

The effect of reduction atmosphere on the LaGaO₃-based solid oxide fuel cell

Jae Yeon Yi and Gyeong Man Choi*

Department of Materials Science and Engineering, Pohang University of Science and Technology, San 31, Hyoja-dong, Pohang, 790-784, South Korea

* Corresponding author

Abstract

Chemical stability of La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) as an electrolyte for solid oxide fuel cells (SOFCs) was investigated during the electrochemical measurement. At low oxygen-partial pressure (0.003 atm), the LSGM electrolyte partly decomposed due to the development of high overpotential, and thus the induced reduction atmosphere near cathode. The morphology of LSGM grain near cathode changed due to the formation of new phases. The main decomposition phases were La₂O₃, La(OH)₃, and LaSrGaO₄. The polarization conductance increased due to the microstructural change in LSM and thus the increase in the specific area of the LSM electrode.

Keywords : SOFC(E), LaGaO₃, Electrical conductivity(C), Decomposition, Chemical stability

1. Introduction

The solid oxide fuel cells are under development for the generation of electricity with little environmental pollution. Since lowering the operating temperature has many advantages, such as the broad choice of cheap interconnect materials and the long-term stability of cell components, much efforts thus have been concentrated on finding an electrolyte material with higher ion conductivity than YSZ (Ytria Stabilized Zirconia) that is commercially used as an electrolyte for SOFCs [1-3].

An electrolyte for SOFCs is required not only to have high oxygen-ion conductivity but also to have a high stability under severe operating conditions, such as high temperature and large oxygen-partial pressure (Po₂) gradient for a long time. Previous studies [4-7] showed the degradation of LSGM electrolyte during sintering at high temperature or operating in reducing atmosphere. LSGM easily decomposes, especially when sintered at temperature greater than 1600 °C, due to the tendency of gallium (III) oxide reduction to gallium (I) oxide [4]. Yamaji et al. [5-7] examined the chemical stability of LSGM in reducing atmosphere. They showed that the migration of Si and Al from Pyrex sealant and Pt from electrode into the surface of LSGM electrolyte gives rise to the depletion of Ga from LSGM electrolyte [5]. The reaction of Ga₂O₃ with H₂ in very low Po₂ resulted in the formation of Ga₂O and H₂O (vaporization of Ga) [6]. Doping of lanthanum gallate with Sr and the existence of Pt enhanced the depletion of Ga from the electrolyte in the reducing atmosphere [7].

Examination of Po₂ dependence of overpotential is one method to determine the reduction mechanism of LSGM. As Po₂ decreases, the cathodic overpotential increases with applied current. High cathodic overpotential tends to reduce the electrolyte. However, the effect of high potential on the cathode and electrolyte due to the applied current is not yet clear for LSGM electrolyte-based fuel cells. In this study, the change in cathode performance and electrolyte properties under high overpotential condition was examined.

2. Experimental

Stoichiometric amount of La₂O₃ (99.99%, Strem Chemicals, USA), SrCO₃ (99.9%, High Purity Chemicals, Japan), and Mn₂O₃ (99.9%, High Purity Chemicals) powders were mixed to prepare LSM (La_{0.9}Sr_{0.1}MnO₃) electrode, and La₂O₃, SrCO₃, Ga₂O₃ (99.9%, High Purity Chemicals), and MgO (99.9%, High Purity Chemicals) powders for LSGM electrolyte.

The powder mixtures were ball-milled with zirconia balls in distilled water for 12 h, and calcined at 1200 °C for 6 h. The calcined LSGM powder was formed into disc-shape by die pressing, followed by cold isostatic pressing at 200 Mpa and sintering at 1500 °C for 6 h in air with the heating/cooling rate of 3 °C/min. Sintered LSGM pellet was sliced into thin disks of ~ 500µm.

