

Short communication

Electrochemical and microstructural characterization of polymeric resin-derived multilayered composite cathode for SOFC

Hwa Seob Song^a, Sang Hoon Hyun^a, Jooho Moon^{a,*}, Rak-Hyun Song^b

^a School of Advanced Materials Engineering, Yonsei University, Seoul 120-749, South Korea

^b Korea Institute of Energy Research, Daejeon 305-343, South Korea

Accepted 1 February 2005

Available online 31 May 2005

Abstract

The multilayered cathodes of functionally graded microstructure for SOFCs were developed using a polymeric resin as a pore former at the nanometer scale. LSM–YSZ composite layer was placed on the interface between electrode/electrolyte as a reaction active layer, subsequently LSM as an intermediate layer and LSCF as a current collector were deposited by screen printing. The type of the LSM–YSZ composite powders used in the cell fabrication influenced the microstructure of the catalytic bottom layer. Furthermore, the addition of the polymeric resin to the particulate paste permits us to produce a nanoporous electrode of high porosity and surface area after thermal decomposition and crystallization. The electrochemical cell of such a microstructural feature showed a significantly improved electrocatalytic activity toward the oxygen reduction. Microstructural evolution and its electrochemical performance of the electrochemical cells with multilayered cathodes were investigated by SEM and impedance spectroscopy.

© 2005 Elsevier B.V. All rights reserved.

Keywords: SOFC; Cathode; Composite electrode; Functionally graded layer

1. Introduction

The solid oxide fuel cells (SOFCs) have represented electrochemical energy conversion from chemical to electrical energy with minimum pollutant emission using various fuels. In this respect, SOFC has shown considerable promise for potential uses in a variety of applications ranging from distributed energy production system to portable power generation. Recent focus has been on the advances of SOFCs through the reduction of operating temperature which is a key technical hurdle in practical development of SOFCs [1–3].

In general, SOFCs are operated at high temperature atmosphere up to $\sim 1000^\circ\text{C}$ based on well-established component systems. Strontium-doped lanthanum manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, LSM) is frequently utilized as a cathode material because of its sufficient electrical conductivity, stability in oxidizing atmosphere, and thermal compatibility

with yttria stabilized zirconia (YSZ) electrolyte. However, LSM does not have adequate electrocatalytic efficiency due to its low oxygen conductivity.

One effective approach for improving the electrochemical performance is to mix another material of higher ionic conductivity, such as YSZ, with LSM to extend the active area over which the oxygen reduction reaction can occur [4,5]. It is demonstrated that such a composite electrode consisting of LSM and YSZ exhibits better performance with lower interfacial resistances that reflect higher electrochemical reduction rate of the oxygen compared to the electrode of LSM alone. 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 developed a novel fabrication method for the production of a multilayered composite electrode with graded microstructure to enhance the performance of the

* Corresponding author. Tel.: +82 2 2123 2855; fax: +81 2 365 5882.
E-mail address: jmoon@yonsei.ac.kr (J. Moon).

LSM-based cathode at lower temperatures [6–8]. The cathodes were consisted of three layers of different compositions: LSM–YSZ/LSM/La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF). In addition, the microstructure associated with each layer gradually varied from macroporous to nanoporous structures. Nanoporous LSM–YSZ catalytic bottom layer was placed on the YSZ electrolyte, followed by LSM intermediate layer and macroporous LSCF top layer as a current collector [9]. It is expected that increase in gas permeability and extension of the triple phase boundary can be simultaneously achieved by employing such a cathode with graded microstructures. For investigating electrochemical performance depending upon the microstructural variations, we have analyzed cathodic polarization resistance of the solid state half-cells.

2. Experimental

All the particulate materials used in the current study had been synthesized in our laboratory by a polymerizable complex method [10–11] with stoichiometric amounts of corresponding nitrate salts. Physical and chemical characteristics of three synthesized powders: LSM, LSM (La_{0.85}Sr_{0.15}MnO₃)–YSZ composite particles and LSCF are summarized in Table 1. LSM–YSZ composite particles were synthesized by pyrolyzing the polymeric resin that contains all the metal cations in a stoichiometric ratio (denoted as a *co-pyrolyzed LSM–YSZ*). Two other types of the LSM–YSZ composite powders were also prepared. One is a simple mixture of LSM and YSZ by ball milling that had been separately synthesized by the polymerizable complex method, which is denoted as a *mixed LSM–YSZ*. Another type is a *coated LSM–YSZ* prepared in a manner that YSZ polymeric resin was coated on the surface of the resin-derived LSM particles, dispersed in yttrium and zirconium nitrates-containing solution prior to polymerization, followed by pyrolysis.

