A Study on Sintering Inhibition of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ Cathode Material for Cathode-Supported Fuel Cells

Bilal Ahmed***, Seung-Bok Lee***†, Rak-Hyun Song***, Jong-Won Lee***,
Tak-Hyoung Lim***, and Seok-Joo Park***

*Fuel Cell Research Center, Korea Institute of Energy Research, Daejeon 34129, Korea

**Department of Advanced Energy Technology, University of Science and Technology, Daejeon 34113, Korea

(Received August 12, 2016; Accepted September 7, 2016)

ABSTRACT

In this work, the effects of different sintering inhibitors added to $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) were studied to obtain an optimum cathode material for cathode-supported type of Solid oxide fuel cell (SOFC) in terms of phase stability, mechanical strength, electric conductivity and porosity. Four different sintering inhibitors of Al_2O_3 , CeO_2 , NiO and gadolinium doped ceria (GDC) were mixed with LSM powder, sintered at 1300°C and then they were evaluated. The phase stability, sintering behavior, electrical conductivity, mechanical strength and microstructure were evaluated in order to assess the performance of the mixture powder as cathode support material. It has been found that the addition of Al_2O_3 undesirably decreased the electrical conductivity of LSM; other sintering inhibitors, however, showed sufficient levels of electrical conductivity. GDC and NiO addition showed a promising increase in mechanical strength of the LSM material, which is one of the basic requirements in cathode-supported designs of fuel cells. However, NiO showed a high reactivity with LSM during high temperature (1300°C) sintering. So, this study concluded that GDC is a potential candidate for use as a sintering inhibitor for high temperature sintering of cathode materials.

Key words : Cathode support, Sintering inhibition, SOFC

1. Introduction

Sr²⁺ substituted lanthanum manganite perovskite oxides ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$, LSM) have been widely studied because of their fascinating applications in oxi-reduction catalysts, ceramic fuel cells, sensors and memories.¹⁻⁶⁾ LSM is extensively used as cathode material for solid oxide fuel cells (SOFCs) because it offers high electronic conductivity, high catalytic activity for oxygen reduction and chemical and thermal compatibility with commonly known electrolytes such as yttria-stabilized zirconia (YSZ) and gadolinium doped ceria (GDC) at the operating temperatures.²⁾

In SOFCs, LSM-based materials are mostly used in electrolyte-supported and anode-supported configurations in which a thin cathode layer is coated over a sintered electrolyte layer and the whole cell assembly is co-fired at $1000 - 1100^\circ\text{C}$. However, the electrolyte – supported cell configuration is not preferred because most of the ohmic loss comes from the resistance of the thick electrolyte layer; the anode – supported cell configuration has the disadvantages of redox cycling and microstructural degradation during fabrication and operation. To solve these problems, cathode – supported cell designs are most commonly used because

cathode – supported cells do not suffer from redox cycling or microstructural degradation. Moreover, the low cost of LSM-based cathode materials gives these materials a potential advantage in the commercialization of SOFCs.

However, cathode – supported designs require co-firing of the cathode substrate with an electrolyte layer at high temperatures ($1300 - 1400^\circ\text{C}$) to obtain a dense electrolyte layer; however, due to the low sintering temperature of LSM materials, co-firing with an electrolyte is not possible. Some groups have reported cathode – supported cell configurations that have used LSM/YSZ composites as cathode support material; however, LSM reacts with zirconia based electrolytes (YSZ and ScSZ) and forms insulating phases such as $\text{La}_2\text{Zr}_2\text{O}_7$ (LZO) and SrZrO_3 (SZO) during co – firing at temperatures over 1100°C . Therefore, LSM can be used as a cathode support material only if the sintering temperature is increased from the usual sintering temperature and undesirable phase formation between LSM and YSZ is avoided.

In the present study, we have approached this problem by employing different sintering inhibitors and studying the effect of the addition of sintering inhibitors on the electrical conductivity, sintering behavior, chemical compatibility and mechanical strength of LSM. Al_2O_3 , CeO_2 , NiO and GDC were added as sintering inhibitors and mixtures of LSM + the respective sintering inhibitor were sintered at 1300°C .