The calcined LSM powders was screen-printed on LSGM electrolyte and heat treated or sintered at 1300 °C in air for 2 h. Three-electrode configuration cells were fabricated; the working electrode is a cathode under investigation and the counter and the reference electrodes are platinum on the opposite side of the working electrode. The cell was heated for 1 h at 1000 °C after Pt pasting (Engelhard No. 6926, USA). Pt mesh (Aldrich 52 mesh, USA), as a current collector, was bonded at 1000 °C for 1 h to three electrodes.

The ohmic- and the over-potential values were measured by using a current interruption device (Doosung Induction, DSI-10, Korea), a current source (Solartron, SI 1287, UK) and digitizing oscilloscope (Tektronix, TDS 3032, USA). The electrochemical measurement was performed between 800 and 900 °C in Po₂ between 1 and 0.003. The cathodic overpotential changed with time and reached its steady state value within 10 min at high Po₂, and within 1 h at Po₂ = 0.003 atm. Microstructure was observed by a field-emission scanning electron microscope (JEOL, model 6330F, Japan).

3. Results and Discussion

The cathodic overpotential of LSM electrode as a function of current density is shown in Fig. 1. The cathodic overpotential at 1 atm of Po₂ (1 atm (before)) increased slowly as the current density increased. The curves obtained at Po₂ greater than 0.015 atm showed the similar trend as the 1 atm curve. However, at Po₂ = 0.003 atm, the cathodic overpotential increased sharply with current density. Such an increase is often due to a diffusion limiting process. Oxygen cannot be supplied fast enough from cathode to electrolyte with increasing current density. The cathodic overpotential value at 100 mA/cm² of current density was ~ 1.85 V. Hereafter, we refer the measurement under 1.85 V at 800 °C, Po₂ = 0.003 atm as the low Po₂ measurement. The cathodic overpotential value was measured again at 1 atm after the low Po₂ measurement and it (1 atm (after)) was smaller than the initial value (1 atm (before)). The decrease in overpotential after the low Po₂ measurement needs explanation. Gharbage et al. [8] reported that oxygen vacancies were created in the LSM electrode at high polarization, and the cathodic reaction was progressively delocalized over the whole surface of the electrode. During the low Po₂ measurement, specimen was maintained under high overpotential (~1.85 V) and thus oxygen vacancies may have been created in LSM electrode. The Po₂ equilibrated with external electromotive force (e.m.f.) follows the Nernst equation:

$$e.m.f. = -\frac{RT}{4F} \ln \frac{P_{O_2}'}{P_{O_2}''} \quad (1)$$

where R, T, P'_{O₂}, and P''_{O₂} are the gas constant, the absolute temperature, the reference Po₂, and the equilibrated Po₂. Since the reference Po₂ was 0.003 atm and the emf value was 1.85 V, the P''_{O₂} may be as low as 3.65x10⁻³⁶ atm at 800 °C. Such a highly reducing Po₂ enhances the formation of oxygen vacancies in LSM electrode.

The effect of reduction potential on the cathode performance was examined. Fig. 2 shows the temperature dependence of polarization conductance (G_p) at 40 mA/cm² of current density. The polarization conductance was defined as:

$$\frac{1}{G_p} = R_p = \frac{\eta_c}{J} \quad (2)$$

where R_p is the polarization resistance, η_c is the cathodic overpotential and J is the current density.

The polarization conductance at 1 atm increased after the low P_{O_2} measurement at 0.003 atm. The activation energy of G_p of LSM electrode at 1 atm is similar before and after the low P_{O_2} measurement (0.73 ~ 0.75 eV). The reported activation energy values of G_p are known to be varying depending on the combination of electrode and electrolyte. For YSZ electrolyte, $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ electrodes showed 1.87 and 2.28 eV [9], respectively, and $La_{0.8}Sr_{0.2}MnO_3$ -YSZ composite electrode showed 1.49 eV [10]. $La_{0.6}Sr_{0.4}CoO_3$ and $La_{0.9}Sr_{0.1}Ga_{0.5}Ni_{0.5}O_3$ electrodes on LSGM electrolyte showed 0.96 and 1.816 eV [11]. $La_{0.6}Sr_{0.4}Co_{0.98}Ni_{0.02}O_3$, $La_{0.6}Sr_{0.4}CoO_3$ and Pt electrodes on $(CeO_2)_{0.9}(CaO)_{0.1}$ electrolyte showed 0.5, 0.63 and 1.13 eV, respectively [12]. Generally, the electrodes having the charge transfer reaction as the rate-determining step of oxygen reduction show high activation energy of G_p . Thus no electrode composition or oxygen-reduction mechanism has been changed after the low P_{O_2} measurement.

