CHARACTERISTICS OF POLYMERIC RESIN-DERIVED MULTILAYER COMPOSITE CATHODE FOR SOFC

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ABSTRACT

The multilayered cathodes of nanoporous microstructure for SOFCs were developed using a polymeric resin as a nanoscale pore former that was prepared by a modified Pechini method. An LSM-YSZ composite layer was placed on the interface between electrode/electrolyte as a reaction active layer, then LSCF as a current collector was deposited by screen printing. Adding the polymeric resin component to the particulate paste permits us to produce a nanoporous electrode with high porosity and large surface area after heat treatment. The pore structure of a composite cathode is a function of the polymeric resin added in the paste. The electrochemical cell of this microstructural feature showed significantly improved electrocatalytic activity toward oxygen reduction. Microstructural evolution and the performance of the electrochemical cells with multilayered cathodes were investigated by SEM and impedance spectroscopy.

INTRODUCTION

Conventional SOFCs are operated in a high-temperature atmosphere up to ~1000°C based on well-established component systems. Strontium-doped lanthanum manganite (La_xSr_yMnO_3, LSM) is frequently used as a cathode material because of its high electrochemical activity for the O_2 reduction reaction and good stability and compatibility with yttria stabilized zirconia (YSZ) electrolyte. However, LSM is limited in the application of cathodes for low-temperature SOFCs due to its low oxygen ion conductivity and high activation energy.

Several strategies have been adopted to improve the electrochemical performance of the LSM based system. One effective approach is to add a secondary phase of higher ionic conductivity, such as YSZ, with LSM to extend the active area over which the oxygen reduction reaction can occur (1,2). Such electrodes are referred to as composite cathodes and were first reported by Kenjo et. al. (3). It was shown that by adding 50 wt% YSZ to the LSM cathode, the polarization resistance could be reduced to 25% of its original value. But it is not certain whether the performance of these cathodes will be sufficient at lower temperatures due to depreciation of oxygen ionic diffusivity of YSZ. Consequently, the performance of the electrodes must be significantly advanced to reduce the operating temperature, either through development of new materials or formation of novel microstructures.

We have researched a novel method for producing a bilayered composite electrode with
graded microstructure to enhance the performance of the LSM-based cathode. Recently, the concept of functionally graded materials, which have a porosity gradient consisting of fine grains close to the cathode-electrolyte interface and large grains at air side, was introduced to fabricate SOFC components (4,5). It has been shown that nanoporous electrodes with high surface area offer excellent electrochemical performance as long as large enough pore size and enough porosity are generated (6,7).

In this study the cathodes consisted of two layers of different composition: LSM-YSZ/LSCF. In addition, the microstructure associated with each layer varied from macroporous to nanoporous. A nanoporous LSM-YSZ catalytic layer was deposited at the cathode-electrolyte interface, followed by a macroporous LSCF top layer as a current collector (8). It is expected that increased gas permeability and extension of the triple phase boundary can be achieved simultaneously by using such a cathode with graded microstructures. For investigating electrochemical electrode performance depending upon the microstructural variations, we measured the cathodic polarization resistance of the solid-state half cells.

EXPERIMENTAL

The particulate cathode materials were synthesized by a polymerizable complex method (9,10) with stoichiometric amounts of corresponding nitrate salts. Particle size and specific surface area of two synthesized powders, LSM-YSZ composite particles and LSCF particles, are summarized in Table I. LSM-YSZ composite particles were synthesized by pyrolyzing the polymeric resin containing all the metal cations in a stoichiometric ratio.

| Powder | Compositions confirmed by ICP | Mean particle size | Standard deviation | Surface area |
|--------|-------------------------------|--------------------|--------------------|--------------|
| LSM-YSZ | \((La_{0.8}Sr_{0.2}MnO_3):(8\text{mol}\%Y_2O_3/92\text{mol}\%\text{ZrO}_2)=6/4\) (weight ratio) | 0.24 µm | 0.11 µm | 2.53 m²/g |
| LSCF  | \(La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3\) | 0.11 µm | 0.05 µm | 11.59 m²/g |

The electrochemical cells were prepared such that nanoporous LSM-YSZ structures were derived from the polymeric resin before pyrolysis added the paste together with the particulate materials. The polymeric resin was used as a nanopore former to control a graded microstructure of the composite cathodes. The LSM-YSZ paste materials were prepared by mixing the synthesized powders dispersed in solvent with the polymeric complex resin of the same metal cation compositions.

