Formation of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films as SOFC cathodes by electrophoretic deposition

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$\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) cathode films for a solid oxide fuel cell (SOFC) were formed on a solid electrolyte sheet using the electrophoretic deposition (EPD) technique. The EPD process was undertaken in methanol suspensions containing LSM particles with different mean particle sizes. The zeta potentials of the LSM dispersions in methanol tended to decrease with increased sintering temperature during powder preparation. The morphology of the cathodic films was significantly dependent on the mean particle size and the grain sizes in the films after sintering at 1100°C were in the order of LSM600 > LSM1000 > LSM800, with corresponding cathodic performance in the order of LSM800 > LSM1000 > LSM600. The morphology of the LSM 800 films varied with the DC voltage applied during the EPD process (7.5 and 15 V), and a more densely deposited phase with finer pores was achieved with lower applied voltage. Increase in applied voltage tended to induce particle growth; therefore, the film applied at low voltage exhibited the highest cathodic performance. The cathodic performance was not dependent on the film thickness in the range between 5 and 15 μm , which implies that the LSM800 film was sufficiently porous to provide a suitable rate of oxygen gas diffusion.

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1. Introduction

The solid oxide fuel cell (SOFC) is a promising technology for power generation because of its high energy conversion efficiency, high energy density and low usage of noble metals. SOFC is generally operated at high temperatures around 900–1000°C, which allows for the use of various fuels such as natural gas without requiring sophisticated gas reformers. Because of its high temperature operation, it requires thermally durable and costly materials to assure a long-term stability. Therefore a lowering an operation temperature is currently one of the mainstreams of development among SOFC researchers. Although operation at lower temperatures enables the use of low cost materials, such as metallic interconnects, it incurs a reduction of power density. For this reason, lowering the temperature without reducing the cell performance has been an issue among SOFC researchers. One of the decisive factors to achieve a reduction of the operating temperature is to suppress electrode overpotential, i.e., increase electrode activity, especially in the cathode. It is generally accepted that electrode microstructure at the boundary between the electrode, electrolyte and oxygen (three phase boundary; TBP) has significant correspondence to the electrode overpotential.^{1),2)}

Electrophoretic deposition (EPD) is an attractive technique, which is applied for the formation of thin or thick ceramic films.³⁾ EPD is based on particle migration and deposition under an applied DC electric field. The EPD technique has been successfully applied in SOFC applications to form thin, dense electrolyte films on electrode supports, with an aim to reduce the

ohmic resistance of the electrolyte.^{4)–8)} However, there have been few reports on the deposition of electrode films on electrolyte substrates by EPD. Electrode films for SOFC required appropriate morphology control to achieve low electrode overpotential.^{2),9)} Santillán et al.¹⁰⁾ successfully formed $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) films on Au- or Ag-sputtered $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ and concluded that the microstructure of the LSCF film can be controlled by EPD parameters such as applied voltage, deposition time. EPD can be a practical process of not only a film formation but also morphology control. In this study, to have knowledge for morphology control of a cathode film and their relation to a cathodic performance, some $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM) SOFC cathode films were prepared on an yttria-stabilized zirconia sheet using EPD with different conditions such as LSM particle size and applied voltage.

2. Experimental

2.1 Preparation of LSM powders

LSM powders were prepared by the sol-gel route starting from a stoichiometric molar ratio of $\text{La}[\text{CH}_3\text{COO}]_3 \cdot 1.5\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Mn}[\text{CH}_3\text{COO}]_2 \cdot 4\text{H}_2\text{O}$.¹¹⁾ The gel precursors were calcined in air at 600 (LSM600), 800 (LSM800), and 1000°C (LSM1000) for 24 h. In order to obtain homogeneous powders, the products were ball-milled with 2.3 mm diameter zirconia balls in methanol for 12 h. The powders were characterized by powder X-ray diffraction (XRD; Rigaku Rint 2200V). Particle size distributions were measured in water with laser diffraction and dynamic light scattering (Horiba LA-950). In order to obtain a good dispersion, small amount of sodium hexamethaphosphate was added into the aqueous dispersions. Zeta-potentials of the particles in methanol were evaluated with laser-Doppler electrophoresis (Nikkiso Co.; UPA-UZ).

