



Electrochemical properties of $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ ($0.1 \leq x \leq 0.4$) – GDC composite cathodes for IT-SOFCs

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Abstract

The electrochemical properties of $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ (SCM, $0.1 \leq x \leq 0.4$)– $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-x}$ (GDC) composite cathodes were determined by impedance spectroscopy. The study focused on the doping effect of Ce in the composite cathodes. Single-phase perovskite was obtained for $0.1 \leq x \leq 0.3$ in SCM. No reaction occurred between the $\text{Sr}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ electrode and the GDC electrolyte at an operating temperature of 800 °C for 100 h. In the single phase perovskite region, lattice expansion occurred due to the reduction of Mn^{4+} to Mn^{3+} at B-sites, and this was attributed to an increase in Ce content. Ce doping enhanced the electrode performance of SCM–GDC composite cathodes, and best electrode performance was achieved for the $\text{Sr}_{0.7}\text{Ce}_{0.3}\text{MnO}_3$ –GDC composite cathode ($0.93 \Omega \text{ cm}^2$ and $0.47 \Omega \text{ cm}^2$ at 750 °C and 800 °C, respectively). The improvement in electrode performance was attributed to increases in charge carriers induced by a shift of some Mn from +4 to +3 and to the formation of surface oxygen vacancies caused by Mn^{4+} to Mn^{3+} conversion at high temperatures.

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1. Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices with high energy conversion efficiencies and power densities. Many attempts have been made to develop intermediate-temperature SOFCs (IT-SOFCs) that are capable of operating at 600–800 °C to expand the commercial applications of such devices. However, reducing the operation temperature decreases cathode catalytic activity with respect to the oxygen reduction reaction (ORR). At these lower temperatures, new highly catalytic active cathodes must replace traditional cathodes, such as, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM)-based materials [1–3].

Considerable efforts are being made to develop cathode materials with mixed ionic and electronic conductivity for IT-SOFCs. Among these new cathode materials, $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$

(SCM) is a promising candidate. The partial substitution of Ce at Sr-sites can stabilize the perovskite structure down to room temperature. Hashimoto et al. reported that SCM exhibits higher conductivity (270 Scm^{-1} at 800 °C) than $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM, about 175 Scm^{-1}). Furthermore, its thermal expansion coefficient is similar to that of CeO_2 -based electrolytes, and its chemical compatibility with the electrolytes is good. However, $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ does not show sufficient catalytic activity in a cell test [4–10].

In order to improve the performance of cathodes at lower operating temperatures, a number of investigators have considered composite cathodes, which are composed of mixtures of an electrode and a second ionically conducting phase. A composite cathode can increase the length of three-phase boundaries (TPBs) where gas, electrolyte, and electrode are in contact. Furthermore, the area-specific resistance (ASR) of a composite cathode is decreased by increasing the number of TPBs, and this, results in a considerable lowering of the

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over-potential required for oxygen reduction, as compared to a single phase cathode [11,12].

In the current study, a composite cathode of $\text{Sr}_{1-x}\text{Ce}_x\text{MnO}_3$ (SCM, $0.1 \leq x \leq 0.4$)– $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$ (GDC) was designed as a candidate cathode material. The electrochemical properties of this composite cathode were investigated in an intermediate-temperature range (650–800 °C). SCM powders with different Ce contents were synthesized using a modified the sol–gel method and structural changes were investigated by Rietveld refinement. Composite cathodes were made by mixing SCM with GDC electrolyte, and the electrochemical properties of these composite cathodes were determined at high temperatures using impedance measurements. The Ce doping effect at A-sites and the valence change of B-site ions are discussed.

2. Experimental procedure

2.1. Synthesis of SCM powders

All SCM ($\text{Sr}_{1-x}\text{Sr}_x\text{MnO}_3$, $0.1 \leq x \leq 0.4$) powders were synthesized using an EDTA combined citrate process (ECCP). The calculated amounts of $\text{Sr}(\text{NO}_3)_2$ (Sigma-Aldrich, $\geq 99\%$), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, $\geq 99.5\%$), and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99\%$) metal precursors were dissolved in distilled water. An NH_3 -EDTA buffer solution was prepared by mixing ethylenediaminetetraacetic acid powder (EDTA, Alfa Aesar) in a 1 N NH_4OH solution. NH_3 -EDTA and citric acid (Samchun Chemical, $\geq 99.5\%$) were added to the metal precursor solution in sequence at a mole ratio of total metal ions: EDTA: citric acid of 1:1:1.5. The solution was then heated at 80 °C with continuous stirring, and NH_3OH was added to adjust the pH ~ 8 . A brown opaque viscous gel was obtained after this heating and stirring process. The gel was solidified by firing in an oven at 1000 °C for 4 h. The solidified precursors were then calcined at 1450 °C for 4 h to produce a perovskite structure.

