COMPREHENSIVE DEVELOPMENT OF HIGH PERFORMANCE SOLID OXIDE FUEL CELLS FOR INTERMEDIATE AND LOW TEMPERATURE APPLICATIONS

By

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To my mom and wife
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<tr>
<td>AFL</td>
<td>Anode functional layer</td>
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<tr>
<td>ASR</td>
<td>Area specific resistance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller method</td>
</tr>
<tr>
<td>BRO</td>
<td>Bismuth ruthenate</td>
</tr>
<tr>
<td>BSCF</td>
<td>Barium strontium cobalt ferrite</td>
</tr>
<tr>
<td>DBP</td>
<td>Di-butyl phthalate</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray analysis</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ESB</td>
<td>Erbium stabilized bismuth oxide</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
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<tr>
<td>GDC</td>
<td>Gadolina doped ceria</td>
</tr>
<tr>
<td>IT</td>
<td>Intermediate temperature</td>
</tr>
<tr>
<td>LMIS</td>
<td>Liquid metal-organic ion source</td>
</tr>
<tr>
<td>LSCF</td>
<td>Lanthanum strontium cobalt ferrite</td>
</tr>
<tr>
<td>LSM</td>
<td>Lanthanum strontium manganite</td>
</tr>
<tr>
<td>MIEC</td>
<td>Mixed ionic-electronic conductor</td>
</tr>
<tr>
<td>MPD</td>
<td>Maximum power density</td>
</tr>
<tr>
<td>OCP</td>
<td>Open circuit potential</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
</tr>
<tr>
<td>PVB</td>
<td>Polyvinyl butyral</td>
</tr>
<tr>
<td>ROI</td>
<td>Region of interest</td>
</tr>
<tr>
<td>ScSZ</td>
<td>Scandia stabilized zirconia</td>
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<tr>
<td>SDC</td>
<td>Samaria doped ceria</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid oxide fuel cell</td>
</tr>
<tr>
<td>TLD</td>
<td>Through-lens-detector</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>YSB</td>
<td>Yttrium stabilized bismuth oxide</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttrium stabilized zirconia</td>
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In order to develop high performance solid oxide fuel cells (SOFCs) operating at low to intermediate temperatures, the three main SOFC components--the anode, electrolyte, and cathode--were comprehensively studied.

In order to lower anodic polarization losses in anode-supported SOFCs, a novel composite anode functional layer (AFL) having bimodal (nano/micro) structure was developed. Application of this AFL involved a simple process where a precursor solution was coated onto a conventional submicron sized colloidally-deposited Ni-GDC AFL. Cells prepared in this manner yielded maximum power densities (MPD) of 1.29, 1.16, 0.7 and 0.38 W/cm² at 650, 600, 550 and 500 °C, respectively. Electrochemical impedance results showed a striking decrease in both ohmic and non-ohmic area specific resistances (ASRs) for these cells compared to those with either no AFL, or a conventional AFL.

In addition, the effect composition of the conventional submironized AFL on performance was examined. The highest MPD (1.15 W/cm² at 650 °C) was achieved at a composition of 60wt% NiO. This composition had the best performance over the intermediate temperature range (450 to 650 °C). For the potentiostatic test, the cell
exhibited stable performance over 200 hrs of operation at 1.1 W/cm². It was also revealed that electrode ASR has an inverse linear relationship with maximum power density at 650°C.

To better understand the effect of AFL composition, microstructural features of AFLs having various Ni-GDC compositions were quantified by a 3 dimensional (3D) reconstruction technique using a FIB/SEM dual beam system. Of the compositions tested, the highest triple phase boundary (TPB) density was achieved at 60wt% NiO, which corresponds to a 1:1 volume ratio of Ni to GDC phase. The quantified TPB density showed an inverse proportionality to electrode ASR.

Using a wet chemical co-precipitation method, nano-sized ESB particles were successfully synthesized at temperatures as low as ~ 500 °C. Due to the high sinterability of this powder, a dense erbia stabilized bismuth oxide (ESB) layer was successfully formed on a gadolinia doped ceria (GDC) electrolyte by a simple colloidal coating method. A systematic study on the sintering behavior of ESB was conducted to determine the optimum sintering conditions for these materials. I-V measurement a cell using this bilayered electrolyte system showed a high power density ( ~ 1.5 W/cm²) at 650 °C due to an enhancement in OCP and a significant reduction in ASR when compared to a GDC single cell.

The performance of conventional (La₀.₈₀Sr₀.₂₀)MnO₃-δ (LSM) cathodes were dramatically improved at the IT range by combining it with a highly conductive ESB phase. The electrode ASR measured from a symmetric cell consisting of LSM-ESB electrodes on an ESB electrolyte was only 0.08 Ω-cm² at 700°C which is ~60% lower than that of LSM-ESB on GDC electrolytes (0.19 Ω-cm²). This exemplifies the
synergetic effect the ESB phase has both in the cathode bulk and at the electrolyte/electrode interface. The MPDs of the anode-supported SOFCs with LSM-ESB cathodes on ESB/GDC bilayered electrolytes were ~836 mW/cm² at 650 °C, which is the highest value reported for SOFCs using LSM-bismuth oxide composite cathodes.
A fuel cell is an energy conversion device which directly produces electrical energy from the chemical energy contained in various fuels by electrochemical reactions. In 1838, the basic principle of the fuel cell was written in one of the scientific magazines of the time by German chemist, Christian Friedrich Schönbein. One month later, Sir William Grove reported the first functional fuel cell in 1839. He used a dilute sulfuric acid solution as an electrolyte at room temperature, which produced water and electricity[1]. However the history of SOFCs began much later, in 1899, with the discovery of the solid-oxide electrolyte by Nernst and followed with the first SOFC invented by Baur and Peris in 1937 [2].

Since that time, and especially in the last several decades, tremendous effort and progress has been made to commercialize SOFCs. For instance, Siemens-Westinghouse has successfully developed and operated a 100 kW system for over 20,000 h without significant deterioration in performance [3]. Recently the Solid State Energy Conversion Alliance (SECA), the fuel cell program under United States Department of energy (DOE), announced their road map, including the development of a prototype SOFC stack with megawatt capability and fuel-flexibility by 2015 [4].

One of the biggest challenges to SOFC commercialization is to reduce the operation temperature while maintaining high power densities. At intermediate temperatures (IT, 500~700 °C), the system cost can be significantly reduced by allowing the use of cheap stainless steel for the bipolar plates and the balance-of-plant, as well as the use of high temperature gaskets rather than rigid glass-based seals, which can also enhance mechanical stability and life time [5].
Conventional SOFCs with yttria stabilized zirconia (YSZ) electrolytes operate at high temperatures (over \(~1000^\circ\)C) due to its thermally activated ionic conduction, and thus have unacceptable system cost and slow start-up times [4-7]. Two main strategies have been studied to reduce ohmic losses in the electrolyte at reduced temperatures.

First is the thin electrolyte approach--the electrolyte resistance is inversely proportional to the electrolyte thickness [8]. To accommodate thin electrolyte films, anode supported cells has been developed [5, 9]. In this configuration however, anodic polarization can limit performance due to the relatively high anode thickness. It is believed that most fuel oxidation reactions take place at near the anode/electrolyte interface, indicating that most anodic losses occur in this region [10]. Therefore, engineering of the interfacial region has received much attention as a way to reduce losses at the anode [11-14].

The other approach is to use materials with enhanced ionic conductivity. For example, erbia stabilized bismuth oxide (ESB) and gadolinia doped ceria (GDC) have one to two orders of magnitude higher ionic conductivity in the IT range than YSZ [15]. However, these two materials have disadvantages, including thermodynamic instability at the low Po\(_2\) conditions experienced at the anode side of fuel cell systems [3, 16, 17]. To overcome these limitations, a bismuth oxide/ceria bilayer electrolyte concept has been proposed [18]. In order to produce high power densities in the low to intermediate temperature range, one can combine the bilayer electrolyte concept with a thin film approach. Using this concept with a thin and dense ESB (\(~4\ \mu\)m) and GDC (\(~10\ \mu\)m) bilayered electrolyte, the author and colleagues recently demonstrated a cell having an exceptionally high power density of \(~2\ \text{W/cm}^2\) at 650\(^\circ\)C [19, 20]. In that study, the
dense ESB layer was deposited by pulsed laser deposition (PLD), which is not a viable technique for mass production. Therefore, a more simple and cost-effective fabrication process is necessary.