The microstructures of the LSM electrode (a) before and (b) after the low P_{O_2} measurement are shown in Fig.3. After the low P_{O_2} measurement, more porous morphology was shown. The change in electrode morphology was irreversible and the porous morphology after the low P_{O_2} measurement did not convert to its original morphology in oxygen. Since the activation energy of G_p did not change before and after the low P_{O_2} measurement, the change in G_p is due to the microstructural change rather than the compositional change of electrode. The creation of oxygen vacancies and thus the increase in the specific area of the electrode are the reasons for the increase in the polarization conductance.

In order to see the effect of the low P_{O_2} measurement on the electrolyte, the ohmic conductivity of the electrolyte was examined. Fig. 4 shows the temperature dependence of the ohmic conductivity (σ_{ohm}) of half-cell. The ohmic conductivity is defined as:

$$\sigma_{ohm} = \frac{1}{R_{ohm}} \cdot \frac{t}{A} \quad (3)$$

where R_{ohm} is the ohmic resistance of cell determined from current-interruption measurement, t is the electrolyte thickness, and A is the electrode area. The star symbols (ξ) in the figure represent the conductivity measured by using 4-probe d.c. method of the bulk LSGM in other study [13]. Both open and closed square symbols represent those measured from the current-interruption method in this study. Both the magnitude and the activation energy of ohmic conductivity were smaller than those of bulk LSGM. The smaller value of ohmic conductivity of the cell than that of bulk LSGM may partly be due to the reaction layer formed between LSM electrode and LSGM electrolyte during the cell preparation [14]. The reaction product should show much lower conductivity than either LSM or LSGM. The reaction layer is also responsible for the reduced activation energy from the bulk LSGM [13]. In other words, the contribution of the reaction layer to the ohmic resistance is large enough to change the ohmic conductivity of LSGM electrolyte. After the low P_{O_2} measurement, further decrease in ohmic conductivity was observed as shown by open square symbols in Fig. 4. At first, we thought the decrease was due to the additional reaction between LSM electrode and LSGM electrolyte. To verify the reason for the further decrease in ohmic conductivity after the low P_{O_2} measurement, we fabricated and tested the Pt/LSGM/Pt cell (without LSM electrode). Although the Pt/LSGM/Pt cell does not have LSM electrode, the decrease in ohmic conductivity after the low P_{O_2} measurement was also observed. Thus, the additional decrease after the low P_{O_2} measurement is not due to the further reaction between LSM and LSGM but due to the change in LSGM composition during electrochemical measurement.

We have also examined the dependence of the ohmic conductivity on the P_{O_2} . The ohmic conductivity was nearly constant in all P_{O_2} above 0.01 atm. If the migration of B-site ions continues during electrochemical measurement, the ohmic conductivity may vary with P_{O_2} . This proves that there is no further between LSM and LSGM during 800 ~ 900 °C measurement. The change in ohmic conductivity of LSGM occurs only after the low P_{O_2} measurement.

