1. X-ray diffraction patterns of LSM and LSMCu. Refined lattice parameters for powders are also shown in inset of figure 1.

Figure 2. Refined profile of (a) LSM and (b) LSMCu. In figures 2(a) and (b), the solid line is calculated intensity and the plus is observed intensity (background was not subtracted). Short vertical lines show possible Bragg reflections. Bottom corresponds to difference between observed and calculated intensities.

interaction of Mn–Mn. The most stable state of Cu is Cu^{2+} and the radius of Cu^{2+} (6-coordinated) is about 0.73 Å. This is much larger than the radius of Mn^{3+} (0.645 Å) and Mn^{4+}

(0.53 Å) (Shannon 1976). B-site doping with Cu^{2+} will lead to an expansion of the unit cell rather than a contraction. Cu^{3+} state with a radius of 0.54 Å can exist in certain solids

and especially perovskite structures, but they can only exist at high oxygen partial pressures and low temperature. Therefore, the incorporation of Cu^{2+} in room-temperature air will drive an increase in the valence of Mn, thus accounting for the contraction of the unit cell (Ryu *et al* 2012). The contractions of the unit cell volume with the addition of Cu suggested that Cu doping changed Mn^{3+} ion to Mn^{4+} ion. An increase in the concentration of Mn^{4+} ions leads to a contraction of the unit cell volume. This can be expressed by the following defect reaction (Berenov *et al* 2007).

Figure 3 shows electrical conductivity as a function of temperature obtained from the sintered body with Pt wire. LSMCu exhibited electrical conductivity $>210 \text{ S}\cdot\text{cm}^{-1}$ at 750°C , which reaches an IT-SOFC applicable conductivity level ($>100 \text{ S}\cdot\text{cm}^{-1}$). LSM was $150 \text{ S}\cdot\text{cm}^{-1}$ at 750°C and lower than that of LSMCu. Arrhenius plot of both compositions showed a linear dependence over the entire temperature range studied and a characteristic of small polaron-hopping transport mechanism which occurs in perovskite along the transition metal-oxygen-transition metal chains (Roosmalen *et al* 1993; Mizusaki *et al* 2000). The activation energy calculated from the slopes varied from 0.087 to 0.098 eV and the activation energy (0.098 eV) of LSM was consistent with the value of 0.09 eV reported by Tietz *et al* (2006).

One reason for an increase in the conductivity might be that the substitution of Cu^{2+} for Mn was compensated electronically by the oxidation of Mn^{3+} – Mn^{4+} . An increase in the number of Mn^{3+} – Mn^{4+} couples would lead to an increased amount of available hopping sites. The greater the number of available hopping sites, higher the conductivity

Figure 3. Electrical conductivity of LSM and LSMCu as a function of temperature.

values expected. Thus, the mixed Mn^{3+} – Mn^{4+} could explain the enhanced electronic conductivity. The theoretical maximum conductivity in LSM is expected for 50 mol% Sr substitution for La-site cation. This would result in a maximum Mn^{3+} – Mn^{4+} ratio of 1:1, if only electronic compensation is assumed (Richter *et al* 2009). In our study, A-site (or La-site) and B-site (or Mn-site) were substituted with 20 mol% Sr and 20 mol% Cu, respectively. Thus, the ratio of Mn^{3+} – Mn^{4+} is not 1:1 thus indicating a Mn^{3+} rich state in LSMCu. This means that Mn^{3+} – Mn^{4+} couples increased despite the decrease in Mn^{3+} concentration.

Figure 4 shows electrochemical impedance spectra (EIS) of the symmetrical cells measured under open circuit condition at (a) 750°C and (b) 800°C in air for LSM and LSMCu cathodes. The difference between the intercepts of the low and high frequency parts of the spectra, with the real axis of the Nyquist plots, has been used to determine the polarization resistance (R_p). R_p was $20.24 \Omega\cdot\text{cm}^2$ and $6.25 \Omega\cdot\text{cm}^2$ at 750°C for LSM and LSMCu, respectively. R_p diminished as the temperature was raised. LSMCu exhibited much less polarization resistance ($2.54 \Omega\cdot\text{cm}^2$) than that ($6.99 \Omega\cdot\text{cm}^2$) of LSM at 800°C . This suggests that the electrode performance of LSM improves with the addition of Cu.

Figure 4. Impedance spectra of LSM and LSMCu symmetric cell obtained in air: (a) 750°C and (b) 800°C .