The focus of this dissertation is the development of SOFCs producing high power densities in the IT range and prepared with practical and cost-effective fabrication processes. Each component of the SOFC-- the anode, electrolyte, and cathode--was investigated to reduce its major polarization losses. In order to control anodic polarization losses, a novel AFL was developed at the anode/electrolyte interface by integrating nano- and micron- particle structures. For further improvement of the Ni-GDC AFL, the effect of composition was carried out. Microstructural features of the AFLs were quantified using a state-of-the-art 3D reconstruction technique by a FIB/SEM dual beam system. From this work, the understanding of the relationship between electrochemical performance and microstructures was enhanced.

In order to improve electrolyte performance, the ESB/GDC bilayered electrolyte system was investigated. Cost-effective fabrication of dense ESB electrolytes was achieved by a simple colloidal deposition technique. In order to accomplish this, nanosized ESB particles with high sinterability were synthesized by a wet chemical co-precipitation method. The reproducibility of the high performance exhibited by these bilayered electrolyte cells was carefully demonstrated.

In addition, an (La$_{0.8}$Sr$_{0.2}$)$_{0.9}$MnO$_{3-\delta}$ (LSM)-ESB composite cathode was studied as an alternative cathode for low to intermediate temperatures. The use of conventional LSM cathodes has been limited to high temperature SOFCs due to its low ionic conduction at reduced temperatures [21]. In this work LSM was mixed with the fast ion
conductor, ESB. The performance of the LSM-ESB cathode was investigated in the IT range. This work demonstrated that, coupled to an ESB electrolyte, the performance of LSM-ESB was stable and significantly better than that of the same cathode on conventional GDC or YSZ electrolytes below 650 °C.
CHAPTER 2
BACKGROUND

2.1 Basic Principle of SOFC Operation

In principle, overall SOFC reaction is expressed as a simple reaction formula;

\[ \frac{1}{2}O_2 + H_2 \rightarrow H_2O \]  \hspace{1cm} (2-1)

In order to complete this reaction in the actual fuel cell operation, the reaction is divided into two half cell reactions [2, 3, 9]. Fig. 2-1 shows a schematic diagram of a general SOFC structure and half cell reactions at anode and cathode side [22]. In the cathode side, oxygen which generally comes from air is reduced to \( O^{2-} \) with electrons provided from outside fuel cell which written as;

\[ \frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \]  \hspace{1cm} (2-2)

For this half reaction, a cathode conducts adsorption of oxygen molecules and dissociation of adsorbed oxygen. This is followed by formation of oxygen ion by electron transfer and charge transfer (\( O^{2-} \) and electron) at the triple phase boundaries (TPBs) between gas, ionic, and electronic conducting phases. Therefore, a cathode should be a high catalysis to dissociate molecules and have high ionic and electronic conduction with good compatibility to the electrolyte as well. Related work with high catalytic cathode for IT-SOFC has be done at ch. 7 in this dissertation

Transferred Oxygen ions move to anode via electrolyte, for which high ionic conductivity of the electrolyte is necessary. A driving force of the ion migration is the Nernst potential due to \( P_{O2} \) difference between cathode and anode. Therefore, the electrolyte should be a ‘good barrier’ between the air side and the fuel side to maintain the low \( P_{O2} \) at the anode, which can be achieved by highly dense electrolyte. Highly
dense electrolyte with a special design for high stability and conductivity was researched at ch. 6.

At the anode, the fuel is oxidized with the migrated oxygen ions.

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{2-3}
\]

\[
CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{2-4}
\]

\[
C_nH_{2n+2} + (3n+1)O^{2-} \rightarrow nCO_2 + (n+1)H_2O + (6n+2)e^- \tag{2-5}
\]

Each equation presents the oxidation reaction for different fuels; eq. (2-3) for H\textsubscript{2}, eq. (2-4) for CO, and eq. (2-5) for hydrocarbon fuel. In this case, the catalytic properties of anode is important, which takes place at TPBs. Therefore, concentration and spatial distribution of TPB can be a key factor to improve anode performance for SOFCs. In this dissertation, control and mechanism of TPB extension in anode nearby the anode and electrolyte interface was intensively studied (ch. 3 ~5).

**2.2 Actual SOFCs Operation**

In actual SOFCs operation condition, the performance of SOFCs is commonly measured by voltage out as a function of applied current density. Fig. 2-2 shows a representative voltage-current plot of SOFC [4]. As mentioned above, the Nernst potential by \(P_{O_2}\) difference between anode and cathode produces a driving force to operate SOFCs. However, this ideal voltage can not be maintained under applied current due to various irreversible polarization mechanisms. The actual operational cell voltage \((E)\) as a function of current density can be written as;

\[
E = E_{OCP} - \eta_{act} - \eta_{ohm} - \eta_{conc} \tag{2-6}
\]
where \( E_{OCP} \) is open circuit potential including leakage current and \( \eta_{act} \), \( \eta_{ohm} \) and \( \eta_{conc} \) represent the activation, ohmic, and concentration polarization, respectively. Detailed polarization mechanisms are explained in following sub-sections.

2.2.1 Open-circuit Potential (OCP) and Transference Number (\( t_i \))

The voltage is generated across a cell by various gas mixtures with two different oxygen partial pressures (\( P_{O_2} \)). The open-circuit potential for the oxygen potential gradient cells is given by the well-known Nernst equation in a cell [3],

\[
E = -\frac{RT}{4F} \ln \frac{P_{O_2}'}{P_{O_2}''}
\]

(2-7)

where \( P_{O_2}'' \) and \( P_{O_2}' \) are the equilibrium partial pressure of oxygen at the two sides of the cell, \( R \) is the ideal gas constant, \( F \) is Faraday’s constant and \( T \) is the absolute temperature. The reaction for oxygen is,

\[
O_2(g) + 4e^- \rightarrow 2O^{2-}
\]

(2-8)

If one knows the oxygen partial pressure of the reference electrode (\( P_{O_2}'' \)) and measures the OCP at a given temperature, the equilibrium value of oxygen pressure at the working electrode may be determined from eq. (2-7). Generally, low oxygen pressure can be easily obtained under CO/CO\(_2\) or H\(_2\)/H\(_2\)O mixture [23]. However, previous results showed that in CO/CO\(_2\) gas mixtures, the equilibrium was not readily attained, while H\(_2\)/H\(_2\)O gas mixtures showed equilibration for low Po\(_2\). In this study, H\(_2\)/H\(_2\)O gas mixtures were used to maintain low oxygen partial pressure on the anode side. The hydrogen was bubbled with 3% of H\(_2\)O through a membrane submersed in water. The condition of a controlled oxygen partial pressure can be obtained via thermodynamic relations at equilibrium. At high temperature, H\(_2\) and H\(_2\)O gases react with traces of oxygen as following.
\[ \text{H}_2(g) + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \] \hspace{1cm} (2-9)

And the Gibbs free energy is

\[ \Delta G = \Delta G^0(T) + RT \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} \] \hspace{1cm} (2-10)

where \( \Delta G^0(T) \) is the standard Gibbs free energy of the reaction, \( R \) is ideal gas constant, and \( T \) is temperature. From the thermodynamic data [23],

\[ \Delta G^0(T) = -242,000(J/mol) + 44.7(J/mol - K) \times T(K) \] \hspace{1cm} (2-11)

At equilibrium, \( \Delta G = 0 \),

\[ \Delta G^0(T) = -RT \ln \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{O}_2}^{1/2}} \] \hspace{1cm} (2-12)

\[ P_{\text{O}_2} = \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^2 \left( \exp \left( \frac{\Delta G^0(T)}{RT} \right) \right)^2 \] \hspace{1cm} (2-13)

Therefore, with the reference oxygen potential, temperature, and \( \text{H}_2/\text{H}_2\text{O} \) partial pressures, the controlled oxygen partial pressure can be calculated. For example, the experimental condition can be maintained with reference oxygen partial pressure of 0.21 atm on the cathode side (1 atm air) and 3% of \( \text{H}_2\text{O} \) with \( \text{H}_2 \) on the anode side. Based on these experimental conditions, the theoretical Nernst voltage was calculated by eq. (2-7) to (2-13) over the temperature range of 500 to 700 °C in 50 °C increments as shown in Table 2-1.

The transference number (or transport number), \( t_i \), is defined as the fraction of the total conductivity due to each charged species;
The ionic transference number, $t_i$, is equal to 1 for a purely ionic conductor, such as YSZ. Approaching unity of $t_i$ means that there is no significant electron or hole conduction. Any electronic conductivity causes an internal short circuit in the electrolyte of a fuel cell. The ratio between the measured and the theoretical OCP or Nernst voltage is transference number ($t_i$);

$$t_i = \frac{OCP_{\text{measured}}}{OCP_{\text{theoretical}}} \quad (2-15)$$

The transference number will be evaluated from the experimentally measured OCP values with the theoretical values in Table 2-1.