The microstructures of the cell (Pt/LSM/LSGM/Pt) after the low P_{O_2} measurement are

shown in Fig. 5. The LSGM electrolyte near LSM cathode became porous and small grains are shown. In contrast, the original LSGM electrolyte (far right side of Fig. 6b) is dense and has large grains. This porous area was formed due to the decomposition of LSGM electrolyte. Approximately 100 μm away from LSM electrode, needle-shaped phases were newly formed. We named this area as a decomposition front in Fig. 6b. The decomposition front moves away from the LSM/LSGM interface to the counter electrode (Pt) with time during the low Po_2 measurement. For the cells using either 0.4LSM-0.6LSGM composite (Pt/0.4LSM-0.6LSGM/LSGM/Pt) or Pt (Pt/LSGM/Pt) as a cathode, the same decomposition behavior (i. e., porous decomposition layer and needle-shaped phase in decomposition front) was observed. In all cells, decomposition of the LSGM electrolyte initiates near cathode/electrolyte interface. The decomposition front was found at $\sim 80 \mu\text{m}$ from the Pt cathode for the Pt/LSGM/Pt cell. For this cell, the overpotential due to the applied current of $100\text{mA}/\text{cm}^2$ was 1.65 V. The closer location ($\sim 80 \mu\text{m}$) of the decomposition front from cathode for the Pt cathode than that ($\sim 100 \mu\text{m}$) for the LSM cathode is reasonable considering the smaller potential for the Pt cathode (1.65V) than the LSM cathode (1.85V). As the overpotential increases, the reduction of cathode side become more severe and the wider decomposition layer is expected.

During the low Po_2 measurement, the overpotential may be concentrated on the cathode/electrolyte interface due to the higher overpotential than the ohmic potential. The reducing atmosphere as low as 3.65×10^{-36} atm can be developed at the interface for Pt/LSM/LSGM/Pt cell. This reduction potential is possible if the oxygen flow is partially blocked. The reported decomposition Po_2 for LSGM at 800°C is $\sim 10^{-22}$ atm [5, 15]. Thus, we need only $\sim 1.04\text{V}$ to obtain $\sim 10^{-22}$ atm with respect to the counter electrode potential. Although the actual Po_2 at the decomposition front is not clear due to the unknown potential distribution across the cell, the Po_2 at the decomposition front may be as low as 10^{-22} atm when the cathode works as a current limiting or an ion-blocking electrode.

To determine the phases formed in the decomposition layer, the Pt/LSGM/Pt cell was maintained at low Po_2 (0.003 atm) at 800°C , while supplying $100 \text{ mA}/\text{cm}^2$ ($\sim 1.65\text{V}$ overpotential) for ~ 10 h. The resultant cell was crushed and examined by X-ray diffraction. In addition to the original LSGM phase, La_2O_3 , $\text{La}(\text{OH})_3$, and LaSrGaO_4 were observed. It is noted that white powder, observed on the Pt cathode surface, was identified as La_2O_3 and $\text{La}(\text{OH})_3$. These phases probably formed as a result of Ga evaporation on the cathode surface that was exposed to the reducing atmosphere [6, 7]. LaSrGaO_4 is a Sr-rich LaGaO_3 phase. No Mg-excess phase was observed. Mg is probably contained in La_2O_3 or LaSrGaO_4 as a solid-solution component [6].

4. Conclusions

The cathodic overpotential of LSM/LSGM/Pt cell at low Po_2 (0.003 atm) increased sharply as the current density increased due possibly to the limited oxygen diffusion at the cathode. As a result of reduction, the polarization conductance increased due to the formation of porous LSM cathode. However, the ohmic conductivity of the LSGM electrolyte decreased since LSGM electrolyte decomposed in reducing atmosphere. The decomposition layer formed near cathode was porous and had small grains. The needle-shaped phases were newly formed at the decomposition front. The main decomposition phases of the LSGM electrolyte are La_2O_3 , $\text{La}(\text{OH})_3$, and LaSrGaO_4 .

Acknowledgements

This work was supported by the BK 21 Project. The authors thank to Doosung Induction Co. for the support of electronic switch that enables the current interruption measurement.

References

- [1] N. Q. Minh, J. Am. Ceram. Soc., 76 (1993) 563.

