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Short communication

Influence of microstructure of perovskite-type oxide cathodes on electrochemical performances of proton-conducting solid oxide fuel cells operated at low temperature

Makiko Asamoto, Hiroyuki Yamaura, Hidenori Yahiro*

Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan

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ABSTRACT

The electrochemical performances of proton-conducting SOFCs with the perovskite-type oxide cathodes were investigated at low temperature of 773 K. Among the perovskite-type oxides used in the present study, $La_{0.7}Sr_{0.3}FeO_3$ (LSF) cathode exhibited the lowest overpotential at 773 K. The power density of the SOFC was dependent on the particle size of LSF cathode. The decrease in the particle size resulted in the decrease in overpotential. The power density of the cell with LSF cathode was also dependent on the thickness of LSF cathode; in the present condition, the LSF cathode with 13-μm thickness showed the best electrochemical performance at 773 K.

1. Introduction

The doped perovskite-type oxide protonic conductors such as Yb-doped $SrCeO_3$ and Nd- or Gd-doped $BaCeO_3$ are of interest for their applications in hydrogen sensors [1], hydrogen pumps [2], membrane reactors [3], and fuel cells [4–7]. The use of proton-conducting electrolyte in solid oxide fuel cells (SOFCs) has some advantages compared with that of the oxygen ion-conducting electrolyte in SOFCs. For instance, SOFCs with proton-conducting electrolyte form water at the cathode compartment, that is, the fuel unreacted keeps pure at the anode compartment, requiring no recirculation. In addition, the activation energy of protonic conductors (0.6 eV in doped-$SrCeO_3$ [8] and 0.3–0.5 eV in doped-$BaZrO_3$ [9]) is generally lower than that of oxygen ion-conductor (0.8–1.0 eV in YSZ [10] and 0.8 eV in samarium-doped ceria [11]), indicating that ionic conductivity of former conductor becomes higher than that of the latter conductor at low temperature. In fact, the protonic conductivity of $BaCe_{0.9}Y_{0.1}O_{3-\alpha}$ was reported to be $2 \times 10^{-3}\,S\,cm^{-1}$ at 673 K [12], being comparable to the oxygen ion conductivity of YSZ ($1 \times 10^{-2}\,S\,cm^{-1}$) at 973 K. Accordingly proton-conducting SOFC is advantageous in low temperature use (<773 K), rather than oxygen ion-conducting SOFC.

Recently, much attention is focused on intermediate and low temperature-SOFCs (IT- and LT-SOFCs) operated at less than 1073 K because such an operation enables to use the low cost metallic interconnects and the long-term stable materials and to decrease the corrosion of components. However, the decrease in the operation temperature of a SOFC results in an increase in the overpotential of electrode, mainly cathode [13]. Therefore, the development of a superior cathode becomes an important subject to realize an IT- and LT-SOFC using proton-conducting electrolyte.

Some perovskite-type oxides, $La_{1-x}Sr_xMnO_3$ [14], $La_{1-x}Sr_xCoO_3$ [15], $La_{1-x}Sr_xFeO_3$ [16], and $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ [17], with mixed conducting property have been considered to be one of the most promising cathode materials for SOFCs with oxygen ion-conducting electrolyte. Recently, we have reported that $La_{0.7}Sr_{0.3}FeO_3$ with perovskite-type structure showed the lower cathodic overpotential than $La_{0.7}Sr_{0.3}CoO_3$, $La_{0.7}Sr_{0.3}MnO_3$, and Pt for SOFCs with proton-conducting electrolyte, $SrCe_{0.95}Yb_{0.05}O_3$ [18] and $BaCe_{0.8}Y_{0.2}O_3$ [19], at 973 K. Furthermore, we applied the electrophoretic deposition (EPD) method to fabricate the perovskite-type oxide cathode on $SrCe_{0.95}Yb_{0.05}O_3$ electrolyte surface and first reported that the electrode thickness could be exactly controlled by EPD method [20]. This result indicates that the cathodic performances of proton-conducting SOFC were strongly influenced by the microstructure

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* Corresponding author. Tel.: +81 89 927 9929; fax: +81 89 927 9946.
E-mail address: hyahiro@eng.ehime-u.ac.jp (H. Yahiro).

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of electrode. The aim of the present study is to obtain preliminary results of electrochemical performance of cathode with different particle size and thickness when proton-conducting SOFC was operated at temperature as low as 773 K. Such a low operation temperature was selected to clarify the difference in electrode ability among cathodes affecting both gas diffusion and electro-catalytically reaction although the power densities were decreased with decreasing operation temperature. The results obtained in the present study are expected to be important findings for achieving LT-SOFCs with proton-conducting electrolyte.

2. Experimental

2.1. Sample preparation

The proton-conducting electrolyte, $SrCe_{0.95}Yb_{0.05}O_3$, was prepared by a following method [18]. The mixed powders, $SrCO_3$ (Wako, 95%), CeO_2 (Wako, 99.9%), and Yb_2O_3 (Wako, 99.9%), were calcined at 1673 K for 10 h in air, uniaxially pressed into pellets under a pressure of 2000 kg cm^{-2}, and finally sintered at 1773 K for 10 h in air. The diameter and the thickness of sintered pellets were ca. 9 mm and ca. 2.3 mm, respectively.