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Fig. 1. Schematic diagram showing the three-terminal half-cell configuration.

2.2 EPD process

A solid electrolyte support of 0.2 mm thick 8 mol % yttria-stabilized zirconia (YSZ; Tosoh Co.) sheet with an area of $1 \times 1 \text{ cm}^2$ was used. The YSZ sheet is poorly conductive for the EPD process; therefore, carbon ($0.5 \times 0.5 \text{ cm}^2$) was first vapor-deposited on the surface of the YSZ sheet. The LSM deposit could then be selectively formed on the carbon surface. To prepare the starting EPD bath, 0.5 g of LSM powder was added to 40 mL of methanol, and the mixture was ball-milled with 2.3 mm diameter zirconia balls for 12 h. The resultant LSM dispersion was used as the suspension for EPD without the addition of a charging agent. EPD was performed at a constant voltage of 7.5 or 15 V/cm. The film thickness was fixed to approximately $15 \mu\text{m}$ by adjusting the deposition time. The carbon deposited YSZ sheet and a stainless steel sheet were used as the deposition substrate and counter electrode, respectively. The LSM suspension was sonicated for 20 min, immediately after which the EPD process was conducted. EPD was performed without stirring the suspension using a magnetic bar, due to the magnetism of the LSM powders. The green deposited LSM films were sintered at 1100°C for 2 h. The sputtered carbon is pyrolyzed during this heating process, so that a direct contact is formed between the LSM film and YSZ sheet.

2.3 Cathodic performance

Cathodic performance was examined using the three-terminal half-cell configuration shown in Fig. 1. The apparent electrode areas are 0.025, 0.025, and 0.01 cm^2 for working, counter and reference electrodes, respectively. First, the LSM electrodes are formed on the YSZ sheet with the above-mentioned procedure. Next, counter and reference electrodes were formed. Here, Pt/YSZ composite (Pt:YSZ = 9:1 w/w) was applied for those electrodes to yield a good compatibility with the YSZ electrolyte sheet in terms of the thermal expansion. The Pt/YSZ composite electrode was prepared by screen-printing of the mixed paste consisting of Pt-paste (Tanaka Kikinzoku Co., TR-7907) and 8 mol % YSZ powder (Tosoh Co., TZ-8Y). The Pt/YSZ electrodes were sintered at 600°C for 1 h. Finally, the electrodes were thinly over-coated with Pt-paste as a current collector, and then each of three electrodes was wired with Pt-leads using Pt-paste. To fix them, the cells were fired at 600°C for 1 h. The completed test cell was fixed on the top of an alumina tube, with the counter electrode oriented toward the tube interior, and sealed

Fig. 2. XRD patterns of LSM600, LSM800, and LSM1000 powders. The peaks marked with (024) were analyzed for evaluating the crystallite size by the Sherrer's equation.

Fig. 3. Particle size distributions for LSM600, LSM800, and LSM1000 dispersed in water.

with an inorganic adhesive. Then, 3% H_2/Ar gas bubbled through water was aerated onto the Pt/YSZ counter electrode and compressed air was flowed onto the cathode and Pt/YSZ reference electrodes.¹²⁾ The cathodic potential drop versus the reference electrode was measured at various current densities in the temperature range between 600 and 900°C .