Multilayered composite cathodes were fabricated by screen printing with relevant paste materials that were a mixture of the powders and additives dispersed in an organic solvent mixed by three roller mill (EXAKT 35). The binder and solvent for all the cathode pastes were ethylcellulose and α -terpineol, respectively. Each cathode paste was successively applied on the commercially available YSZ disk (Tosoh TZ8Y, diameter = 20 mm, thickness = 0.5 mm) in the order of LSM–YSZ/LSM/LSCF. Three different cells were prepared by varying the types of LSM–YSZ used in the mul-

Table 2
Powder to resin ratio of the LSM–YSZ pastes used in three different polymeric resin-derived cells

Cell type	First coating	Second coating
Cell 1	8:2 paste	8:2 paste
Cell 2	8:2 paste	7:3 paste
Cell 3	8:2 paste	6:4 paste

tilayered cathode, i.e., the co-pyrolyzed, the mixed, and the coated powders.

Another set of the electrochemical cells was prepared in a way that nanoporous LSM–YSZ structures were derived from the polymeric resin prior to pyrolysis added in the paste together with the particulate materials. The polymeric resin was employed as a nanopore former to control a graded microstructure of the composite cathodes. The LSM–YSZ paste materials were prepared by mixing the co-pyrolyzed powders dispersed in α -terpineol with the polymeric complex resin of the same metal cation compositions. Mixing ratio of the powder to the polymeric resin varied from 8:2 through 7:3 to 6:4 based on the weight. Three different LSM–YSZ layers were fabricated by a double screen printing in which the second layer was deposited over the dried first layer using a different combination of the polymeric resin-containing pastes as described in Table 2. The remaining LSM and LSCF layers were processed with the same paste materials utilized in the first set of the cells.

The prepared multilayered composite electrodes were charred at 400 °C, 2 h and 600 °C, 30 min to remove volatile species resulted from the polymeric resin, followed by crystallization at 800 °C and then firing at 1000 °C. The cross sections of the resulting half-cells were investigated using a scanning electron microscopy (SEM, FE-SEM, S-4200, Hitachi). The image analysis was performed using software (Lica Qwin) to determine the porosity depending upon the paste compositions using with SEM images of the polished cross sections.

For the measurement of electrochemical reduction activity, the Pt 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 Pt current lead line was contacted with the Pt layers at both sides and the cells were fired at 1000 °C, 1 h [12]. The cells were mounted on an alumina tube reactor and electrochemical impedance characterizations were performed at the temperatures from 750 °C to 850 °C in 50 °C

Table 1
Physical and chemical characteristics of three synthesized powders by a polymerizable complex method

Powder	Calcination temperature (°C)	Compositions confirmed by ICP	Mean particle size (μ m)	Standard deviation (μ m)	Surface area (m ² /g)
LSM–YSZ	1000	La _{0.85} Sr _{0.15} MnO ₃ –8 mol% Y ₂ O ₃ /92 mol% ZrO ₂	0.24	0.11	2.53
LSM	800	La _{0.85} Sr _{0.15} MnO ₃	0.21	0.06	15.82
LSCF	800	La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	0.11	0.05	11.59

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 min after the desired temperature was reached. Variation of polarization resistances for two identically prepared cells was less than 5%. Impedance spectra obtained in the frequency range of 0.03 Hz–100 kHz, and the applied ac voltage amplitude was set to 20 mV.

3. Results and discussion

Fig. 1 shows the SEM images for LSM–YSZ layer derived from the particulate pastes involving different composite particles. It was observed that the LSM–YSZ layer made from the co-pyrolyzed powders shows well connected pore structure of submicron pore sizes. The porosity was determined to $\sim 25\%$. On the other hand, relatively dense LSM–YSZ layer was obtained for the paste involving the mechanically mixed LSM–YSZ powders and the coated powder-derived layer. The porosity of each cathode layer was 18% and 20%, respectively. Beside the microstructure observation, a degree of the compositional uniformity also varied depending upon the type of the LSM–YSZ powders as determined by EDX analyses, which were not shown here. The LSM and YSZ phases were not homogeneously distributed for the mechanically mixed powders, whereas two other LSM–YSZ layers exhibited similar distribution in which the two phases were well mixed at the microscale.