### 2.2.2 Irreversible Losses

#### 2.2.2.1 Activation polarization losses

At low current density condition, the slow reaction kinetics at the cathode and the anode can cause the activation polarization. In other words, the excessive energy to overcome a energy barrier for electrode reaction such as the oxygen reduction and hydrogen oxidation produces the voltage drop which is increased with the current density drawn.

The phenomena can be formulated by the Butler-Volmer equation [24];

$$i = i_{0,a} \left[ \exp \left( \frac{\alpha_{a,a} nF \eta_{\text{act},a}}{RT} \right) - \exp \left( \frac{-\alpha_{a,a} nF \eta_{\text{act},a}}{RT} \right) \right] \quad (2-16)$$

$$i = i_{0,c} \left[ \exp \left( \frac{\alpha_{c,c} nF \eta_{\text{act},c}}{RT} \right) - \exp \left( \frac{-\alpha_{c,c} nF \eta_{\text{act},c}}{RT} \right) \right] \quad (2-17)$$
where $i_{0,a}$, $i_{0,c}$ are the exchange current densities of the anode and cathode, respectively, $\alpha_{a,a}$ and $\alpha_{c,a}$ are the anodic ($i>0$) and cathodic ($i<0$) charge transfer coefficients of the anode, and $\alpha_{a,c}$ and $\alpha_{c,c}$ are the anodic and cathodic charge transfer coefficients of the cathode. The charge transfer coefficients depend on the electrocatalytic reaction mechanism and usually ~0.5 is used for SOFCs. It is noted that as shown above, the Butler-Volmer equation should be applied for each electrode separately. This nonlinear Butler-Volmer equation can be simplified as:

$$\eta_{act} \cong \frac{RT}{\alpha nF} i_{0,c} \ln\left(\frac{i_a}{i}\right)$$  \hspace{1cm} (2-18)$$

In this case, this equation only considers on forward direction reaction, that is, reduction at the cathode side and oxidation at the anode side. Surprisingly, this simplified form was already predicted in empirical equation by Tafel in 1905 [25], which is written as:

$$\eta_{act} = a \log \ln\left(\frac{i_0}{i}\right)$$  \hspace{1cm} (2-19)$$

where $a$ is a called the Tafel slope.

### 2.2.2.2 Leakage current polarization losses

In principle, voltage measurement of SOFC under open circuit condition (OCP) should show the theoretical Nernst voltage at the testing temperature. However, the actual measurement of OCP usually has some deviation from the theoretical voltage. Even YSZ known as purely ionic conductor still sometimes shows some OCP deviation, which might be comes from gas leaks across the electrolyte itself or poor seal. For mixed ionic and electronic conductors (MIECs), such as dope-ceria, the partial electronic conduction causes OCP drop from theoretical one. For example, the
theoretical OCP at 650 °C is ~1.14V but the reported OCPs of the GDC electrolyte cells are 0.7 ~ 0.8V [7]. As explained above, the ratio of measured OCP to theoretical one is expressed as transference number, \( t_i \).

2.2.2.3 Ohmic polarization

The ohmic polarization is the losses due to total electrical resistances from electrodes, electrolyte and lead wires. This polarization loss simply follows Ohm’s law (\( V=IR \)). Therefore, ohmic polarization which is function of current can be expressed by

\[
\eta_{\text{ohm}} = I(R_{\text{electrode}} + R_{\text{electrolyte}} + R_{\text{contact}})
\]  \hspace{1cm} (2-20)

where \( R_{\text{electrode}} \), \( R_{\text{electrolyte}} \), and \( R_{\text{contact}} \) are resistances from electrode (both cathode and anode), electrolyte, and electrode-electrolyte contact, respectively, and \( I \) is current density. For SOFC structure, it has been generally accepted that most of the ohmic resistance comes from electrolyte due to much slow conduction process of ion migration rather than that of electrons. In this case, comparison of resistance between electrolytes is difficult due to its thickness dependence. Moreover, performance of SOFC is measured as a function of current density \( (i) \) not current \( (I) \). Therefore, ohmic polarization of electrochemical devices is generally expressed by;

\[
\eta_{\text{ohm}} = I \cdot R_{\text{tot}} = i \cdot A \cdot R_{\text{tot}} = i \cdot ASR_{\text{tot}}
\]  \hspace{1cm} (2-21)

where \( ASR_{\text{tot}} \) is total area specific resistance.

2.2.2.4 Concentration polarization

Concentration polarization is generally observed at high current density regime of I-V curves due to restriction to the transport of the fuel gas molecules to the anodic reaction site. At high current density, excess water byproduct can block the reaction sites. Therefore significant deactivation of reaction sites can be occurred. The
concentration polarization can be alleviated by higher gas pressure to drive out excess water from the reaction sites, reduction of anode thickness to shorten the distance to electrolyte, or higher porosity formation with same reason.

2.3. Materials and Design

2.3.1 Stabilized Zirconia Electrolytes

For high temperature SOFCs, stabilized zirconia, such as yittria-stabilized zirconia (YSZ) has been most widely used as an electrolyte due to its high stability, reasonable ionic conductivity at high temperature (> ~900 °C), and relatively inexpensive cost [6]. Although pure zirconia (ZrO$_2$) is also chemically stable in both oxidizing and reducing conditions, it has not been chosen as a solid electrolyte due to its poor ionic conductivity. In addition to low conduction, pure ZrO$_2$ shows phase transition from monoclinic to tetragonal and from tetragonal to cubic fluorite at 1170 and 2370 °C, respectively, accompanying unacceptable volume change (3 ~ 5%) in the fabrication temperature ranges [26]. However, it has been known that some aliovalent cations, such as cations of Ca, Y, Mg and Sc, can stabilize the ZrO$_2$ phase as cubic fluorite structure from room temperature to high temperature [27]. Moreover, this aliovalent cation doping in ZrO$_2$ produces higher vacancy concentration, leading higher ionic conduction at the wider Po$_2$ ranges. This aliovalent dopant effect on vacancy concentration can be explained by Kroger-Vink notation in which the negative charge produced by substituting a dopant is indicated by prime or a superscript dot if it is positive. The amount of charge is indicated by the number or prime or dot. For neutrality after substituting, it is marked as the superscript ‘x’. For example, the incorporation reaction between trivalent dopant and ZrO$_2$ can be written as [3];
\[ M_2O_3 \overset{zrO_2}{\rightarrow} 2M^{+} + 3O^{2-} + V^{**} \]  

(2-22)

where the \( M \) is trivalent dopant and \( V \) is vacancy, indicating that two \( M \) dopants produce one oxygen vacancy. Various tri- and divalent dopants has been studied to make the stabilize \( ZrO_2 \) with high ionic conduction. It was shown that there is certain dopant concentration to give maximum conductivity. For yttria stabilized zirconia (YSZ), as \( Y \) dopant concentration increases, the conductivity is increased upto 8 mol\%, while over 8 mol\% it shows degradation [28]. As shown in Fig. 2-3 Most of the stabilized zirconia shows similar trend [2]. It is explained that at higher dopant concentration, defect ordering or vacancy clustering occurs leading the reduction of total number of active vacancy [29]. Among the dopants, \( Y \) is most widely used due to cost and stability, while highest conductivity has been reported for Sc dopant (Table 2-2) [29]. The ionic conductivity of YSZ is strongly depends on the concentration and mobility of ions, which is known to a thermally activated process. Therefore, conductivity of YSZ suffers significant conductivity reduction at low temperature, which limits it operational temperature \( \sim1000 \, ^\circ\text{C} \).