3. Results and discussion

3.1 LSM characterizations

LSM powders were prepared by calcination at 600, 800, and 1000°C . Powder X-ray diffraction (XRD) patterns of the LSM powders indicated formation of the typical perovskite-type phase (Fig. 2). The XRD linewidth decreased with an increase in the calcination temperature. The crystallite sizes were evaluated as 0.02, 0.04, and $0.16 \mu\text{m}$, respectively, using Sherrer's equation applied to the (024) peak. Particle size distributions measured by the laser diffraction method in water indicated mean particle sizes of 0.20, 0.29, and $0.51 \mu\text{m}$, respectively (Fig. 3) and shows a similar tendency to the crystallite size. Figures 4(a)–4(c) are the SEM pictures of the deposited surfaces of the LSM particles. It seems that the sizes of the deposited particles are much smaller than those evaluated by the laser diffraction method in water and even close to the crystallite sizes evaluated by XRD. It is deduced that the particles are dispersed in water as secondary particles.

The zeta-potentials of LSM600–1000 particles dispersed in methanol were 44.70, 39.19, and 31.25 mV , respectively, and decreased with an increase in the calcination temperature. The LSM particles exhibited sufficiently high zeta-potentials to obtain a stable suspension without the addition of a charging agent.

Fig. 4. SEM micrographs of the LSM deposit surfaces formed by EPD at a voltage of 15 V/cm using (a, d) LSM600, (b, e) LSM800, and (c, f) LSM1000 powders. The images shown in (a, b, c) and (d, e, f) represent those before and after sintering at 1100°C, respectively.

Fig. 5. (a) Cathodic voltage drops for the cells prepared with LSM600, LSM800, and LSM1000 films observed at 700 and 900°C. (b) Temperature dependence of the voltage drops at a current of 0.1 A/cm².

3.2 EPD films of LSM powders and cathodic properties

Figure 4 shows scanning electron microscopy (SEM) micrographs of the LSM films before and after sintering. All the EPD films were densely deposited and accompanied by the local aggregation of particles. After sintering of the LSM films at 1100°C, SEM observations indicated partial sintering and particle growth. The particle size distributions of the sintered films were clearly dependent on the particle size of the starting LSM powders. The particle size ranges were estimated to be 0.3–0.8 μm (LSM600), 0.25–0.5 μm (LSM800), and 0.5–0.6 μm (LSM1000) from SEM observations. The LSM600 film, which consisted of the smallest particles before sintering, ended in the most grown particle assembly with a wide size distribution. In contrast, the LSM1000 film almost retained its initial particle size. The LSM800 film consisted of the smallest particles with a narrow size distribution.

The cathodic performance of the films was measured and the cathodic potential drops at various current densities are shown in

Fig. 5(a). The LSM800 film exhibited distinctly higher performance than the other films both at 700 and 900°C. The cathodic performance was in the order of LSM800 > LSM1000 > LSM600, which corresponds to the mean particle size of the sintered LSM films. Figure 5(b) shows the temperature dependence of the cathodic performance. The difference in cathodic performance became more prominent at lower temperature, which suggests that the LSM800 film has low activation energy for the cathodic reaction. This result is predictable from the difference in morphology shown in Fig. 6, where the LSM800 film after the sintering is composed of fine particle aggregations. This controlled morphology increased the effective contact area at the electrode/electrolyte interface and elongated the total length of three-phase boundary (TPB). It is generally accepted that elongation of the TPB decreases the resistance overpotential of the electrode.¹²⁾ Therefore, it is concluded that aggregation of the small LSM800 particles results in a reduction of the resistance overpotential.

Fig. 6. SEM micrographs of the LSM800 deposit surfaces formed by EPD at constant voltages of (a, c) 7.5 and (b, d) 15 V/cm. The images shown in (a, b) and (c, d) represent those before and after sintering, respectively.

3.3 Effect of applied voltage on morphology and the cathodic properties

The electrophoretic velocity of a charged particle is proportional to the applied DC voltage. This trend can generally be used for control of the mass deposited and film thickness in EPD.⁵⁾ It is also expected that the electrophoretic velocity affects the microstructure of the deposited film, which can be a decisive factor for determining electrode properties. Therefore, the effect of applied voltage on the LSM film morphology was examined using the LSM800 powder, which exhibited the best cathodic performance as described in the last section.

