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Polarization resistance and composite cathode of Ce doped $SrMnO_3$ system for intermediate temperature solid oxide fuel cells

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ABSTRACT

$Sr_{1-x}Ce_xMnO_3$ (SCM, x = 0.1, 0.2, 0.3) materials synthesized through the EDTA citrate complexing process show a single perovskite structure, and the refined lattice volume increases with the concentration of Ce ions. An increase in the Mn^{3+} concentration with increasing Ce doping was confirmed by Mn $L_{3,2}$-edge analysis, and we observe an expansion of the lattice volume due to the larger ionic radii of Mn^{3+}, as compared to that of Mn^{4+}. The change in the O *K*-edge caused by increasing Ce content presented an increase in the binding force of the oxygen ions. We hypothesize that the decrease in oxygen vacancy concentration caused by the increase in the oxygen binding force impedes the oxygen ion transfer process, which causes an increase in the polarization resistance (R_p) with the increasing concentration of Ce ions in the SCM system. The R_p value of $Sr_{1-x}Ce_xMnO_3/Sm_{0.2}Ce_{0.8}O_2$ (SCM/SDC) composite cathodes was lower than that of pure SCM cathodes at the measured temperature, especially the R_p value of SCM10/SDC (0.88 cm^2 at 800 °C), which is about seven times lower than that of SCM10 at the same temperature.

1. Introduction

Ce-doped $SrMnO_3$ ($Sr_{1-x}Ce_xMnO_3$, SCM) with a perovskite structure has received attention as a cathode material that is capable of operating at intermediate temperatures. Hashimoto et al. have demonstrated that the partial substitution of Ce ions for Sr stabilizes the perovskite structure down to room temperature, and SCM is a potentially attractive cathode material due to its good electrical conductivity (~300 S cm^{-1} for $Sr_{0.7}Ce_{0.3}MnO_3$ at 800 °C) [1,2].

In our previous study of $Sr_{1-x}Ce_xMnO_3$, we investigated the structural and electrochemical properties as a function of the Ce content [3]. We observed an increase in electrical conductivity with increasing Ce content, a finding that is in good agreement with that noted in Hashimoto's study. However, the polarization resistance (R_p), which is determined in part by the oxygen ion transfer, increased with increasing Ce content. We reasoned that the generally high R_p values of the SCM cathodes could be attributed to the small number of triple-phase boundary reaction sites, which were limited to the contact between the cathode and the electrolyte layer. Meanwhile, we hypothesized that R_p increases with Ce content because of further reductions in the oxygen ion transfer.

In this work, we focus on the change in the crystal structure and polarization resistance in the SCM system as a function of the Ce content by means of an electronic structure analysis of manganese and oxygen. This analysis, which provides information on the oxygen vacancy concentration and oxygen bonding structure, enables further insight into the reasons for the increase in R_p with increasing Ce content in the SCM system. To mitigate the high R_p values associated with the SCM system, we then develop and characterize the electrochemical properties of composite cathodes that consist of SCM with samarium-doped ceria (SDC), which show greatly decreased R_p values, as compared to their pure SCM counterparts.

2. Experimental procedure

2.1. Powder preparation

Powders of the three $Sr_{1-x}Ce_xMnO_3$ compositions (SCM, x = 0.1, 0.2, 0.3) were synthesized by the ethylenediaminetetraacetic (EDTA) citrate complexing process using nitrate solutions containing Sr, Ce, and Mn acetate; the detailed procedure for synthesis process is given in a preceding paper [3]. The synthesized SCM powders were mixed in a weight ratio of 1:1 with $Sm_{0.2}Ce_{0.8}O_2$ powder (SDC, Fuel Cell Materials, USA) and ball-milled to obtain the composite cathode powder. To investigate the reactivity of the two-phase mixture, the SCM30/SDC composite powder was annealed at 850 °C for 100 h. Table 1 shows

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Table 1
Composition and abbreviation of $Sr_{1-x}Ce_xMnO_3$ and their composite cathodes according to the Ce content.

Ce content	Phase	Denotation
x = 0.1	$Sr_{0.9}Ce_{0.1}MnO_3$	SCM10
x = 0.2	$Sr_{0.8}Ce_{0.2}MnO_3$	SCM20
x = 0.3	$Sr_{0.7}Ce_{0.3}MnO_3$	SCM30
x = 0.1	$Sr_{0.9}Ce_{0.1}MnO_3$ + SDC	SCM10/SDC
x = 0.2	$Sr_{0.8}Ce_{0.2}MnO_3$ + SDC	SCM20/SDC
x = 0.3	$Sr_{0.7}Ce_{0.3}MnO_3$ + SDC	SCM30/SDC

the denotations of the $Sr_{1-x}Ce_xMnO_3$ composite cathodes according to the Ce content.

2.2. Cell preparation

Symmetric cells were prepared to investigate the electrochemical properties of the SCM10/SDC, SCM20/SDC, and SCM30/SDC composite cathodes supported on SDC electrolyte pellets. The 15 mm diameter and 1.5 mm thick SDC electrolyte pellets were sintered at 1500 °C for 10 h. The SCM/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 brushed on to both sides of the SDC pellets to form symmetric cathode structures with electrode areas of 0.49 cm^2. After drying, the symmetric cells were sintered at 1050 °C for 2 h in air, resulting in porous structure consisting of partially sintered, 1–3 μm sized particle. After sintering, Pt-paste current-collectors were applied on both sides and Pt-mesh connected with Pt-wires was attached to each electrode.