### 2.3.2 Aliovalent Cations-Doped Ceria Electrolytes

Recently, aliovalent cations-doped ceria (\( \text{CeO}_2 \)) has been given much attention as a potential solid electrolyte because of its higher ionic conductivity over a range of high to intermediate temperature. The ionic conductivity of ceria is considerably increased by aliovalent cation doping which increases the oxygen vacancy concentration in ceria [30, 31]. The magnitude of electrical conductivity and the stability under reducing conditions for ceria-based oxides depend greatly on the kind and quantity of doping elements. Alkaline earth oxides(e.g. \( \text{CaO} \) and \( \text{SrO} \)) and rare earth oxides(e.g. \( \text{Gd}_2\text{O}_3 \) and \( \text{Sm}_2\text{O}_3 \))
are highly soluble in the ceria sublattice. Among these, Sm and Gd-doped ceria shows the highest electrical conductivity in ceria based oxides with 10~20% of dopant concentration [31]. It is considered because of the similar ionic radii of Sm$^{3+}$ and Gd$^{3+}$ to that of Ce$^{4+}$. Since Steele calmed the ionic conductivity of Gd$_{0.1}$.Ce$_{0.9}$.O$_{1.95}$. (10GDC) is the highest among various Gd and Sm dopant concentrations at a temperature range of 500~700°C, 10GDC has been paid attention as one of the most suitable candidates for IT-SOFCs electrolyte [7]. Moreover, as shown in Fig. 2-4 the ionic conductivity of doped-ceria is approximately one to two order of magnitude greater than that of stabilized zirconia, which is most widely used electrolyte material up to present [3]. It is considered because Ce$^{4+}$ (0.87 Å) ion has larger ionic radius than Zr$^{4+}$ (0.72 Å) causing easier oxygen ion migration through a more open structure. However, one big drawback of ceria-based electrolyte makes us hesitate to select it as a best electrolyte material for IT-SOFCs despite of its high ionic conductivity. When ceria-based oxides are reduced at low oxygen partial pressures (<10$^{-14}$ atm), Ce$^{4+}$ transfers into Ce$^{3+}$ leading significant n-type electronic conduction with a P(O$_2$)$^{-1/4}$ dependence [7]. This phenomenon reduces the ionic transference number ($t_i$) and the open circuit potential (OCP), thereby making ceria less efficient for application as an IT-SOFCs. To increase the electrolyte domain and to preserve the ionic conductivity of the doped ceria by any means is important.

2.3.3 Stabilized Bismuth Oxide Electrolytes

Various polymorphism in bismuth oxide based materials have been identified with α, β, γ and δ phases [32]. Even though the cubic δ phase at high temperature (> 729 °C) shows an excellent ionic conductivity, attributed to the presence of such a large concentration of oxygen vacancies, it is unstable and transforms into a monoclinic phase with below 729 °C resulting in a discontinuous decrease in conductivity [33].
However, when a solid solution of bismuth oxide is formed with erbia (Er$_2$O$_3$) or several other rare-earth oxides, bismuth oxide is known to remain stable in the cubic phase. 20% erbia stabilized oxide (ESB) has the excellent conductivity among the stabilized-bismuth oxides. The greater conductivity of stabilized-bismuth oxide electrolytes has tremendous potential for lower operating temperature, thus considerably growing the number of applications for SOFCs [34]. Despite the high conductivity of stabilized bismuth oxide electrolytes, they have not been used in solid electrochemical devices such as SOFCs due to their thermodynamic instability. Takahashi et al. indicated that the critical PO$_2$ value below which stabilized bismuth oxide would decompose is the equilibrium oxygen pressure of a Bi/Bi$_2$O$_3$ mixture [16]. The decomposition process may be simplified as:

$$Bi_2O_3 = 2Bi(s) + \frac{3}{2}O_2(g) \quad (2-23)$$

The open-circuit potential from galvanic cells with an air cathode and metal/metal oxide anode were stable in oxygen partial pressures above $10^{-13.1}$ atm at 600$^\circ$C. This result showed that there was no contribution of electronic conduction to the total conductivity above the equilibrium oxygen potential of Bi/Bi$_2$O$_3$ mixture. Therefore, they concluded that the minimum oxygen partial pressure at 600$^\circ$C is $10^{-13.1}$ atm. On the other hand, Wang and other researches reported the ionic conductivity of Bi$_2$O$_3$ could be measured without critical decomposition of Bi/Bi$_2$O$_3$ under an H$_2$/H$_2$O atmosphere [35, 36]. Wachsman et al. reported that the measured conductivity of ESB was independent of Po$_2$ over the range 1 to $10^{-22}$ atm under O$_2$/Ar atmosphere as shown in Fig. 2-5 while ESB was decomposed at low Po$_2$(10$^{-21}$ atm) with H$_2$, which was also confirmed by XRD [37]. It was considered that the stability of ESB in the Ar/O$_2$
atmosphere is probably due to slow heterogeneous kinetics in the absence of an active reducing agent, such as H₂. From these results, it can considered that bismuth oxide based electrolytes may be kinetically stable in the absence of contact with an active reducing agent. Therefore, in order to use bismuth oxide as an IT-SOFC electrolyte, exposure to the reducing environment of the fuel gases must be prevented due to decomposition of the bismuth oxide.

2.3.4 Bilayered Electrolyte Concept for High Performance IT-SOFCs

2.3.4.1 Ceria / Zirconia bilayer electrolyte

Bilayered electrolytes have been proposed as an alternative of overcoming the decomposition by the thermodynamic instability of highly conductive oxides. Yahiro et al. demonstrated that a thin and dense layer of YSZ on the fuel side of ceria avoided the effect of reduction of electrolytes by blocking the electronic conduction and consequently increased the OCP and power density [38]. Alternatively, some researchers have suggested placing the YSZ layer, which has a low electronic conductivity, on the air (i.e., oxidizing) side of the SOFC where its function is only to block electronic flux (thereby increasing the efficiency of the SOFC) [23]. Of the two approaches the latter has been the most successful. However, in both cases the YSZ layer could not be made thin enough for the total ionic conductance of the bilayer to be high enough for efficient power generation at low temperatures. Generally, a YSZ/SDC or SDC/YSZ bilayer electrolyte has no intrinsic advantage over just a thin YSZ electrolyte itself, other than providing a non-porous substrate for YSZ deposition, due to the relatively low conductivity of YSZ [18].
2.3.4.2 Ceria / Bismuth oxide bilayer electrolyte

Wachsman et al. proposed a bilayer electrolyte consisting of a layer of erbia-stabilized bismuth oxide (ESB) on the oxidizing side and a layer of SDC or GDC on the reducing side[9]. In this arrangement, the ceria layer would protect the bismuth oxide layer from decomposing by shielding it from very low Po2 and the ESB layer would serve to block electronic flux. They demonstrated concepts of bilayered electrolytes by using a system, which consists of SDC (Ce0.8Sm0.2O1.5) on the reducing side and ESB (Bi0.8Er0.2O1.5) on the oxidizing side [39]. As shown in Fig. 2-6, it was considered that the gas phase on either side is fixed by the gradient of oxygen partial pressure and the relative electronic conductivity relies on the local oxygen activity. In this bilayer structure, the SDC layer prevents the ESB layer from decomposing at very low Po2. That is, in bilayered bismuth/ceria electrolytes, thermodynamics stability of the bismuth oxide electrolytes can be elevated and ceria can be act as both an electrolyte and anode depending on local oxygen partial pressure. As a result, higher OCP can be obtainable in the bilayered bismuth/ceria electrolytes, since transference number of bismuth oxide electrolyte is unity [18]. Based on the gradient oxygen partial pressure and vacancy transport theory, modeling results showed that the interfacial oxygen partial pressure can be mainly determined by the relative thickness ratio between two oxide electrolyte layers[24]. These results implies that the relative thickness ratio is the key parameter to the electrochemical performance of bilayer electrolytes, since the P02 at the ESB/SDC interface can be controlled by the thickness ratio of SDC and ESB layers. Recently Park et al. reported study result on SDC/ESB bilayer electrolyte [39, 40]. In this paper, they successfully deposited thin ESB layers with pulsed laser deposition (PLD) technique and a dip coating method on 1.7mm thick SDC pellet and
showed that there is no interfacial phase formation. Such a formation can lower the total electrolyte conductivity and cause the ESB layer to be ineffective in blocking electron flow from ceria electrolyte causing higher open-circuit potential. Although the studied relative thickness ratio ($L_{\text{ESB}}/L_{\text{SDC}}$) of the bismuth/ceria bilayer electrolytes was up to $10^{-2}$ level, it was expected that the higher relative thickness ratio can obtain higher electron open circuit potential without loss of high ionic conductivity on electrolyte. Leng et al. also demonstrated the bilayer concept through YDB (yittria-doped bismuth)/ GDC electrolyte system [41]. Their results showed not only higher open-circuit potential but also lowering electrode polarization effect due to the bismuth oxide interlayer. In this study they used relatively higher thickness ratio of 0.3, which implies the possibility of thermodynamic stability of thin film bilayer electrolyte even in higher ratio. However, only one thickness ratio was used and the cathode (Pt) was different from previous studies (Au). The thickness ratio effect cannot be directly compared with other results. Recently, modeling of the transport in ESB/SDC bilayer electrolytes has shown that the thickness of the bismuth oxide layer can be increased relative to the ceria layer, due to the increase in the electrolytic domain with decreasing operation temperature [42]. As shown in Fig. 2-7, it has been expected that, at higher the ESB/SDC electrolyte thickness ratio, the total electrolyte resistance can be dominantly influenced by higher conductivity bismuth oxide layer, from which we can expect a significantly lower ASR (area specific resistance) as well as very high OCP.
Figure 2-1. Schematic diagram of reactions in SOFCs based on oxygen-ion conductors [22]
Figure 2-2. SOFC current-voltage behavior indicating relative polarization losses [4]
Figure 2-3. Variation of ionic conductivity of stabilized ZrO2 with dopant concentration (T=807oC) [2]
Figure 2-4. Conductivities of selected electrolyte materials [3]
Figure 2-5. ESB conductivity versus Po2 in purified argon atmosphere [37]