Cathode materials, $La_{0.7}Sr_{0.3}MO_3$ (M = Mn, Fe, and Co), were prepared by the solid-state reaction. La_2O_3 (Wako, 99.99%), $SrCO_3$ (Wako, 95%), $MnCO_3$ (Wako, 99%), Fe_2O_3 (Wako, 99.5%), and Co_3O_4 (Wako, >90%) were used as starting materials. These powders were mixed in appropriate ratio and ground in a ball mill with ethanol for 24 h. After drying, the mixed powders were calcined at 1673 K for 10 h in air. The resulting powders were ground by ball-milling for 10 and 30 h to obtain homogeneous and fine particles. The particle size distribution was measured with a laser diffraction particle size analyzer (HORIBA LA-950). XRD analysis was performed to confirm the crystalline phase of samples using a Rigaku RINT2200HF diffractometer with CuKα radiation. The microstructures of cathodes were observed by a scanning electron microscope (SEM, JEOL JSL-5310).

2.2. Cathode fabrication methods

Two methods, a slurry coating method (SC method) and an electrophoretic deposition method (EPD method), were utilized for fabricating cathode on the surface of electrolyte. SC method was performed as follows. $La_{0.7}Sr_{0.3}MO_3$ oxide powders were dispersed into turpentine oil (Wako, 90%) and painted on one face of electrolyte. After drying at room temperature for several hours, the sample was heat-treated at 1173 K for 3 h to obtain good adherence between cathode and electrolyte. EPD method was performed according to the previous literature [21]. The cathode samples were added to acetylacetone containing I_2 as a charging agent and sonicated for 30 min. A constant voltage of 10–70 V was applied for 1 min between stainless electrode and electrolyte with carbon-coated surface. The thickness of electrode was controlled by changing an applied voltage. The sample was finally heat-treated at 1023 K for 3 h.

2.3. Measurement of electrochemical performance

The construction of a fuel cell was essentially the same as that reported elsewhere [18]. After Pt paste (Nilaco) was painted into one surface of electrolyte and heat-treated at 1273 K for 0.5 h in air to obtain anode, the electrolyte pellet with both electrodes was placed between silica tubes with glass gaskets to separate two compartments. A Pt wire as a reference electrode was fixed around the side of the electrolyte. After Ar gas saturated with water vapor at 298 K was supplied to the anode compartment with a flow rate of 30 cm^3 min^{-1} for 1 h, H_2 gas was supplied with a flow rate of 50 cm^3 min^{-1}. The air as an oxidant gas was supplied to the cathode compartment with a flow rate of 50 cm^3 min^{-1}. A current interruption method was employed to obtain cathodic overpotential under the operation of a fuel cell at 773 K [18].

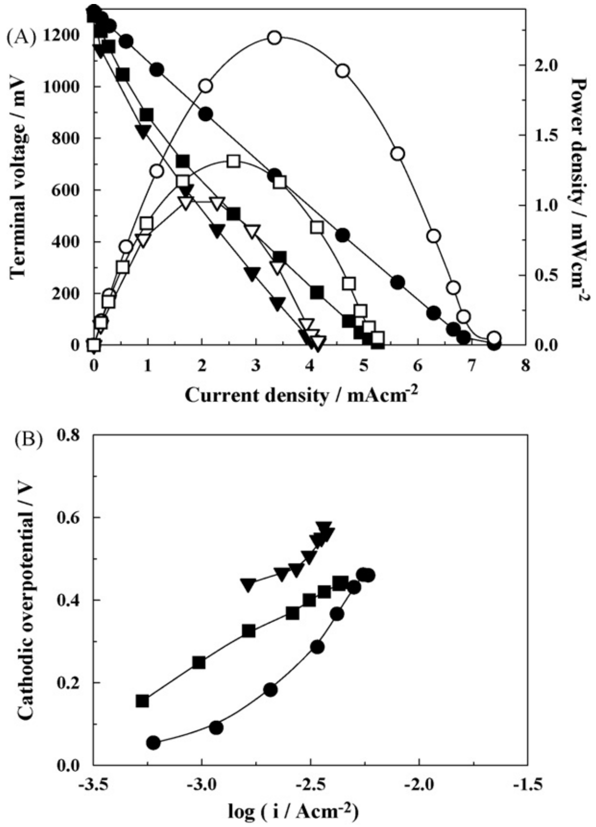

Fig. 1. (A) *I–V* (closed symbols) and *I–P* (open symbols) curves of SOFCs with (■, □) SC-LSM, (●, ○) SC-LSF, and (▼, ▽) SC-LSC cathodes at 773 K. (B) Cathodic overpotentials of (■) SC-LSM, (●) SC-LSF, and (▼) SC-LSC at 773 K.

3. Results and discussion

3.1. Electrochemical performance of perovskite-type oxide cathode

The XRD patterns of $La_{0.7}Sr_{0.3}MnO_3$ (LSM), $La_{0.7}Sr_{0.3}FeO_3$ (LSF), and $La_{0.7}Sr_{0.3}CoO_3$ (LSC) samples calcined at 1673 K provided the single phase assigned to the perovskite-type structure; no diffraction peak from a secondary phase or from the starting materials was observed. The mean diameters of LSM, LSF, and LSC particles ground by ball-milling for 30 h were estimated to be 0.4, 0.8, and 0.5 μm, respectively. These powders were utilized to elucidate cathodic performance.

Current–voltage (*I–V*) and current–power (*I–P*) curves and cathodic overpotentials for H_2–O_2 SOFCs using $La_{0.7}Sr_{0.3}MO_3$ cathodes fabricated by SC method were measured at 773 K. The results are shown in Fig. 1(A). The power densities were strongly influenced by the kind of B-site cation in perovskite-type oxide. The order of maximum power density was SC-LSF > SC-LSM > SC-LSC. Fig. 1(B) shows the cathodic overpotentials of $La_{0.7}Sr_{0.3}MO_3$ at the same temperature. The order of the cathodic overpotential was SC-LSF < SC-LSM < SC-LSC, agreeing with that of maximum power density. This suggests that the power density is dominated by the cathodic overpotential and that LSF cathode is a potential candidate for cathode material of proton-conducting SOFCs operated at low temperature.