2.3. Characterization

X-ray diffraction patterns of the sintered powders were recorded at room temperature using a step scan procedure (0.02°/2θ step, 0.5 s time per step) in the 2θ range of 10–150° (Ultima IV, Rigaku). Rietveld refinement, based on the X-ray diffraction patterns, was calculated using the FullProf software package. In the final run stage, the following parameters were refined: five background coefficients, scale factors, and unit cell parameters. Site occupancies were fixed according to the results of the chemical analysis.

An XAS analysis was performed on the 10D-XAS KIST beam line of the Pohang accelerator laboratory (PAL, Korea) operated at 2.5 GeV with a maximum storage current of 200 mA. The powder samples were loaded on an indium metal tape since the commonly used carbon tape support can affect the O *K*-edge spectrum. All spectra were collected in total-electron yield (TEY) mode. The measurements were performed at room temperature (RT) under a base pressure less than 3×10^{-10} Torr, and a resolution of 0.01 eV. XAS spectra were recorded for the O *K*-edge (520–580 eV) and the Mn $L_{3,2}$-edge (630–665 eV), respectively.

Impedance measurements were carried out using an IviumStat (Ivium, Netherlands) instrument over the frequency range from 10^6 to 0.01 Hz with a 10 mV excitation voltage at operating temperatures of 600, 700, and 800 °C in air. The impedance measurements were acquired under an open circuit condition. The electrochemical impedance spectra (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.

Fig. 1. Equivalent circuit model for fitting the impedance spectra of the SCM–SDC composite cathodes.

The equivalent circuit consisted of the resistance in series with the inductance (L) and two parallel resistance/constant phase elements (R/Q) in series with one another as shown in Fig. 1. R_1, R_2, and R_Ω refer to the high- and low-frequency resistances and the ohmic resistance, respectively.

3. Results and discussion

3.1. Crystal structure

Fig. 2 shows the XRD spectra and results of Rietveld refinements of the SCM10, SCM20, and SCM30 powders sintered at 1450 °C for 4 h. The refined lattice parameters and their reliability factors are presented in Table 2. The perovskite characteristic peaks were well identified in all samples, which showed the I4/mmm tetragonal space group. It is reported that the change of lattice volume in doped perovskite systems can be ascribed to the change of ionic radius of the transition metal cation due to charge compensation effects induced by the doping element [4,5]. We hypothesize that partial reduction of the Mn^{4+} ions to Mn^{3+} occurs upon doping Ce into $SrMnO_3$, resulting in the observed lattice expansion. This is consistent with the contention of Sundaresan et al. [6] that the reduction of Mn ions from Mn^{4+} (0.53 Å) to Mn^{3+} (0.645 Å) can occur when Ce^{3+} ions, having a higher oxidation state than Sr^{2+} ions, are substituted into $SrMnO_3$. To further understand the valence change according to the Ce content, we investigated the reduction of Mn^{4+} ions to Mn^{3+} ions by means of an X-ray absorption spectroscopy (XAS) analysis of the Mn $L_{3,2}$-edge.

3.2. X-ray absorption spectroscopy

Fig. 3 shows the Mn $L_{3,2}$-edge spectra of SCM powders and reference standards of manganese oxides (Mn_2O_3 and MnO_2) to investigate how the Mn valence state is affected by the addition of Ce ions. The spin–orbit interaction of the Mn 2p core hole splits the spectrum into two multiplets (L_3 and L_2 edge), reflecting the oxidation state of the Mn ions.

The Mn L_3 peak positions were detected at 644.4 eV for SCM10, at 644.2 eV for SCM20, and at 644.1 eV for SCM30. Thus, the SCM spectra shifted slightly toward the Mn_2O_3 reference (lower energy) with an increase in the Ce content. The 3d transition metals exhibit a valence-specific multiplet structure and chemical shift toward lower energy with a decreasing oxidization state [7]. Therefore, the shift in the Mn $L_{3,2}$-edge with the addition of Ce suggests that Ce doping leads to an increase in Mn^{3+} in the SCM system. As the Mn^{3+} ions (0.645 Å) possess larger ionic radii than Mn^{4+} ions (0.53 Å), this would cause the lattice volume expansion of Ce-doped $SrMnO_3$.

We also analyzed the O *K*-edge of SCM10, SCM20, and SCM30 in an effort to probe the reasons underlying the increasing polarization resistance with increasing Ce content in the SCM system through the analysis of oxygen vacancy and bonding structure. The normalized X-ray absorption spectra in the region of the O *K*-edge for each SCM composition and the difference spectra obtained after subtracting the spectrum of SCM10 are shown in Fig. 4(a) and (b), respectively. The O *K*-edge spectra correspond to transitions from the O 1s to the unoccupied O 2p states in the conduction band [8]. The feature around 528–534 eV is attributed to the hybridization of the O 2p and unoccupied 3d states of the Mn ions [8–10].

The pre-edge peaks are located at 530.1, 530.2, and 530.3 eV for SCM10, SCM20, and SCM30, respectively. Asokan et al. reported a chemical shift toward higher energy due to an increase in the negative charge on the oxygen ions in Ca-doped $LaMnO_3$ system [9]. For the Ce-doped $SrMnO_3$ system in this study, we can similarly explain the peak shift as caused by an increase in the negative charge on the oxygen, which would lead to an increase in the oxygen binding energy.

The enhancement of the spectra at 535 eV with an increase in the Ce content can be clearly seen in the difference spectra as calculated by subtracting the spectrum of SCM10 from the spectra for SCM 20 and