Effect of microstructural features on the electrode performance can be evaluated by an impedance spectroscopy. It is a powerful method to understand 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.

The interfacial polarization resistances were resolved for the electrochemical cells with different LSM–YSZ layers, which were summarized in Table 3. It increased with the decreasing measurement temperature regardless the types of the cells due to depreciation of oxygen conduction and catalytic activity. The multilayered composite cathode involving the co-pyrolyzed LSM–YSZ powders exhibited higher

electrocatalytic activity toward the oxygen reduction as characterized by the lowest polarization resistance $\sim 1.63 \Omega \text{ cm}^2$ at 750°C as compared to the other cells (Fig. 2b). Higher polarization resistance of $6.84 \Omega \text{ cm}^2$ was obtained for the cell with the mechanically mixed LSM–YSZ powders, while $2.99 \Omega \text{ cm}^2$ for the cell with the coated LSM–YSZ powders at 750°C . These results were directly correlated with the

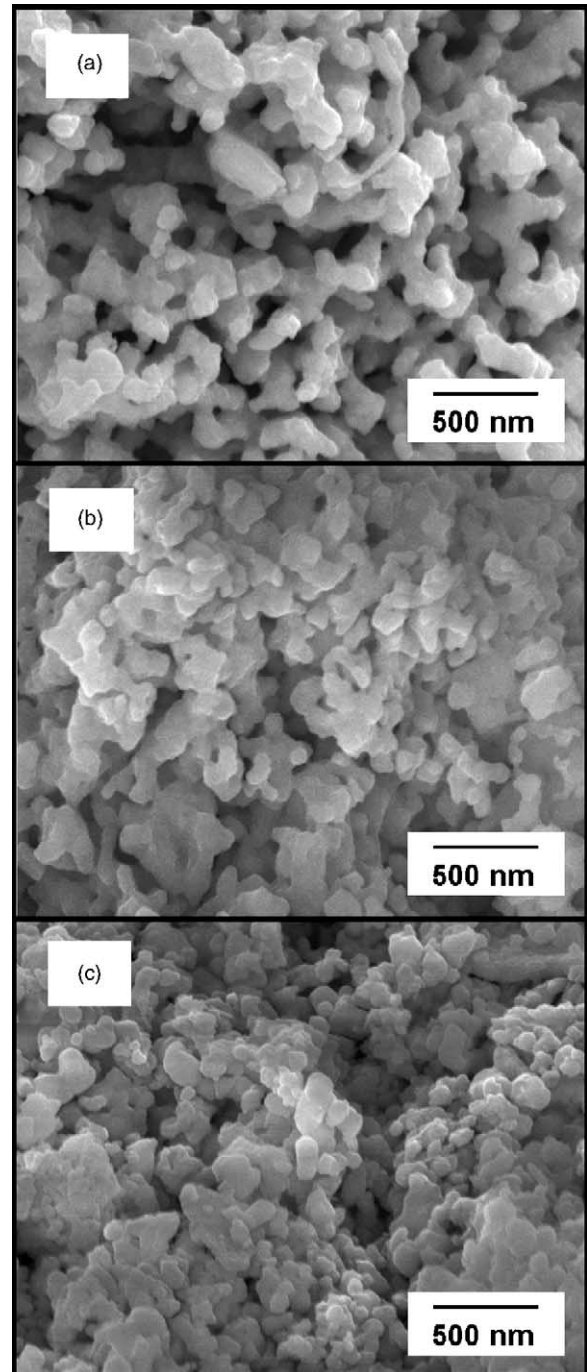


Fig. 1. The cross sectional SEM images for the LSM–YSZ layers derived from three different pastes involving the composite particles: (a) the co-pyrolyzed powders; (b) the coated powders; and (c) the mixed powders. The firing temperature was 1000°C , 3 h.

Table 3

Interfacial polarization resistances measured at different temperatures for the multilayered cathodes in which the bottom layers were prepared with different LSM–YSZ powders

Powder type	850°C	800°C	750°C
Co-pyrolyzed LSM–YSZ ($\Omega \text{ cm}^2$)	0.19	0.58	1.63
Coated LSM–YSZ ($\Omega \text{ cm}^2$)	0.47	1.19	2.99
Mixed LSM–YSZ ($\Omega \text{ cm}^2$)	0.80	2.40	6.84