†Corresponding author : Seung-Bok Lee

E-mail : sblee@kier.re.kr

Tel : +82-42-860-3466 Fax : +82-42-860-3180

2. Experimental Procedure

Commercially available $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM; Fuel Cell Materials, USA) was used as base material for this study. Four different sintering inhibitors including Al_2O_3 (Aluminum Oxide, Sigma-Aldrich, Co. LLC.), CeO_2 (Cerium (IV) Oxide, Sigma-Aldrich, Co. LLC.), $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (Gadolinia doped Ceria, GDC; Fuel Cell Materials, USA) and NiO (Nikel Oxide Powder, Fuel Cell Materials, USA) powders were used to study the effect of the addition of sintering inhibitors to the LSM. Four composite compositions were prepared with 80 wt.% of LSM and 20 wt.% of the corresponding sintering inhibitor. Mixtures were ball-milled in ethanol for 48 h and dried at 90°C. The dried powders were sieved through a mesh with a size of 100 μm and pelletized in the form of bars via uniaxial pressing at 250 MPa for 45 sec. The bar type pellets were sintered at 1300°C for 5 h in air before characterization. Bar type pellets with dimensions of 2 mm $\times$ 6 mm $\times$ 25 mm were used for electrical and mechanical properties assessment, while cylindrical pellets with diameters of 8 mm and heights of 2.1 mm were fabricated to study the sintering behavior and the thermal expansion coefficient.

Chemical stability of the sintered powders was examined using an automated Rigaku diffractometer (2500 D/MAX; Rigaku, Japan) with Cu-K_α radiation. The data were recorded over a scanning angle range of 20° to 80° using a step width of 0.025° and a holding time of 5 s. The sintering behavior was analyzed using a dilatometer (DIL 402C; Netzsch GmbH, Germany) in a temperature range from 30 to 1400°C with a heating rate of 2°C/min. The surface morphology of the sintered samples was observed via scanning electronic microscopy (S-4700; Hitachi Ltd., Japan). Before the scanning electronic microscopy measurements, the samples were polished and thermally etched at 1200°C.

The flexural strengths of the composite materials were determined using the three-point flexural test technique, in which a rectangular sample is bent until a fracture occurs. The specimen was bent at a crosshead speed of 1 mm/min using a universal test machine (Instron 5544A; Instron Corp., USA). In order to avoid stress concentration at any specific point, the specimens were polished prior to testing in order to remove surface scratches. The porous structures of the sintered samples were characterized using a Mercury Porosimeter (AutoPore 9500; Micromeritics, USA). The electrical conductivity was measured in air using the DC four-probe technique (Keithley 2400; Keithley, USA) over a temperature range of 500 to 900°C; the electrical contacts were created with Pt wires and Pt paste.

3. Results and Discussion

3.1. Electrical Conductivity

In SOFCs, pure oxygen or oxygen from air is reduced into oxygen ions at the cathode side after receiving electrons coming from the anode side. Therefore, one of the prime

requirements for a cathode material is electronic conductivity. The electrical conductivity levels of pure LSM and of sintering inhibitor added LSM were measured in oxygen atmosphere. Fig. 1 shows the electrical conductivity levels of pure LSM, LSM + 20 wt.% GDC, LSM + 20 wt.% CeO_2 , LSM + 20 wt.% NiO and LSM + 20 wt.% Al_2O_3 at different temperatures. The electrical conductivity of pure LSM the highest among all samples; the electrical conductivity decreases with the addition of a sintering inhibitor. The electrical conductivity consists of electronic conductivity and ionic conductivity. In the case of pure LSM, the total electrical conductivity is considered simply to be the electronic conductivity because LSM does not conduct ions. However, in the case of sintering inhibitor added LSM, the electrical conductivity comes from the electronic conductivity of LSM and the ionic conductivity of Al_2O_3 , NiO, GDC and CeO_2 . But, as the ionic conductivities of the abovementioned sintering inhibitors are very low, one can easily conclude that the major contribution to the electrical conductivity is the electronic conductivity of LSM. On the other hand, decreases in electrical conductivity can be explained in terms of sintering inhibition of LSM. With the addition of sintering inhibitors, LSM is not completely sintered and this results in lower values of electrical conductivity.