Figure 2-6. Conceptual representation of a bilayer electrolyte showing the effect of relative thickness on interfacial oxygen partial pressure (Po2 ) [39]
Figure 2-7. Bulk electrolyte ASR at 500 oC as a function of relative ($t = \frac{L_{ESB}}{L_{SDC}}$) and total thickness for bilayers.
Table 2-1. Calculated Po$_2$ and Nernst voltage at open-circuit condition (T=500~700$^\circ$C)

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>$\Delta G^0$ (T) (J/mol)</th>
<th>Po$_2$ (atm)</th>
<th>Nernst Voltage; OCP theoretical (V)</th>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>-198507</td>
<td>4.641x10$^{-25}$</td>
<td>1.1415</td>
<td>$P_{H_2O}$/ $P_{H_2} = 0.0309$</td>
</tr>
<tr>
<td>650</td>
<td>-200742</td>
<td>1.816 x10$^{-26}$</td>
<td>1.1473</td>
<td>$P_{O_2, ref}=0.21$ atm</td>
</tr>
<tr>
<td>600</td>
<td>-202977</td>
<td>4.900 x10$^{-28}$</td>
<td>1.1531</td>
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</tr>
<tr>
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<td>-205212</td>
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<td>1.1588</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>-207447</td>
<td>8.784 x10$^{-32}$</td>
<td>1.1646</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-2. Conductivity Data for Stabilized ZrO$_2$ Doped with Rare-Earth Oxides [43]

<table>
<thead>
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<th>Activation energy (kJ/mol)</th>
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CHAPTER 3
INTERGRATING NANO- AND MICRO- STRUCTURED ANODE FUNCTIONAL LAYERS FOR IMPROVED IT-SOFC PERFORMANCE

3.1 Introduction

The commercialization of solid oxide fuel cells (SOFCs) as highly efficient, low pollution power sources can be realized by lowering operational temperatures [3]. As Steele claimed, in the lower temperature operation regime (< ~ 700 °C), the system cost can be significantly reduced with the use of cheap stainless steel for the bipolar plates and the balance of the plant, combined with the use of high temperature gaskets rather than rigid glass-based seals. The lower operation temperature can also enhance the SOFC’s mechanical stability and life time [5]. However, critical points to achieve this goal are to alleviate the significantly increased ohmic and activation polarizations at reduced temperatures due to their thermally activated nature [9, 44].

An anode-supported designs for low (~ 500 °C) to intermediate (~ 600 °C) temperature SOFCs have recently received much attention since they can accommodate very thin electrolytes (< ~ 10 μm), thereby eliminating a large fraction of the cell’s ohmic resistance [5]. Until now, many anode-supported SOFCs with state-of-the-art thin, highly conductive electrolytes, and highly electrocatalytic cathodes have been shown to obtain high power density at intermediate temperatures (IT). For example, Shao and Haile reported a high performance of ~ 1.01 W/cm² at 600 °C with a barium doped perovskite cathode (Ba₀.₅Sr₀.₅-Co₀.₈Fe₀.₂O₃-δ, BSCF) accompanied with thin doped ceria-electrolyte [45]. Recent study also demonstrated a nickel and gadolinia doped ceria (Ce₀.₉Gd₀.₁O₁.₉₅, GDC) composite anode-supported SOFC with ~10 μm thick of bismuth/ceria bilayered electrolyte coupled to a bismuth-ruthenate cathode that achieved a high maximum power density (MPD) of ~ 1.95 W/cm² at 650 °C [20]. In the
anode-supported design, however, anodic polarization at the interface between electrolyte and anode can dominate due to its relatively high volume fraction compared to the electrolyte and cathode.

Generally the SOFC anode provides the conducting phase for charge transfer as well as reaction sites for the electrochemical oxidation of the fuel [2]. For example with hydrogen as the fuel, the following reaction occurs

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (3-1)$$

For low temperature SOFC application, Ni-GDC cermet anode has been widely used due to high electrocatalytic effect of Ni both for the direct oxidation of hydrogen and for steam reforming of methane [46]. The GDC in the cermet anode, which high ionic conductivity at low temperature, extends the reaction zone and compatibility with GDC electrolyte in addition to preventing Ni sintering. Moreover, it has been reported that doped ceria showed high resistance to carbon deposition in hydrocarbon fuel [47]. In this composite structure, to achieve higher anode performance, the anode microstructures should be carefully controlled. Recent research by Suzuki et al. showed that high MPD of ~ 1.1 and 0.5 W/cm² at 600 and 550 °C with a anode-supported microtubular fuel cell using ~3 μm thick Sc-doped zirconia (ScSZ) and a GDC interlayer as electrolyte [48]. In this study, they demonstrated that IT-SOFC performance greatly depends on anode microstructural factors. For example, porosity and size of Ni particles in anode influenced concentration polarization and amount of triple phase boundary (TPB) which is believed as anodic reaction sites between the gas phase, ionic and electronic conduction phases. Moreover, it is generally accepted that most of the fuel oxidation reaction, such as eq.(3-1), take place in a limited zone inside ~ 10 μm
thickness of anode adjacent to the anode/electrolyte interface [10]. For this reason, interfacial anode functional layers (AFLs) have been explored to increase the TPB length. To date many studies have successfully demonstrated that graded AFL interlayers with submicron sized NiO particles at the anode/electrolyte interface can effectively extend active TPB site reducing anodic polarization and give higher mechanical and chemical stability [11, 49]. Most of these AFLs were fabricated by conventional colloidal slurry deposition.

In the previous work author and co-workers introduced a new method for fabricating AFLs by dispersing a GDC precursor at the interface between the anode and the electrolyte [14]. The resulting nano-sized particles formed a smooth interfacial region between the anode and electrolyte by filling in pores and crevices and also extending TPBs. This resulted in an improvement in electrolyte deposition quality as well as higher electrochemical performance.

Based on this study, the author developed a novel AFL which combines a conventional particle size (~ < 1 μm) AFL applied by colloidal deposition and a nano-sized Ni-GDC applied by a precursor solution coating. Due to the nature of the precursor solution, the nano-scale Ni-GDC can penetrate into the AFL and be well distributed. As shown in Fig. 3-1 we expect two major benefits from this bimodally integrated AFL concept. First, the TPB length of the AFL can be significantly higher than that of the conventional AFL because very fine Ni-GDC particles surround the submicron-size Ni-GDC AFL particles. Secondly, precursor solutions form very fine particles which fill submicron-sized pores at the interfacial region and thereby increase the actual 2-dimensional contact area with the electrolyte (2-phase boundaries) so that
it is in closer agreement with the nominal measured contact area, thus reducing the interfacial ohmic resistance. In addition to higher electrochemical performance, this novel AFL is very attractive for mass production of IT-SOFCs because all materials are commercially available (NiO and GDC powder, and metal cation nitrates) and this simple process is readily applicable to most anode-supported fuel cell designs with precise control.

In this chapter, the cost-effective and high performance novel AFL for IT-SOFCs is described. To investigate the effect of the novel AFL on SOFC performance, three cells all from the same anode tape were compared. These include no AFL, conventional AFL (referred to as C-AFL), and one sprayed precursor onto the conventional AFL to form a nano/micro composite AFL (referred to as N+C-AFL). Thin GDC electrolyte and $\text{La}_{0.6}\text{Sr}_{0.4}\text{C}_{0.2}\text{F}_{0.8}\text{O}_{3-\delta}$ (LSCF)-GDC composite cathodes were used for the balance of the button cells. The microstructural evolution was analyzed and the electrochemical performance of the SOFC with this novel AFL were measured and characterized.

### 3.2 Experimental

The NiO-GDC anode support was fabricated by tape-casting using a 65:35 (wt%) mixture of NiO (micron-scale, Alfa Aesar) and GDC (Rhodia) powders. Based on the ethanol solvent, an appropriate binder system was prepared with Solsperse, di-n-butyl phthalate (DBP) and poly-vinyl butyral (PVB), with mixing ratio of 5.9 : 44.1 : 49.9 wt%, as the dispersant, plasticizer, and binder respectively. For a homogeneous slurry with proper viscosity and strength before and after tape casting, the binder system was mixed with the powder mixture and ball-milled for 24 hrs. After a de-airing step to avoid cracks or defects caused by air bubbles during the tape-casting process, a Procast tape casting system (DHI, Inc) produced a NiO-GDC anode tape from the slurry. To make a
button type fuel cell, the dried tape was punched out into a circular shape with a 32 mm
diameter and pre-sintered at 900 °C for 2 hrs.