Figure 6 shows the surface morphologies of sintered LSM800 films prepared at applied voltages of 7.5 and 15 V/cm. The morphology of the LSM film is clearly affected by the applied voltage. LSM particles are densely and uniformly deposited on the YSZ sheet under application of 7.5 V/cm, and the surface becomes rougher with the increase in applied voltage to 15 V/cm. Consequently, the pore size of the films after firing became larger with an increase in the applied voltage. Similar behavior has been reported previously.¹⁰⁾ The difference in morphology could be related to the particle coagulation process in the deposited electrode film. Particle coagulation in an electric field can be described using a modified DLVO interaction force,¹³⁾ where increase in an electric field decreases the minimum force of particle coagulation onto the substrate. Therefore, the EPD process at the 15 V/cm will exert a higher rate of particle coagulation than that at 7.5 V/cm. Furthermore, the particle concentration near the deposit surface increases at the higher voltage.

Since LSM is highly resistive at room temperature ($\sim 30 \text{ S cm}^{-1}$ at 25°C and 1 atm O_2), it is deduced that the electric field penetrating the LSM-deposited layer would be weakened to some extent. Conversely, electric field at a void on the deposited surface is stronger than that at the periphery. Under this situation, the migrating particles may be preferentially thrust onto a void on the deposited surface. Therefore, applying high voltage would reduce such the deposition site selectivity and yield a non-close-packed structure. **Figure 7** shows the cathodic potential drops of the films prepared at 7.5 and 15 V/cm. The 7.5 V/cm film

Fig. 7. Cathodic voltage drops of cells with LSM800 formed at constant voltages of 7.5 and 15 V/cm, and measured at 700, 800, and 900°C .

exhibited better performance than the 15 V/cm film, and this difference was accentuated at lower temperature. This can be explained by better contact at the electrode/electrolyte interface from close packing of the LSM particles and elongation of the effective TPB. It should be noted that close packing occasionally results in a large diffusion barrier for oxygen; however, in the present case, the closer packed film exhibited better performance, which suggests that the microstructure at the interface plays a predominant role in the cathodic properties.

Although the film prepared at high applied voltage is inferior in the cathodic activity to that prepared at low applied voltage, it can be expected that the former film might be superior in the gas permeability because of its higher porosity than the latter film. Thus we are now conducting a further examination of double-layered cathode formation by EPD, where a film with high applied voltage as a gas diffusive current collecting layer formed on a film with a low applied voltage.

3.4 Film thickness dependence

The thickness of an electrode layer sometimes has an influence on the electrode properties.¹⁴⁾ EPD is an effective method for the control of film thickness; therefore, the effect of film thickness on the cathodic properties was examined in the region between 5 and $15 \mu\text{m}$. **Figure 8** shows the cathodic drops of LSM films with different film thicknesses. No significant difference in the potential drop was observed for cathode film thicknesses between 5 and $15 \mu\text{m}$ measured at 600 and 900°C . Film thickness can affect gas diffusion and the current collection properties; however, the result indicates that the LSM films are sufficiently porous and the film thickness does not act as a diffusion barrier. Furthermore, the thin film exhibited acceptable current collection, which suggests that $5 \mu\text{m}$ is sufficiently thick to form effective conjunctions between LSM particles to form current paths.

4. Conclusion

EPD was applied for LSM cathode film formation on YSZ sheets using different size LSM particles and different applied voltages. The LSM particles prepared at 600 (LSM600), 800

Fig. 8. Cathodic voltage drops for cells with 5, 10, and 15 μm thick LSM800 films formed at a constant voltage of 7.5 V/cm and measured at 600 and 900°C.

(LSM800), and 1000°C (LSM1000) exhibited different film morphologies. LSM800 had the smallest particle aggregations and the best cathodic performance among the three LSM electrode types. The EPD process was carried out for LSM800 particles using different applied DC voltages. The LSM particles were densely deposited at lower voltage and became rough with an increase in the voltage. Better performance was obtained for

the film prepared at low voltage. No significant effect of film thickness on the cathodic properties was observed in the range between 5 and 15 μm .

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