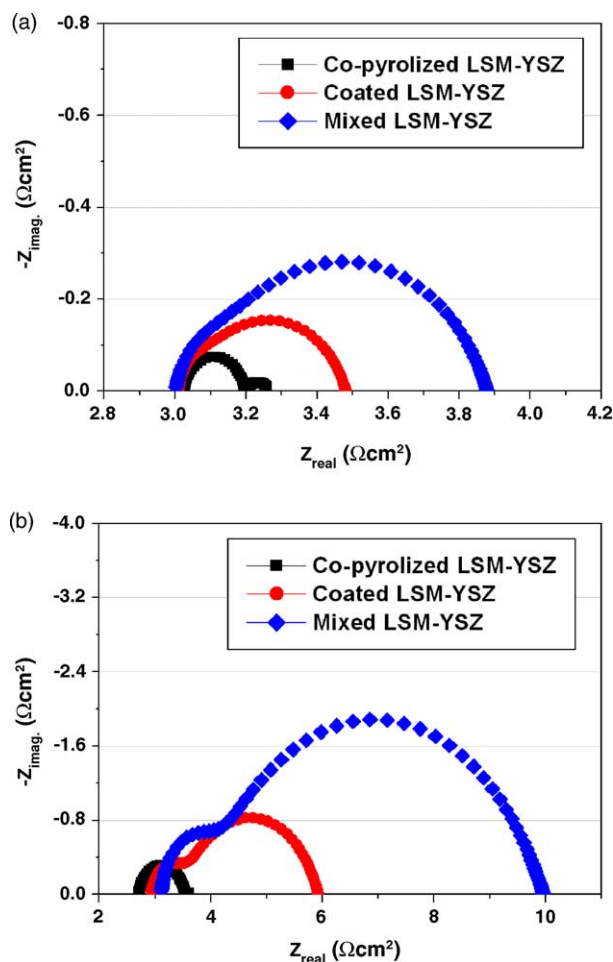


Fig. 2. Impedance spectra for three different cells involving the multilayered composite cathode in which various LSM–YSZ powders were used. The spectra were measured at (a) 850 °C and (b) 750 °C in air.

microstructural features of the composite cathodes. The cell involving the bottom LSM–YSZ layer in which sufficient porosity is present and the ionic and electron conducting phases are uniformly distributed reveals higher cathodic performance. This improvement can be attributed to an increased

length of the triple phase boundary in a porous electrode structure.

Electrocatalytic activity of the cathode can be further enhanced by introducing a nanopore structure within the composite electrode. The microstructures of the LSM–YSZ layer prepared from the polymeric resin-added pastes with the varying mixture ratios are shown in Fig. 3. The porosity of two prepared cathode layer is almost similar as 21%. The LSM–YSZ layer derived from the paste containing the co-pyrolyzed powder:the resin = 8:2 displayed similar microstructure as those prepared from the powder-based pastes as shown in Fig. 3b. In contrast, Fig. 3a show that the cathode layer has uniform nanoporous structures as the portion of the resin increased to 50 wt.%. Polymeric complex resin decomposes into relevant metal hydrous oxides or hydroxides that subsequently transform into the desired crystalline metal oxide compounds. Such a transformation can be utilized to produce a nanoporous electrode in which the length of the triple phase boundary is significantly extended. However, the large pore ‘valley’ was occasionally observed in the polymeric resin-derived cathode layer because of non-uniform volumetric shrinkage associated with the difference between the particulate materials and the polymeric resins. The addition of higher amount of the resin may weaken the resulting layer due to excess weight loss. Therefore, a mixture ratio of the powder and the polymeric resin must be well-controlled to achieve the nanoporous robust electrode with sufficient overall porosity required for better electrocatalytic reaction.

Influence of the nanoporous microstructure on the cathodic performance was investigated for the electrochemical cells involving three different polymeric resin-derived LSM–YSZ. Fig. 4 shows a cross sectional view of the multilayered LSM–YSZ/LSM/LSCF cathode in the *Cell 3* fabricated by screen printing. It was shown that the cathode layer is adhered to the electrolyte and the particles themselves are well connected each other. The composite electrode had a relatively uniform thickness of $\sim 30 \mu\text{m}$ without a delamination in which each layer was approximately $10 \mu\text{m}$. The detailed microstructural features associated with each layer are