Fabrication of the N+C-AFL on anode substrate involved two steps. First, a NiO-
GDC colloidal slurry containing submicron size NiO (JT Baker) and GDC (Rhodia)
(65:35wt%) mixed with the proper binder system was deposited on one side of anode
support by spin coating. The binder system consisted of Solsperse, di-n-butyl phthalate
(DBP) and poly-vinyl buteral (PVB), with mixing ratio of 52.2 : 28.2 : 19.6 wt% as the
dispersant, plasticizer, and binder respectively. In this work, the C-AFL thickness was
maintained by coating the support two times at 1500 rpm for 15 s. Subsequent heat
treatment at 400 °C was carried out for the removal of the binder system. Next, the Ni-
GDC nitrate precursor was coated onto the first AFL. A 1 M solution of Ni-GDC
precursor having the same mole ratio of each element as the anode substrate was
synthesized by dissolving Ni(NO$_3$)$_2$·6H$_2$O, Gd(NO$_3$)$_3$·6H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O in ethyl
alcohol using ultra-sonication for 30 min. The precursor solution was transferred to a
spray gun (Excell), sprayed onto the C-AFL surface and pre-sintered at 900 °C for 1 hr.

Thin and even GDC electrolytes were deposited by spin coating with a GDC
colloidal slurry. For the GDC colloidal slurry, the Rhodia GDC powder was ball milled for
48 hrs with a binder system based on an ethanol solution. As a binder system, for 10 g
of GDC powder, 0.5g of Solsperse (dispersant), 0.3g of PVB (binder) and 0.2g of DBP
(plasticizer) were used with 70cc of ethanol. The spin coating was conducted at 1500
rpm for 15s for each deposition. After drying at room temperature for 10 hrs the
anode/N+C-AFL/electrolyte multilayer structure was sintered at 1450 °C for 4 hrs using
a 3 °C /minute ramp rate in air.
A La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) - GDC composite cathode was prepared and applied on the GDC electrolyte surface. Cathode inks were synthesized by mixing LSCF (Praxair) and GDC (Rhodia) at 50:50wt%. For a solvent, Alpha-terpiniol and ethanol were used. DBP and PVB were used as the plastisizer and binder, respectively. After mixing and grinding the cathode ink for 1 hour, the ink was brush-painted onto the GDC electrolyte evenly. The first layer of cathode ink was dried in an oven for 1 hour at 120 °C, and a second layer of the same cathode ink was brush painted onto the first layer. The active cathode area was ~0.4 cm$^2$. The cathode was fired at 1100 °C for 1 hour. Ag mesh and Pt wire were bonded onto both electrode surfaces using Pt paste for current collecting and then fired at 900 °C for 1 hour.

The AFL microstructures on Ni-GDC anode supports were observed using scanning electron microscope (SEM, JEOL 6400 / 6335F). For electrochemical performance, fuel cell samples were loaded in sealed fuel cell testing apparatuses. Current-voltage (I-V) characteristics were conducted by a Solartron 1287 using 30 sccm of dry air on the cathode side and 30 sccm of humidified (3 vol% H$_2$O) hydrogen on the anode side. In addition to the I-V measurement, 2-point electrochemical impedance analysis was carried out under open circuit condition using a Par-stat 2273 (Princeton Applied Research) with a frequency range of 100 KHz to 100 mHz.

**3.3 Result and Discussion**

Fig. 3-2 shows the microstructures of the anode substrate surfaces after application of the different AFL types and the evolution of these microstructures after various heat treatments. The AFL surfaces were compared after deposition and presintering at 900 °C (Fig. 3-2-a, c, e) in order to inspect and compare the initial morphological state of N+C-AFL deposition on the anode. As seen in Fig. 3-2-a, the
substrate with no AFL has numerous micron-sized pores. Such a microstructure can cause poor mechanical contact between the anode and electrolyte and lead to micro-cracking during high temperature operation [11]. In contrast, the microstructure of the N+C-AFL-covered surface (Fig. 3-2-e) exhibits little if any micron-sized porosity and the surface particles are fine and well distributed. The surface coated with C-AFL still exhibits a degree of micron size porosity (Fig. 3-2-c).

Next, we sought to observe the microstructure of the N+C-AFL coating after testing. However, due to the presence of the electrolyte on the surface, it is difficult to observe the reduced anode surface after electrochemical testing. Therefore, in order to simulate the effect of testing, the three anode samples were sintered at 1450 °C with no electrolyte coating and were reduced at 650 °C under simulated operational gas flow conditions for 10 hrs. Fig. 3-2-b shows again that the bare anode forms big pores on the interfacial surface, compounded by the reduction of large NiO particles into Ni metal. The conventional C-AFL exhibits a much finer particulate microstructure (Fig. 3-2-d). The characteristic microstructure of the N+C-AFL is presented in Fig. 3-2-f. Compared with Fig. 3-2-d, the very fine Ni and GDC particles (marked as dotted circles) appear to be better distributed between pores of the submicron size Ni-GDC AFL network structure, indicating likelihood for extended TPB lengths and 2-phase contact area with the electrolyte. Fig. 3-2-g exhibits a characteristic N+C-AFL structure magnified from Fig. 3-2-f. In this figure it is clearly shown that a nanosized particle is necking with submicron or micron sized AFL particles, which corresponds well with the schematic diagram of N+C-AFL in Fig. 3-1-b. Fig. 3-2-h shows the cross-sectional view of actual anode/N+C-
AFL/electrolyte multilayered structure after cell testing, indicating the very fine AFL structure is well constructed with dense electrolyte and porous anode.

Fig. 3-3 shows the I-V characteristics and power densities for the three different types of samples at the temperature ranges from 500 to 650 °C. In Fig. 3-3-a, I-V plots of 3 cells were compared at 600 °C and the detailed values are tabulated in Table 3-1. The C-AFL sample exhibited a maximum power density (MPD) of 681 mW/cm², an increase of 127% compared to the sample which used no AFL, which measured only 300mW/cm². In addition, the open circuit potential (OCP) of increased from 0.82 V for the cell without an AFL to 0.86 V for the cell using the conventional AFL. This supports the theory that particle size graded anode functional layers may improve the quality of GDC electrolyte deposition by partial filling the interfacial porosity [14]. Although the OCP of the Ni-GDC AFL sample was about 0.04 V higher than the sample with no AFL, as shown I-V plot in Fig. 3-3-a, the major contribution to the improvement in electrochemical performance comes from its lower area specific resistance (ASR).

For the novel N+C-AFL cell, the MPD reached 1160 mW/cm²—a 287% increase compared to sample with no AFL and 70% higher than that of sample using a C-AFL, while its OCP (0.85 V) was comparable to that of the C-AFL sample (0.86 V). Again, the highly improved performance is caused by the further reduction of the polarization losses. This result indicate that the precursor solution penetrated into the graded anode functional layer (Ni-GDC AFL) and formed nano-particles with proper percolation and distribution of both GDC and Ni particles, thus increasing active TPB length effectively at the interface between anode and GDC electrolyte.
To further investigate the effect of the N+C-AFL on performance enhancement, electrochemical impedance testing was conducted under open circuit condition on each sample at the same temperature range as used for I-V measurement (Fig. 3-4). Comparison of the nyquist plots of the three samples at 600 °C are shown in Fig. 3-4-b. The total, ohmic, and electrode ASR values at 600 °C were extracted and are given in Table 3-1. As expected from the I-V curves, the total ASR value of the N+C-AFL sample (0.206 Ω-cm²) was much less than that of the C-AFL sample (0.387 Ω-cm²) and the sample with no AFL (0.607 Ω-cm²), showing and ASR reduction of 47% and 66% respectively, which came largely from reduced electrode polarization drops. The electrode ASR of the N+C-AFL sample was reduced by 52% and 70%, respectively, compared to C-AFL and AFL-less samples, suggesting again that the use of the N+C-AFL did have a positive effect on extending TBP lengths. In addition, it should be noted that the ohmic ASR (0.070 Ω-cm²) of the N+C-AFL cell was also reduced by 31% and 53%, respectively, compared with C-AFL and no AFL cells. Based on previously reported ionic conductivity of GDC, ohmic ASR of ~10 μm thick GDC electrolyte is 0.054 Ω-cm², which is close to that of N+C AFL, while the ohmic ASRs of no AFL (0.149 Ω-cm²) and C-AFL (0.102 Ω-cm²) cell shows much higher values. As reported by Koide et al, these additional IR resistance can be caused by higher interfacial contact resistance between anode and electrolyte [50]. Therefore, this ohmic ASR drop of the novel AFL cell indicates that the N+C-AFL effectively improved the interfacial wetting and expended the active contact area of two phase (electrolyte and anode) boundaries at the GDC electrolyte/Ni-GDC anode interface, causing the lower resistance to the flow of
oxygen ions through the electrolyte to anode, as well as a two-phase boundary area that more closely matches the nominal active area used in power density calculations.