- [2] T. Ishihara, H. Matsuda, and Y. Takita, *J. Am. Chem. Soc.*, 116 (1994) 3801.
- [3] E. D. Wachsman, P. Jayaweera, N. Jiang, D. M. Lowe, and B. G. Pound, *J. Electrochem. Soc.*, 144 (1997) 233.
- [4] J. W. Stevenson, T. R. Armstrong, L. R. Pederson, J. Li, C. A. Lewinsohn, and S. Baskaran, *Solid State Ionics*, 113-115 (1998) 571.
- [5] K. Yamaji, T. Horita, M. Ishikawa, N. Sakai, and H. Yokokawa, *ibid.*, 108 (1998) 415.
- [6] K. Yamaji, T. Horita, M. Ishikawa, N. Sakai, and H. Yokokawa, *ibid.*, 121 (1999) 217.
- [7] K. Yamaji, H. Negishi, T. Horita, N. Sakai, and H. Yokokawa, *ibid.*, 135 (2000) 389.
- [6] K. Tsuneyoshi, K. Mori, A. Sawata, J. Mizusaki, and H. Tagawa, *ibid.*, 35 (1989) 263
- [7] M. J. L. Østergård and M. Mogensen, *Electrochimica Acta*, 38 (1993) 2015
- [8] B. Garbage, T. Pannier, and A. Hammer, *ibid.*, 141 (1994) 2118.
- [9] Y. Takeda, R. Kino, M. Noda, Y. Tumid, and O. Yamamoto, *J. Electrochem. Soc.*, 134 (1987) 2656.
- [10] E. P. Murray, T. Tsai, and S. A. Barnett, *Solid State Ionics*, 110 (1998), 235.
- [11] F. Lecarpentier, H. L. Tuller, and N. Long, *J. Electroceramics*, 5 (2000), 225.
- [12] T. Inoue, N. Seki, K. Eguchi, and H. Arai, *J. Electrochem. Soc.*, 137 (1990), 2523.
- [13] J. Y. Yi and G. M. Choi, *Solid State Ionics*, 148 (2002) 557.
- [14] J. Y. Yi and G. M. Choi, *J. Eur. Ceram. Soc.*, 24 (2004) 1359.
- [15] K. Huang, M. Feng, J. B. Goodenough, and M. Schmerling, *J. Electrochem. Soc.*, 143 (1996) 3630.

Figure Captions

Fig. 1. The cathodic overpotential of Pt/LSM/LSGM/Pt cell measured at 800 °C as a function of current density in $P_{O_2} = 1$ and 0.003 atm. It was measured in sequence of 1 atm (before), 0.003 atm, and 1 atm (after).

Fig. 2. Temperature dependence of polarization conductance of LSM cathode measured at 40 mA/cm² of current density before and after the low P_{O_2} measurement.

Fig. 3. Micrographs of LSM electrode (a) before and (b) after the low P_{O_2} measurement.

Fig. 4. Temperature dependence of ohmic conductivity of LSGM electrolyte before and after the low P_{O_2} measurement.

Fig. 5. Micrographs of (a) decomposition layer and (b) decomposition front of Pt/LSM/LSGM/Pt cell after the low P_{O_2} measurement.