The graph also shows that the addition of Al_2O_3 severely affects the electrical conductivity; the electrical conductivity of the LSM/ Al_2O_3 mixture dropped drastically. In a way, Al_2O_3 acts as the most effective sintering inhibitor but any material with an electrical conductivity less than 100 S/cm cannot be used as an electrode material in fuel cells. On the other hand, mixtures of LSM and GDC, NiO and CeO_2 show conductivity levels between 100 - 175 S/cm; therefore, in terms of electrical conductivity, any of the above mentioned mixtures can be used as a cathode material in direct carbon fuel cells, except Al_2O_3 . The Arrhenius plots of the electrical

Fig. 1. Plots of the electrical conductivities for pure LSM and sintering inhibitor added LSM after sintering at 1300°C at various temperatures.

Fig. 2. Arrhenius plots of the electrical conductivities of the pure LSM and sintering inhibitor added LSM after sintering at 1300°C.

conductivity for the mixtures of LSM and different sintering inhibitors are presented in Fig. 2. The linear relationships between $\ln(\sigma T)$ and $1/T$ demonstrate that the electronic conductivity follows the small polaron conduction principle in the 550°C to 850°C temperature range.

3.2. Mechanical Characterization

The cathode substrate in cathode – supported fuel cells should have a high level of mechanical strength because the electrolyte and anode layers are coated over the cathode support and the cathode support acts as a basic structural unit. The mechanical strengths of pure LSM and sintering inhibitor added LSM were assessed by three point bending tests. Mechanical strength was defined as the maximum value of the stress on the recorded load-strain curve just prior to the fracture point.

It is well-known that the strength values of brittle ceramics show a large variation; this type of strength variation is expressed by the Weibull distribution,^{7,8)} which is based on the "weakest link theory," which implies that the most critical flaw in a sample controls the failure rate and the mechanical strength. From the Weibull distribution, we can evaluate the characteristic strength (σ_0) and the Weibull modulus (m). The Weibull modulus (m) determines the reliability of a material's strength data; a higher value of m corresponds to a higher reliability of the measured data.

Figure 3 presents Weibull plots for the pure LSM and the sintering inhibitor added LSM after sintering at 1300°C. The linear relationship between $\ln\{1/(1-P)\}$ and $\ln(\sigma)$ is the key feature of Weibull distribution. The characteristic strength (σ_0) and Weibull modulus (m) are presented in Table 1. Interestingly, the Weibull distribution shows that additions of Al_2O_3 and CeO_2 have almost the same effect on the mechanical strength; the strength decrease values for the LSM mixtures of CeO_2 and Al_2O_3 are almost the same. However, with the addition of GDC and NiO, the strength

Fig. 3. Weibull plots determined from the three point flexural strength distributions of pure LSM and sintering inhibitor added LSM after sintering at 1300°C.

Table 1. Weibull Parameters for the Pure LSM and Sintering Inhibitor Added LSM Mixtures after Sintering at 1300°C

Sample Name	Characteristic Strength (MPa)	Weibull Modulus (m)
Pure LSM	46.54	4.24
LSM + 20 wt.% Al_2O_3	27.21	5.17
LSM + 20 wt.% CeO_2	27.70	6.32
LSM + 20 wt.% NiO	60.92	4.98
LSM + 20 wt.% GDC	47.73	4.48

value increased and the LSM + 20 wt.% NiO sample yielded the maximum strength value of 60.9 MPa. The mechanical strength will be further correlated with the microstructure and porosity of the sintering inhibitor added LSM.