This ASR analysis implies two additional points with respect to anode-supported SOFCs. First, the anodic polarization in this SOFC design is a very large portion of the total electrode polarization, since modifying the anode alone using N+C-AFL reduced electrode ASR by 70%. Second, the fact that only ~5 μm of N+C-AFL lowered the total ASR by 66% shows that most of this anodic polarization occurs near the electrolyte/anode interfacial region (~μm of depth) which can be mitigated by the use of a proper anode functional layer at the interface.

Fig. 3-5 summarizes MPD obtained from I-V plots shown in Fig. 3-3 and total ASR values given in Fig. 4 of SOFCs with N+C-AFL, C-AFL, and no AFL at temperatures ranging from 650 °C down to 500 °C. The MPD of the N+C-AFL cell reached 1296, 697, and 380 mW/cm² at 650, 550, and 500 °C (Fig. 3-5-a). Thus, the improvement in performance becomes even greater at lower temperatures—the power density of the N+C-AFL cell compared to that of the cell with no AFL increased by 107% (625 to 1296 mW/cm²) at 650 °C and by 407% (75 to 380 mW/cm²) at 500 °C. The same trend is observed for the total ASR values as shown in Fig. 3-5-b. The total ASRs of the N+C-AFL were 0.091, 0.497 and 0.654 Ω-cm² at 650, 550 and 500 °C, respectively, showing total ASR reduction of 67.2 and 80.2% at 650 and 500 °C. This implies that at the low end of the IT range (below 650 °C), the ability of the N+C-AFL to reduce the ASR and improve MPD was confirmed and the improvements were significant. On the other hand, for all samples, the portion of electrode ASR in total ASR is getting greater as decreasing temperature (Fig. 3-4). Even N+C-AFL showed electrode ASR fraction
increase in total ASR from 54.8% at 650 °C to 75.8% at 500 °C. We believe this is because the sluggish oxygen reduction reaction occurred at the conventional perovskite cathode due to high activation energy at the lower temperature. Coupled with recently reported highly catalytic cathodes, even higher performance of this SOFC is expected at low temperature.

3.4 Conclusions

In conclusion, bimodally integrated nano-/micron- composite AFL was developed by simple spray coating a precursor solution into conventional submicron sized Ni-GDC in a functional layer. This combined structure produced a novel N+C-AFL. Microstructural analysis revealed that very fine Ni and GDC particles were homogeneously distributed into the conventional AFL and formed network structures in 3D, leading to a significant increase in TBP length. A SOFC using this novel AFL exhibited a MPD of 1.16 W/cm² at 600°C. Due to its characteristic structure, N+C-AFL reduced both electrode and ohmic ASR. Compared with the performance of a SOFC without AFL, the cell using the N+C-AFL showed a 287% increase in power density as well as a 66% reduction in total ASR. This effect was observed throughout the IT range tested, indicating the N+C-AFL is an excellent structure for use in high performance IT-SOFCs.
Figure 3-1. Schematic illustration of the proposed N+C-AFL structure on anode-supported SOFC and effect of N+C-AFL on expending TPB length. Yellow triangles represent TPBs in conventional AFL (C-AFL) and red triangles represent TPBs by N+C-AFL.
Figure 3-2. SEM micrographs of the anode surface after deposition and pre-sintering (a, c, e) and after full sintering followed by simulated testing atmospheric conditions (b, d, f) for samples with no AFL (a, b), C-AFL (c, d) and N+C-AFL (e, f). Highly magnified image shows the characteristic N+C-AFL structure (g). The cross sectional image presents actual multilayered fuel cell with N+C-AFL(h).
Figure 3-3. Comparison of I-V characteristics for the fuel cell samples with N+C AFL, C-AFL, and no AFL at 600 °C. (a) I-V plots at the temperature ranging from 650 to 500 oC for N+C-AFL (b), C-AFL (c), and no AFL (d).
Figure 3-3. Continued
Figure 3-4. Electrochemical impedance spectra of the testing samples with N+C AFL, C-AFL and no AFL at various temperature; 650 °C (a), 600 °C (b), 550 °C (c), and 500 °C (d).
Figure 3-5. MPD (a) and ASR plots (b) for the different samples tested between 500 and 650 °C.
Table 3-1. Detailed OCP, MPD and ASR values of the fuel cell samples with N+C-AFL, C-AFL, no AFL at 600°C.

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<th>MPD (mW/cm²)</th>
<th>Total ASR (Ωcm²)</th>
<th>Ohmic ASR (Ωcm²)</th>
<th>Electrode ASR (Ωcm²)</th>
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</tr>
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CHAPTER 4
EFFECT OF NI-GDC AFL COMPOSITION ON PERFORMANCE OF IT-SOFCs

4.1 Introduction

Wider commercialization of solid oxide fuel cells (SOFCs) can be achieved by lowering the operation temperature [5]. Critical points to achieve this goal are to alleviate the significantly increased ohmic and activation polarizations at reduced temperatures due to their thermally activated nature [5, 7, 44]. Anode-supported designs for solid oxide fuel cells operating at intermediate temperatures (IT, 500 ~ 650 °C) are widely used due to their ability to utilize a very thin electrolyte (below ~10 μm), eliminating a large fraction of the ohmic polarization loss [51, 52]. Currently, state of the art thin electrolytes and highly electrocatalytic cathodes are applied on anode-supported cells, showing high performance at IT ranges. For example, we reported that anode supported SOFCs using a Ni/ Ce0.9Gd0.1O1.95 (GDC) composite anode, bismuth oxide/GDC bilayered electrolyte and bismuth/ruthenate composite cathode achieved an exceptionally high maximum power density (MPD) of ~ 2 W/cm² at 650 °C [20]. In the anode-supported design, however, anodic polarization at the interface can dominate due to its relatively high fraction of volume compared to the electrolyte and cathode. Generally, the anode-support is fabricated using submicron-sized NiO particles with pore-former to increase porosity in the anode [11, 53]. Even though sufficient porosity is readily achieved, the large sized pores at the electrolyte interface cause a large interfacial anodic loss and low mechanical strength due to the poor quality of electrolyte deposition [11]. To overcome these problems, interfacial anode functional layers have been developed. Up to this date, many researchers have reported that thin anode functional layers (<10 μm) using fine particles without pore-former effectively reduce
activation polarization by increasing triple phase boundary (TPB) density, strengthening mechanical properties and lowering ohmic losses by improving the quality of electrolyte deposition due to significantly reducing interfacial porosity [11, 53-56].

For the last several years, we have concentrated on developing high performance IT-SOFCs with a tape cast Ni-GDC anode using large micron-sized NiO particles [14]. Although this anode design provided sufficient mechanical properties and porosity without additional pore-former, it still suffered from low performance. The low performance is due to the coarse microstructure with large size pores at the electrolyte interface, causing poor electrolyte deposition. Recently, Ahn et al. introduced a new method to establish AFLs by dispersing a GDC precursor solution at the anode/electrolyte interface by simple spray coating. This resulted in ultra fine particles forming a much smoother interface, leading to extended TPB density [14]. Based on this study, Lee et al. developed a novel AFL integrating a nanosized Ni-GDC particles into a submicron-sized AFL by a simple precursor solution coating [57]. Because of the nature of the precursor solution, very fine Ni-GDC particles were well-distributed and formed a bimodally structured AFL. The AFL led to a high performance of ~1.3 W/cm² at 650 °C with a 10 μm thick GDC electrolyte. We have shown how microstructural changes due to different particle sizes influence the electrochemical performance for SOFCs with respect to the surface porosity and anode active reaction sites, TPBs. However, the spatial distribution, amount of porosity and TPBs in two phase composite anodes can be significantly affected by the amount of each phase [12, 58]. In this study, we fabricated and investigated IT-SOFCs having AFLs of various compositions using submicron-sized NiO and GDC particles at the electrolyte interface. Electrochemical
performance studies were conducted by current-voltage (I-V) and impedance testing. The optimal composition of this AFL was investigated, and the relationships between composition and performance were analyzed.