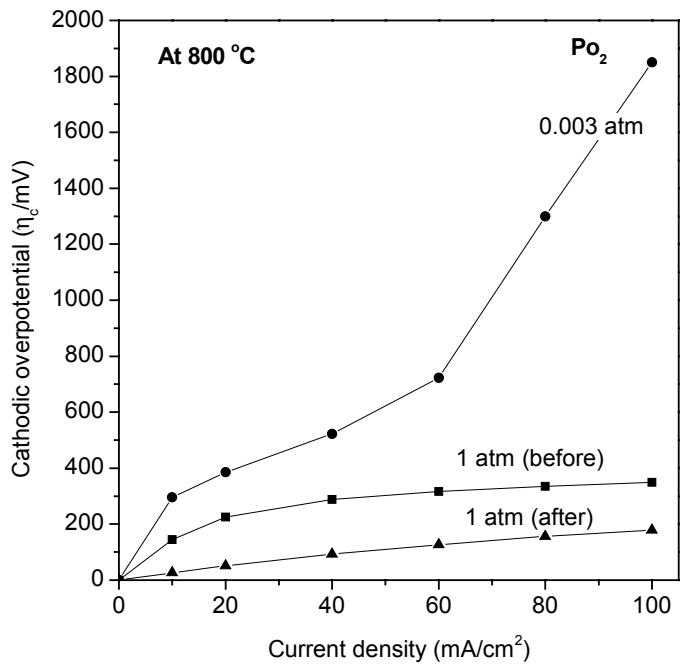


Fig. 1

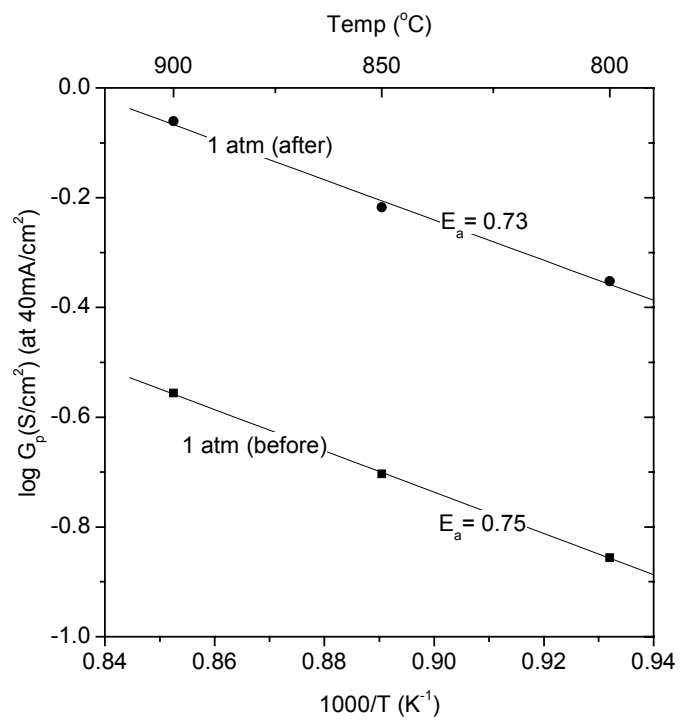


Fig. 2

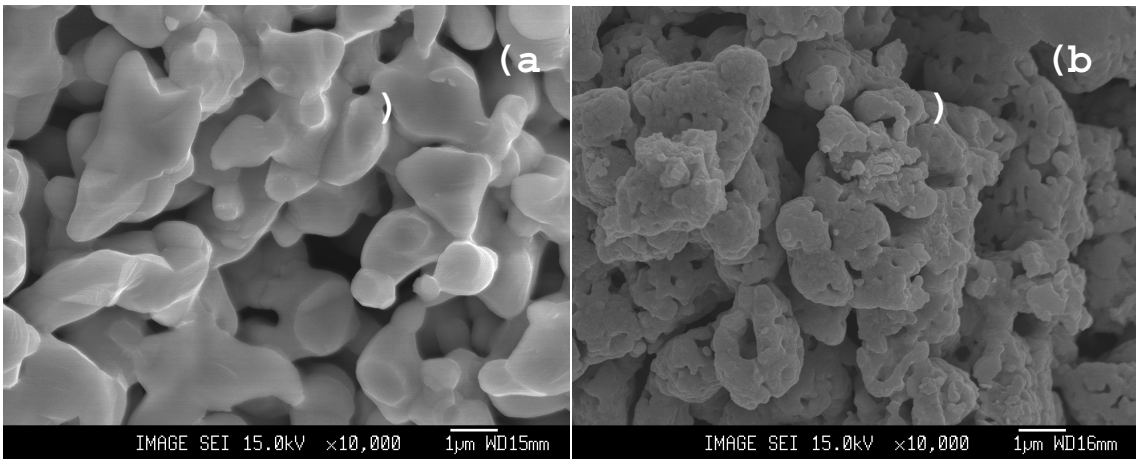


Fig.