To investigate the reactivity against an electrolyte material, the SCM30 and $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_2$ (GDC, Fuelcell Materials, USA) powders were mixed and ball-milled at a weight ratio of 1:1, pressed into pellet and then annealed at 800 °C for 100 h. Table 1 provides the composition and names of the four materials produced.

2.2. Characterization

Powder x-ray diffraction patterns of the calcined powders were obtained at room temperature using a step scan procedure ($0.01^\circ/2\theta$ step, time per step 0.5 s) in the 2θ range 10 – 90°

Table 1
Compositions and names of the materials used in the current study.

Composition	Label
$\text{Sr}_{0.9}\text{Ce}_{0.1}\text{MnO}_3 + \text{GDC}$	SCM10-GDC
$\text{Sr}_{0.8}\text{Ce}_{0.2}\text{MnO}_3 + \text{GDC}$	SCM20-GDC
$\text{Sr}_{0.7}\text{Ce}_{0.3}\text{MnO}_3 + \text{GDC}$	SCM30-GDC
$\text{Sr}_{0.6}\text{Ce}_{0.4}\text{MnO}_3 + \text{GDC}$	SCM40-GDC

(Rigaku Ultima-IV using $\text{Cu K}\alpha$ radiation, Rigaku). Lattice parameters were evaluated using the whole pattern refinement module in PANalytical X-Pert Plus software, in which the lattice parameter was refined to the optimum fit to the entire diffraction pattern. XRD peak shapes were fitted to a pseudo-Voigt function, and the background was fitted to a fifth-degree polynomial.

Symmetric cells were prepared to study the electrochemical properties of SCM-GDC composite cathodes on GDC electrolytes. The GDC powder was pressed into pellets and then sintered at 1500 °C for 10 h. The GDC pellet was 15 mm in diameter and 1.5 mm thick. The compositions of the composite cathodes were fixed at a SCM to GDC weight ratio of 1:1. The composite powders were ball-milled and mixed with a binder prepared from α -terpineol and ethyl-cellulose, and pastes were then screen-printed on GDC pellets (area 0.49 cm^2). After drying, the cells were sintered at 1200 °C for 2 h in air. Pt-paste current-collectors were applied to both sides of the cells, and a Pt-mesh connected to Pt-wires was attached to each electrode. AC impedance measurements were carried out using an IviumStat (Ivium, The Netherlands) over the frequency range 10^6 to 0.1 Hz using a 10 mV excitation voltage at operating temperatures from 650 to 800 °C at intervals of 50 °C in air. ASR values were calculated from differences between the high- and low-frequency intercepts on impedance spectra. Fractured cross-sectional images of tested samples were observed by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

3. Results and discussion

Fig. 1 shows the XRD patterns of SCM powders synthesized by ECCP after calcination at 1450 °C for 4 h. A single perovskite structure was identified for samples with $0.1 \leq x \leq 0.3$. The powders showed peaks characteristic of the $I4/mcm$ tetragonal space group. The ECCP successfully introduced dopant atoms into the samples with $0.1 \leq x \leq 0.3$ without impacting the perovskite structure. It has been reported that the ECCP method allows the homogeneous mixing of metal ions at the molecular level, which leads to faster reaction rates and low energy requirements [13,14]. In the current study, the ECCP synthetic procedure required a short calcination time of 4 h, as compared to a solid state reaction method [5,10]. A small number of additional peaks were observed in the SCM40 samples, as shown in Fig. 1. The additional peaks (marked by arrows) at 2θ values of 28.5° and 56.2° are indicative of the CeO_2 phase (JCPDS No. 34-0394). The limit of Ce content in SCM concurs with that found in a previous study of the SCM system [5].

Fig. 2 shows the XRD patterns of GDC and of the SCM30-GDC mixture after heating at 800 °C for 100 h. The diffraction peaks of the reaction products were visible in SCM30-GDC. No reaction occurred between the electrode and the electrolyte, since no additional peaks were detected in the XRD pattern after heating. The SCM powders were found to be compatible with the GDC electrolyte.

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