In order to investigate the detailed electronic structure, we obtained near edge X-ray absorption fine structure (NEXAFS) spectra for Mn $L_{2,3}$ and O K edges. Figure 5(a) represents Mn $L_{2,3}$ edge spectra of the samples and of Mn_2O_3 as the reference material containing solely Mn^{3+} . $L_{2,3}$ edge spectra of Mn reflect the transitions to the unoccupied $3d$ orbitals and the specific oxidation states. For LSM, Mn $L_{2,3}$ peaks were found at 643.2 and 653.8 eV and for LSMCu, the peaks were at 643.4 and 654.1 eV. The peaks of both compositions were shifted to a higher energy compared with that of Mn_2O_3 reference. Thus, we were able to presume a mixed valence state of Mn^{3+} – Mn^{4+} for LSM and LSMCu systems. Saitoh *et al* (1995) reported a shift to higher photon energies of both L_3 and L_2 absorption edges with increasing Sr concentration in a LaMnO_3 system. This chemical shift was due to higher Mn $2p$ core level binding energies resulting from a decrease in the number of Mn $3d$ electrons. Similarly, we observed a shift of $L_{2,3}$ main peaks to higher energies with the addition of Cu. Usually, $L_{2,3}$ edge positions would shift to higher energy with increased valence, which indicates the

presence of Mn^{4+} ions (Gilbert *et al* 2003). Therefore, the shift in Mn $L_{2,3}$ -edges with the addition of Cu suggested that Cu doping has an effect on the increasing Mn^{4+} ions in LSM system.

O K -edge spectra of LSM and LSMCu systems, as shown in figure 5(b), are composed of three distinct peaks. A pre-edge region is associated with covalent mixing of O $2p$ and Mn $3d$ unoccupied states (528–532 eV) and an intense asymmetric peak is due to both hybridized O $2p$ –La $5d$ and O $2p$ –Sr $4d$ unoccupied states (532–538 eV). The first peak of O K -edge was less intense in LSMCu than that of LSM. The decrease of the first peak corresponds to greater filling of the Mn $3d$ orbital, which indicates a change in Mn–O environment or less oxygen in the coordination shell of Mn. In the case of our LSMCu system, this was explained by the presence of oxygen vacancies, which can affect the electrode performance of ORR.

The additional Mn^{4+} promotes the formation of surface oxygen vacancies when Mn^{4+} is converted to Mn^{3+} at relatively high temperatures (above 600 °C) according to the following reaction (Zhi *et al* 2011):

A greater abundance of Mn^{4+} cations is beneficial for the generation of more oxygen vacancies and the presence of surface oxygen vacancies promotes ORR. The relatively easy valence change performed by the manganese ions provides the basis for the greater electronic conductivity due to the small polaron hopping mechanism. The addition of Cu^{2+} ions increases the total conductivity due to an increase of the percolating Mn^{3+} – Mn^{4+} couples. A partial oxidation of Mn^{3+} – Mn^{4+} with simultaneous generation of oxygen vacancies can lead to enhanced oxygen ion transport, making it suitable as a cathode for IT–SOFC applications.

Figure 5. (a) Manganese L edge and (b) oxygen K edge X-ray absorption spectra of samples. Highlighted hybridized Mn $3d$ -O $2p$ pre-peak region (dashed line) is shown.

4. Conclusions

The perovskite-type structure of LSM and LSMCu was synthesized using an ECCP. A single-phase perovskite structure was identified at both compositions and the unit cell volume decreased with the addition of Cu ion. LSMCu exhibited an enhanced electrical conductivity ($210 \text{ S}\cdot\text{cm}^{-1}$ at 750 °C) and the value was higher than that of LSM ($150 \text{ S}\cdot\text{cm}^{-1}$ at 750 °C). LSMCu exhibited much less polarization resistance ($2.54 \Omega\cdot\text{cm}^2$) than that of LSM ($6.99 \Omega\cdot\text{cm}^2$) at 800 °C. This suggests that LSM electrode performance improves with the addition of Cu. NEXAFS analysis showed that oxidation state of Mn ions increased with the addition of Cu ion. We suspect that the enhanced electrical conductivity was due to an increase of Mn^{3+} – Mn^{4+} couples and the formation of oxygen vacancies. These changes will promote the oxygen ion transport by making it suitable as a cathode for IT–SOFC applications.

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