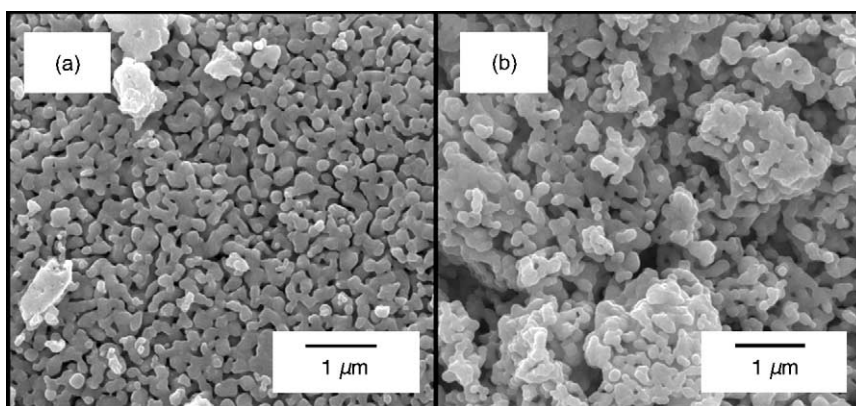


Fig. 3. The cross sectional SEM images for the LSM–YSZ layers derived from the polymeric resin-added pastes with the varying powder to the resin ratio: (a) 5:5 paste and (b) 8:2 paste.

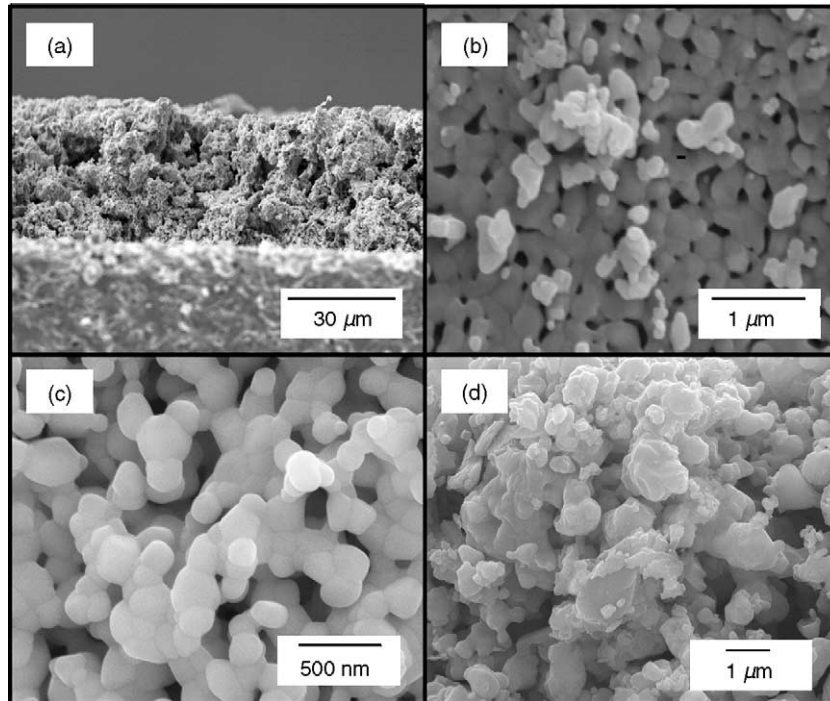


Fig. 4. SEM micrographs showing cross sectional view of the multilayered LSM–YSZ/LSM/LSCF cathodes (Cell 3): (a) the entire cathode; (b) the LSM–YSZ layer; (c) the LSM layer; and (d) the LSCF layer.

presented in high-magnification SEM images of Fig. 4b–d. The multilayered cathode had a grade microstructure in which a nanoporous LSM–YSZ catalytic layer of 50–100 nm in pore size was in contact with the LSM intermediate layer of high level of interconnected porosity of 100–250 nm in pore size, followed by the current collecting LSCF gas permeable layer of three-dimensionally interconnected macro pores of 1–2 μm.

Impedance spectra were analyzed for three cells listed in Table 2 and the polarization resistance for each cell was shown in Fig. 5. It was determined that the interfacial polarization of the cell decreased with the increasing polymeric resin content. The catalytic activity toward the reduction of the oxygen significantly improved as indicated by the diminished polarization resistances from 4.01 Ω cm² to 0.97 Ω cm² at 750 °C when the LSM–YSZ layer was made from the polymeric resin-added paste of higher resin ratio. However, relatively high resistance was observed for the Cells 1 and 2 that were prepared from the polymeric resin-added paste at lower resin ratio. Electrochemical performance was even worse than the cathode layer without the resin (i.e., the copolymerized LSM–YSZ).