3.3. Porosity Measurements

To transport oxygen gas and overcome concentration losses, a cathode substrate should have a sufficient level of porosity after sintering at high temperatures. Therefore, the porosity levels of pure LSM and of sintering inhibitor added LSM were measured using a Mercury Porosimeter; results are presented in Fig. 4. As was anticipated, the porosity increased with the addition of sintering inhibitors because additions of NiO, GDC, Al_2O_3 and CeO_2 retard the sintering of LSM grains, resulting in porous sintered specimens.

It is worth mentioning that these porosity results are in close agreement with the electrical and mechanical data presented in earlier sections. The addition of Al_2O_3 to LSM led to the highest level of porosity, which is ~ 17%. One can easily conclude that this high level of porosity is responsible for the low mechanical strength and electrical conductivity. Similarly, the CeO_2 added LSM mixture also showed porosity of ~ 12%, which again must be responsible for the decrease in mechanical strength. On the other hand, GDC

Fig. 4. Porosity of the pure LSM and sintering inhibitor added LSM after sintering at 1300°C determined by Mercury porosimeter.

and NiO showed porosity levels of 8% and 4%, respectively.

3.4. Sintering Behavior Study

The sintering behaviors of the pure LSM and of the sintering inhibitor added LSM were studied using a dilatometer. Dilatometric data can be used to determine the sintering temperature, amount of shrinkage and thermal expansion behavior of the mixture powder. The dilatometric analysis was carried out in air from room temperature to 1400°C. Fig. 5 shows the dilatometric sintering curves for the pure LSM and for the prepared mixture of LSM and sintering inhibitors. The sintering curve can be divided into two distinct regions: from room temperature to 900°C, shrinkage was not detectable; from 900°C to 1400°C, sintering process proceeded along with shrinkage. As anticipated, sintering temperature increases with the addition of sintering inhibitors and amount of shrinkage varies from 15 - 19%. The observed sintering temperatures of the LSM + 20 wt.% NiO and the LSM + 20 wt.% GDC were 1080 and 1075°C, respectively. The dilatometric data confirmed the hypothesis made earlier in the section on electrical conductivity of sintering inhibition of LSM via the presence of added Al₂O₃, CeO₂, GDC and NiO.

3.5. X-Ray Diffraction Analysis

X-ray diffraction analysis was carried out to determine whether the sintering inhibitors being used in this study are chemically compatible with LSM after sintering at high temperature. For this purpose, the XRD patterns of pure LSM, pure GDC, pure NiO, pure Al₂O₃, pure CeO₂ and mixtures of LSM and sintering inhibitors are presented in Fig. 6(a) - (d). Fig. 6(a) shows the XRD patterns for pure LSM, pure GDC and LSM + 20 wt.% GDC after sintering at 1300°C. The XRD pattern of the mixture of

Fig. 5. Dilatometric sintering curves for pure LSM and sintering inhibitor added LSM.

LSM and GDC shows that all peaks correspond to either LSM or GDC, which means that no secondary phases are formed after sintering at high temperatures. Similarly, the mixture of LSM and CeO₂ showed identical behavior. There are no reactions between LSM and CeO₂ even after sintering at 1300°C. On the other hand, the mixtures of LSM with NiO and Al₂O₃ showed the formation of some secondary phases during the sintering process. This feature indicates that LSM does not react with ceria – based materials but does react with NiO or Al₂O₃.

3.6. Microstructural Analysis

Figure 7(a) - (e) present the surface morphologies of the pure LSM and of the sintering inhibitor added LSM after sintering at 1300°C in air. Fully sintered LSM grains, with a large grain size, are shown in Fig. 7 (a), while a two-phase microstructure is shown in Fig. 7 ((b) and (c)). In the two-phase structure, the dark phase corresponds to LSM and the light phase corresponds to GDC.

It is obvious from the grain size that GDC and NiO inhibit the sintering of LSM materials and that the resulting grain size is much smaller than that seen in pure LSM grains. The reason for this grain growth restriction is that GDC and NiO both have high sintering temperatures (> 1400°C) and they prohibit LSM sintering. Another interesting feature is that, as can be seen in Fig. 7(c), LSM and NiO phases constitute a network of LSM and NiO grains. In addition to having a lower level of porosity, this network like structure is the reason for the high mechanical strength values exhibited by the LSM + NiO mixture. It can be predicted that, in the LSM + NiO composite, NiO will be the component responsible for the strength, and the mechanical strength will be far higher than that of pure LSM materials.