Bilayered composite cathodes were fabricated by screen printing with relevant paste materials that were a mixture of the powders, polymeric resin, and additives dispersed in an organic solvent mixed by a three-roller mill (EXAKT 35). The binder, dispersant, and solvent for all the cathode pastes were ethylenecellulose, fish oil, and α-terpineol, respectively. Each cathode paste was successively applied to the commercially available YSZ disk (Tosoh TZ28Y, diameter = 20 mm, thickness = 0.5 mm) in the order of LSM-YSZ/LSCF.
Two different cells were prepared by varying the mixing ratio of the powder to the polymeric resin of LSM-YSZ. The mixing ratio of the powder to the polymeric resin varied from 1:0.75 to 1:0.33 based on the weight, as described in Table II. The polymeric resin undergoes about 67% weight loss during heat treatment. Subsequently, 20 wt% of the LSM-YSZ composite layer in cell 1 was derived from the polymeric resin, whereas 10 wt% was in cell 2. The LSM-YSZ layers were fabricated by a double screen printing using polymeric resin-containing pastes. The second layer was deposited over the first layer after drying at 80°C for 30 minutes. The LSCF layer was then processed on the top of the LSM-YSZ layers.

Table II. Powder-to-resin ratio of the LSM-YSZ pastes used in two polymeric resin-derived cells.

| Cell Type | Paste Composition (weight ratio) |
|-----------|----------------------------------|
| Cell 1    | Powder : Resin = 1 : 0.75        |
| Cell 2    | Powder : Resin = 1 : 0.33        |

The prepared multilayered composite electrodes were charred at 400°C for 2 hr, followed by crystallization at 800°C and then firing at 1100°C for 3 hr. The microscopic features of the prepared electrodes were investigated using scanning electron microscopy (SEM) (FE-SEM, S-4200, Hitachi).

For measuring electrochemical reduction activity, the platinum paste was screen-printed on the other side of the YSZ as well as on top of the LSCF layer. The platinum mesh connected with the platinum current lead line was contacted with the platinum layers at both sides, and the cells were fired at 1000°C for 1 hr (11). The cells were mounted on an alumina tube reactor, and electrochemical impedance characterizations were performed at temperatures from 750°C to 850°C in 50° intervals. AC impedance spectroscopy (Solatron SI 1260/ SI 1287) was used to measure the polarization resistance of the electrochemical cells. All data were taken 30 minutes after the desired temperature was reached. Impedance spectra were obtained in the frequency range of 0.03 Hz to 100 kHz, and the applied AC voltage amplitude was set to 20 mV.

RESULTS AND DISCUSSION

The microstructures of the LSM-YSZ layer prepared from the polymeric resin-added pastes with the varying mixture ratios are shown in Figure 1. The microstructure of the cathode layer showed evidence of the effect of the resin contained ratio. SEM microscopy revealed that the microstructure of cathode with higher concentration of resin indicated a well-distributed nanoporous structure. However, the microcrack in the electrode was occasionally shown in the polymeric resin-derived cathode layer because of nonuniform volumetric shrinkage associated with the difference between the particulate materials and the polymeric resins. Adding a large amount of resin may weaken the resulting layer due to excess weight loss (i.e., powder to resin ratio = 1:2). On the contrary, adding a lesser amount of the resin did not greatly affect the microstructure of the cathode. Polymeric complex resin decomposes into relevant metal hydrous oxides or carbonates that subsequently transform into the desired crystalline metal oxide compounds. Such a transformation can be used to produce a nanoporous
Figure 1. SEM images for the LSM-YSZ layers derived from the polymeric resinadded pastes with the varying powder to resin ratio: (a) 1:0.75 and (b) 1:0.33 paste.

The electrode in which the length of the triple phase boundary is significantly extended. Therefore, a mixture ratio of the powder and the polymeric resin must be well-controlled to achieve the nanoporous electrode with adequately pore distribution and strength of cathode layer required for better electrocatalytic reaction.

Figure 2 illustrates a cross-sectional view of the multilayered LSM-YSZ/LSCF cathode in the cell fabricated by screen printing. It was shown that the particles themselves are well connected each other. The composite electrode had a relatively uniform thickness of ~25 μm without delamination in which LSM-YSZ layer was approximately 15 ~ 0. The microstructural features associated with each layer as marked by dotted circles are observed in high-magnification SEM images of Figure 2(b) and 2(c). The multilayered cathode had a grade microstructure that was composed of LSM-YSZ catalytic layer with nano pores of 50 ~100 nm in size, followed by the current collecting LSCF gas permeable layer with three-dimensionally interconnected macro pores of 1 ~ 1.5 μm in size.

The influence of the nanoporous microstructure on electrochemical performance was investigated for electrochemical cells involving two different polymeric resin-derived LSM-YSZ. The effect of microstructural features on electrode performance can be evaluated by impedance spectroscopy. It is an effective method of understanding the influence of resistance of the electrochemical cell on its electrocatalytic activity. The intercept of the impedance arc with the real axis at high frequencies corresponds to the ohmic resistance of the cell, which includes the resistance of the electrolyte and the lead
wire, whereas the one at low frequencies relates to the total resistance of the cell. In
general, the interfacial polarization resistance can be given by subtracting the low
frequency intercept from the high frequency intercept.