It is considered that this results from inhomogeneous microstructure of the electrode. The polymeric resin introduced as a nanopore former undergoes significant volumetric shrinkage together with weight loss, so that its relative amount to the powder strongly influences the sintered microstructure of the electrode. When small amount of the resin is added in the cathode paste, the resin transforms

into an isolated nanoporous domain, which disturbs the continuous connectivity of the particulate phase during sintering as shown Fig. 3b. If proper amount of the resin exists in the paste, the three dimensionally well connected nanopore structure (Fig. 3a) is intimately mixed with the particulate neck structure of larger pore sizes. However, the presence of the excess resin (i.e., more than the powder to the resin ratio = 5:5) weakens the structural integrity of the electrode as well as the introduction of many larger pores and even cracks. Therefore, the Cell 3 in which

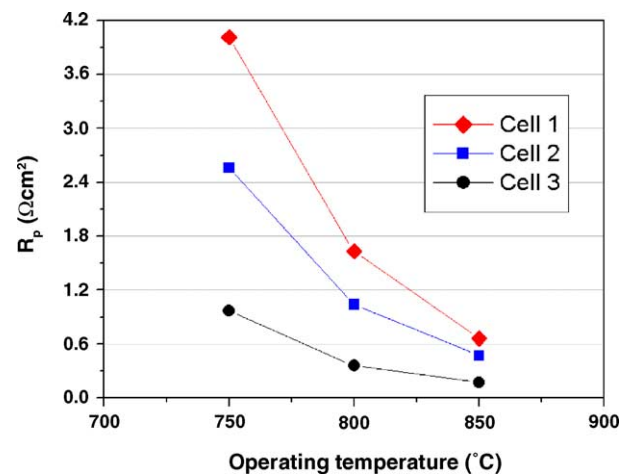


Fig. 5. The impedance spectroscopy of three cells in Table 2 measured at the varying temperatures of 750–850 °C in air.

LSM–YSZ layer is characterized by three dimensionally interconnected pore structures with high specific surface area exhibits better electrochemical performance at lower temperatures.

4. Conclusions

The multilayered composite cathodes derived from a polymeric resin for SOFC were investigated. Special attention was focused on the microstructural influence of the LSM–YSZ catalytic layer on the electrochemical activity. The spatial distribution of ionic and electron conducting phases and their microstructures play an important role in determining the electrocatalytic activity of the cathode. The use of the co-pyrolyzed composite powders enabled us producing the uniform LSM–YSZ layer with relatively sufficient porosity, which exhibited lower interfacial resistances as compared to the cells made from either the coated or mechanically mixed powders. The microstructure of the cathode could be further improved by adding the polymeric resin to the powder-based paste materials. Nanoporous LSM–YSZ catalytic layer of high porosity and large surface area was formed as the polymeric resin decomposed. The electrochemical performance of such a polymeric resin-derived cathode displayed significant lower interfacial resistances of $\sim 0.97 \Omega \text{ cm}^2$ measured at 750°C in air.

Acknowledgements

This work was supported by the Core technology Development Program for Fuel Cell of Ministry of Science and Technology and Korea Institute of Science and Technology Evaluation and Planning.

References

- [1] B.C.H. Steele, *Solid State Ionics* 129 (2000) 95–110.
- [2] S.C. Singhal, *Solid State Ionics* 135 (2000) 305–313.
- [3] B.C.H. Steele, K.M. Hori, S. Uchino, *Solid State Ionics* 135 (2000) 445–450.
- [4] T. Tasi, S.A. Barnett, *Solid State Ionics* 93 (1997) 207–217.
- [5] E.P. Murry, S.A. Barnett, *Solid State Ionics* 143 (2001) 265–273.
- [6] Y. Liu, C. Compson, M. Liu, *J. Power Sources* 138 (2004) 194–198.
- [7] N.T. Hart, N.P. Brandon, M.J. Day, N. Lapena-Rey, *J. Power Sources* 106 (2002) 42–50.
- [8] M.J.L. Ostergard, C. Clausen, C. Bagger, M. Mogensen, *Electrochim. Acta* 40 (1995) 1971–1981.
- [9] C. Xia, W. Rauch, W. Wellborn, M. Liu, *Electrochem. Solid State Lett.* 5 (2002) A217–A220.
- [10] M. Popa, J. Frantti, M. Kakihana, *Solid State Ionics* 154–155 (2002) 437–445.
- [11] M. Kakihana, M. Arima, M. Yoshimura, N. Ikeda, Y. Sugitani, *J. Alloys Compd.* 283 (1999) 102–105.
- [12] 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 (2001) 379–389.