4. Conclusions

In this work, the addition of different sintering inhibitors

Fig. 6. X-ray diffraction patterns for pure LSM, pure GDC, pure NiO, pure Al_2O_3 , pure CeO_2 and mixtures of LSM with GDC, NiO, Al_2O_3 and CeO_2 after sintering at 1300°C for 5 h.

Fig. 7. Scanning electron micrographs of the fracture surfaces of (a) pure LSM, (b) LSM + 20 wt.% GDC, (c) LSM + 20 wt.% NiO, (d) LSM + 20 wt.% CeO_2 and (e) LSM + 20 wt.% Al_2O_3 after sintering at 1300°C .

to LSM was studied to obtain a cathode material with high sintering temperature. Al_2O_3 , CeO_2 , NiO and GDC were mixed with LSM powder and sintered at 1300°C . Sintering inhibition study of LSM cathodes indicated that Al_2O_3 is the most effective sintering inhibitor in terms of sintering retardation and porous structure, but with higher level of porosity, electrical conductivity and mechanical strength

decreased drastically, which is highly undesirable in case of cathode support materials. Similarly, CeO_2 cannot be used because of lower mechanical strengths, although it provided sufficient level of electrical conductivity and porosity. Chemical compatibility studies carried out by XRD analysis, indicated that NiO is not compatible with LSM materials and forms undesirable secondary phases. GDC was selected as

optimum sintering inhibitor because it provided sufficient level of electrical conductivity, mechanical strength and porosity along with chemical stability after high temperature sintering. So, finally we concluded that GDC are potential candidates for use as sintering inhibitors for high temperature sintering of cathode materials

Acknowledgements

This work was conducted under the framework of the research and development program of the Korea Institute of Energy Research (B6-2517).

REFERENCES

- 1 D. Cao, Y. Sun, and G. Wang, "Direct Carbon Fuel Cell: Fundamentals and Recent Developments," *J. Power Sources*, **167** [2] 250-57 (2007).
- 2 A. Gondolini, E. Mercadelli, P. Pinasco, C. Zanelli, C. Melandri, and A. Sanson, "Alternative Production Route for Supporting $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ - $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (LSM-GDC)," *Int. J. Hydrogen Energy*, **37** [10] 8572-81 (2012).
- 3 C. W. Sun, R. Hui, and J. Roller, "Cathode Materials for Solid Oxide Fuel Cells: A Review," *J. Solid State Electrochem.*, **14** [7] 1125-44 (2010).
- 4 H. Y. Lee and S. M. Oh, "Origin of Cathodic Degradation and New Phase Formation at the $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3/\text{YSZ}$ Interface," *Solid State Ionics*, **90** [1] 133-40 (1996).
- 5 W. Wang, M. D. Gross, J. M. Vohs, and R. J. Gorte, "The Stability of LSF-YSZ Electrodes Prepared by Infiltration," *J. Electrochem. Soc.*, **154** [5] B439-45 (2007).
- 6 S. P. Simner, J. P. Shelton, M. D. Anderson, and J. W. Stevenson, "Interaction between $\text{La}(\text{Sr})\text{FeO}_3$ SOFC Cathode and YSZ Electrolyte," *Solid State Ionics*, **161** [1] 11-8 (2003).
- 7 N. M. Sammes, R. Ratnaraj, and M. G. Fee, "The Effect of Sintering on the Mechanical Properties of SOFC Ceramic Interconnect Materials," *J. Mater. Sci.*, **29** [16] 4319-24 (1994).
- 8 J. M. Villora, P. Callejas, M. F. Barba, and C. Baudin, "Statistical Analysis of the Fracture Behavior of Porous Ceramic Raschig Rings," *J. Eur. Ceram. Soc.*, **24** [3] 589-94 (2004).