Interfacial polarization resistances were resolved for electrochemical cells with different
LSM-YSZ layers, as summarized in Table III. Interfacial polarization increased with
decreasing temperature regardless of the powder-resin composition of the cell. This was
due to depreciation of oxygen conduction and electrode catalytic activity. The bilayered
composite cathode involving cell 1 composition exhibited higher electrocatalytic activity
toward oxygen reduction, as characterized by the lowest polarization resistance, ~0.72
Ωcm² at 750°C compared with cell 2. A higher polarization resistance of 1.124 Ωcm²
was acquired for cell 2; i.e., a lesser amount of resin was added. Figure 3 presents the
impedance spectra for cell 1 measured at various temperatures in air.

Table III. Polarization resistances at various temperatures for bilayered cathodes
with bottom layers prepared with polymeric resin pastes at different compositions.

| Cell Type | 850°C  | 800°C  | 750°C  |
|-----------|--------|--------|--------|
| Cell 1    | 0.043  Ωcm² | 0.18  Ωcm² | 0.72  Ωcm² |
| Cell 2    | 0.117  Ωcm² | 0.445  Ωcm² | 1.124  Ωcm² |

Figure 3. Impedance spectroscopy for cell 1 measured at various temperatures
between 750°C and 850°C in air.

The cell involving the bottom LSM-YSZ layer in which sufficient porosity and well-
distributed nanopore structure is present reveals higher cathodic performance, an im-
provement attributed to increased length of the triple phase boundary in a porous
electrode structure. The nanoporous structure derived from the polymeric resin is more
effective in improving catalytic activity and reducing oxygen at lower temperatures.

This result was directly correlated with the microstructural features of the composite
cathodes. As described above, the well-distributed nanoporous LSM-YSZ layer can be
obtained by controlling the concentration of resin component. Thus, as seen in Figure 1
and Table III, the 3D interconnected pore structures with high specific surface area plays
a critical role in enhancing the electrochemical performance of the electrode at lower
temperatures, but the amount of polymeric resin must be controlled. Indeed, fairly high resistance was observed for the cell derived from the paste with excess polymeric resin (result not shown). Poor performance associated with such a cell results from improper microstructural development where occasional larger pores/macrocracks and weak interfacial adhesion occur due to significant weight loss during burnout of the polymeric resin.

CONCLUSIONS

The bilayered composite cathodes derived from a polymeric resin for SOFCs were investigated. A homogeneous, nanoporous cathode layer was prepared on a YSZ substrate using a polymeric resin-containing paste. Correlations between powder-to-resin ratio and microstructure of the corresponding cathode layer were observed. It was demonstrated that well-distributed and nanosized pore structure is acquired by controlling the powder-resin ratio. The nanoporous microstructure of the LSM-YSZ catalytic layer plays an important role in enhancing the electrocatalytic activity of the cathode. The electrochemical performance of this polymeric resin-derived cathode displayed significant lower interfacial resistance, ~0.72 Ωcm², measured at 750°C in air.

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REFERENCES

1. T. Tsai, S. A. Barnett, Solid State Ionics, 93, 207 (1997).
2. E. P. Murry, S. A. Barnett, Solid State Ionics, 143, 265 (2001).
3. T. Kenjo, M. Nishiya, Solid State Ionics, 57, 295 (1992).
4. Y. Liu, C. Compson, M. Liu, J. Power Sources, 138, 194 (2004).
5. N. T. Hart, N. P. Brandon, M. J. Day, N. Lapena-Ray, J. Power Sources, 106, 42 (2002).
6. E. Ivers-Tiffee, A. Weber, D. Herbstritt, J. Eur. Ceram. Soc., 21, 1805 (2001).
7. C. W. Tanner, K. Z. Fung, A. V. Virkar, J. Electrochem. Soc., 144, 21 (1997).
8. C. Xia, W. Rauch, W. Wellborn, M. Liu, Electrochem. and Solid State Lett., 5, A217 (2002).
9. M. Popa, J. Frantti, M. Kakihana, Solid State Ionics, 154-155, 437 (2002).
10. M. Kakihana, M. Arima, M. Yoshimura, N. Ikeda, Y. Sugitani, J. Alloys and Compounds, 283, 102 (1999).
11. J.-D. Kim, G.-D. Kim, J.-W. Moon, Y. Park, W.-H. Lee, K. Kobayashi, M. Nagai, C.-E. Kim, Solid State Ionics, 143, 379 (2001).