3

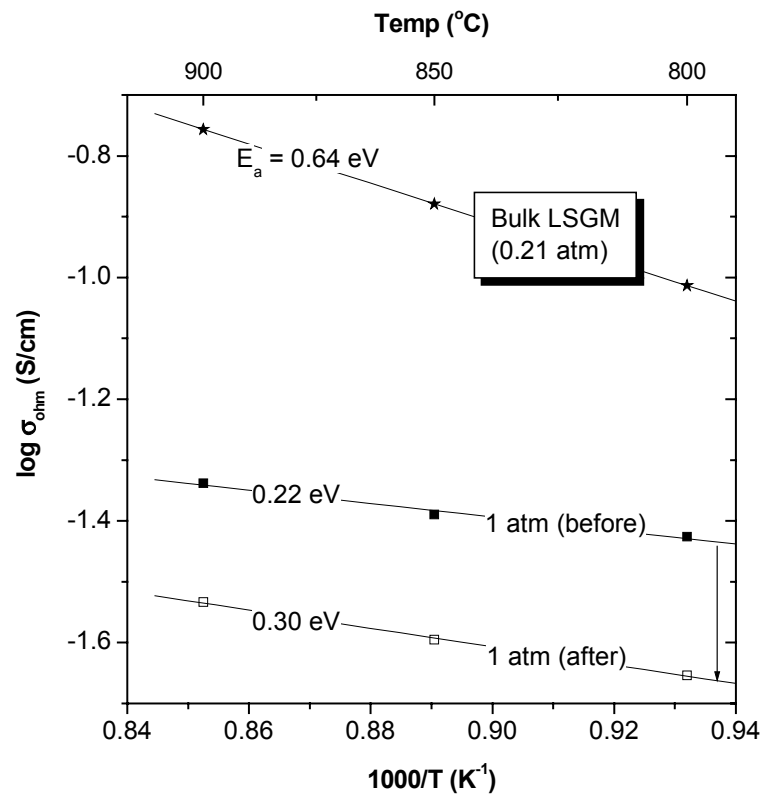


Fig. 4

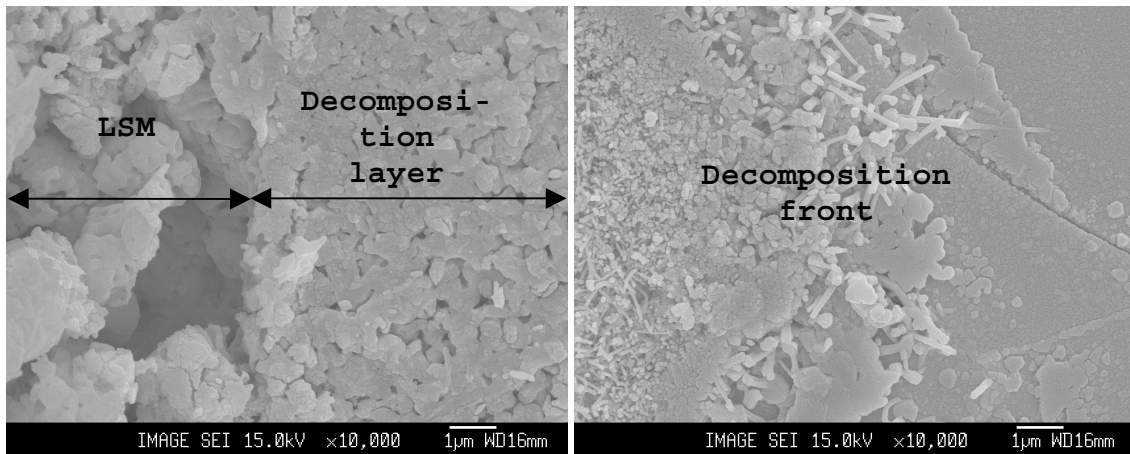


Fig.

5