4.2 Experimental

4.2.1 Cell Fabrication

Flat NiO-GDC anode supports were fabricated by the tape-casting method. In order to provide a sufficient gas channel without the aid of pore-former, micron-sized large NiO particles (Alfa Aesar) were mixed with nano sized GDC from Rhodia. In this study, the composition of the anode support was fixed at 65 to 35wt% of NiO to GDC. Based on the ethanol solvent, an appropriate binder system was prepared with Solsperse, di-n-butyl phthalate (DBP) and poly-vinyl butyral (PVB) as the dispersant, plasticizer, and binder respectively. For a homogeneous slurry with proper viscosity and strength before and after tape casting, the binder system was mixed with the powder mixture and ball-milled for 24 hrs. After a de-airing step to avoid cracks or defects caused by air bubbles during the tape-casting process, a Procast tape casting system (DHI, Inc) produced a NiO-GDC anode tape from the slurry. To make a button type fuel cell, the dried tape was punched out into a circular shape with a 32 mm diameter and pre-sintered at 900 °C for 2 hrs.

For a finer and graded AFL structure, submicron-sized NiO (JT-Baker) was mixed with nano-sized GDC (Rhodia). To investigate the effect of the composition of the AFL, various NiO-GDC AFL contents, from 40wt% to 80wt% of NiO, were fabricated on the anode surface by spin coating. Similar to the tape casting slurry, a proper binder system was added to each AFL powder, leading to a well dispersed colloidal slurry. During the spin coating process, the thickness of the Ni-GDC AFL layer was controlled by the
number of depositions at the same spin speed and time. In this work, we produced the same thickness of AFL by applying 3 coats at 1500 rpm for 15s. After deposition, the AFL layer was pre-sintered at 900 °C for 1 hour to remove the binder system.

For the electrolyte, the same GDC powder for the anode and AFL was ball milled for 48 hrs with a binder system based on an ethanol solution. As a binder system, Solsperse (dispersant), PVB (binder) and DBP (plasticizer) were used. The thin GDC electrolyte was coated by the spin coating method with same process as the AFL deposition. After deposition, samples were dried at room temperature for 10 hrs. After drying the multilayer anode/AFL/electrolyte structure was sintered at 1450 °C for 4 hrs.

A La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) - GDC composite cathode was prepared and applied on the GDC electrolyte surface. Cathode inks were synthesized by mixing LSCF (Praxair) and GDC (Rhodia) at 50:50wt%. For a solvent, Alpha-terpiniol and ethanol were used. DBP and PVB were used as the plastisizer and binder, respectively. After mixing and grinding the cathode ink for 1 hour, the ink was brush-painted onto the GDC electrolyte evenly. The first layer of cathode ink was dried in an oven for 1 hour at 120 °C, and a second layer of the same cathode ink was brush painted onto the first layer. The active cathode area was ~0.4 cm². The cathode was fired at 1100 °C for 1 hour. Ag mesh and Pt wire were bonded onto both electrode surfaces using Pt paste for current collecting and then fired at 900 °C for 1 hour.

4.2.3 Characterization

For electrochemical performance, the prepared cells were loaded on a fuel cell testing set-up. In order to obtain the gas-tight sealing, the edge of the cell and testing tube were covered with a mixture of two parts ceramic sealant using ceramabond-517 (Aremco). I-V tests were carried out by a Solartron 1407E with 3% wet hydrogen as a
fuel on the anode side and dry air as an oxidant on the cathode side at various temperatures. The gas flow rate was controlled by a mass flow controller (MKS 647C). In addition to current-voltage characteristics, electrochemical impedance spectroscopy with a two-point probe was measured by a Solartron 1400 using a frequency range of 100 kHz to 100 mHz under the same gas and temperature conditions.

For microstructural analysis, the tested fuel cells were fractured and the cross-sections of the multilayered structures were observed using a scanning electron microscope (SEM, JEOL 6400 / 6335F) with the back-scattering mode.

4.3 Results and Discussion

In this study, five kinds of fuel cells with AFLs containing 40, 50, 60, 65, and 80 wt% of NiO were prepared in order to investigate the effect of AFL composition on the microstructure and electrochemical performance. At the same time, a cell without AFL was tested as a reference cell.

4.3.1 Microstructural Analysis

Figure 4-1 shows the microstructures from a cross-sectional view of the samples with different AFL compositions after reducing and testing under 90 sccm of air on the cathode side and hydrogen on the anode side. In order to directly compare the effect of the AFL, the thickness of the electrolyte, anode, cathode, and active cathode area were designed to be the same between the different samples. As seen in Figure 4-1-a~f, the dense GDC electrolyte for each cell shows an even thickness of 17 to 19 μm, with a few closed pores. For the other anode and cathode, the thicknesses were measured by SEM and found to be nearly identical between the samples at 290 μm to 300 μm for anode and ~30 μm for cathode. For the AFLs, each AFL thickness measured was about 10 μm. In addition, it is clearly shown that interfaces between the AFLs and GDC
electrolyte (Fig. 4-1-b~f) look very flat and continuous while the interface between the GDC electrolyte and anode support (no AFL sample, Fig. 4-1-a) shows a very irregular and discontinuous morphology due to large pores caused by reduction of large size NiO into Ni.

In Fig. 4-2, the magnified microstructures of the anode/AFLs nearby the GDC electrolyte after reducing and testing are presented. In comparing Fig. 4-2-a to 4-2-b~f, particulate size differences between the AFLs and anode are clearly shown indicating that submicron-sized NiO successfully formed a very fine Ni-GDC AFL structure. Using backscattered mode the Ni (dark gray), GDC (white), and pore (black) phases are well distinguishable due to contrast difference. As shown in Fig. 4-2-b~f, it is observed that the amount of both Ni phase and porosity due to reduction of NiO into Ni during the operation increased with higher NiOwt% in AFL.

4.3.2 Effect of AFL Composition on Power Density
4.3.2.1 I-V characteristics at 650 °C

Fig. 4-3 shows I-V characteristics of fuel cells with various compositions of AFL at 650 °C. The open circuit potential of the tested cells were 0.806, 0.834, 0.838, 0.814, 0.807, and 0.801 V for the cells with no AFL, 40, 50, 60, 65, and 80wt% NiO AFL. It has been commonly reported that formation of AFL at the interface between the anode and thin electrolyte enhances OCP [13, 14, 57]. Generally the theoretical Nernst voltage for thin electrolytes below 10 μm can be lowered by gas permeation through electrolyte which is caused by various structural defects such as open pores and microcracks in addition to inherent internal shorting of a mixed ionic and electronic conductor (MIEC) such as doped ceria. In that case, AFL can help to enhance the quality of the electrolyte deposition by reducing the possibility of crack and pore formation at the interface due to
its finer and reduced surface porosity [14, 57]. In addition, as Chen et al. reported, AFL itself can act as a barrier to gas permeation along with the electrolyte although this can cause concentration polarization [13].

In this study, however, the OCP does not increase only by the existence of the AFL, as shown between the AFL cell (0.806V) and 65% wt NiO AFL cell (0.807 V). It is considered that the electrolyte thickness (~20μm) was much larger than the size of bare anode surface pore (below 5 μm), suggesting a similar gas permeability in all electrolytes regardless of AFL existence. Instead, the observed OCP seems to be influenced by AFL composition.

Fig. 4-4 shows the plot of OCP versus NiO composition of the AFL or anode at the anode/electrolyte interface. Higher OCP is observed with decreasing NiO wt% in the AFL. SEM observation of the anode and AFL structure before reduction reveals that the anode without pore-former and AFL are relatively dense with little porosity. Therefore, it is considered that the total pore volume in the anode or AFL after testing increases proportionally with NiO content because the only source to produce porosity is the reduction of NiO under operational conditions. This indicates that an AFL with lower NiO content forms less porosity after reduction and is a better barrier of gas permeation, leading to a higher OCP. In addition, the higher Ni content can cause lower OCP because of greater electronic conductivity. It has been reported that for thin MIEC electrolyte, OCP greatly depends on electrolyte thickness [59, 60]. Therefore it is noted that for the ultra thin electrolyte system, the OCP change with AFL composition can be much greater and have a significant impact on cell performance.
The maximum power densities (MPDs) of cells with no AFL, 40, 50, 60, 65, and 80 wt% NiO AFL were obtained from the power density curves in Fig. 4-3 as 882, 732, 1033, 1147, 1077, and 711 mW/cm², respectively. In addition to MPDs, total area specific resistance (ASR) value for each cell also estimated from the IV curves near OCP region. Resultant MPDs and total ASRs are plotted in Fig. 4-5. Compared to the no AFL cell, cells with 50, 60, and 65wt% NiO AFL showed significant improvement in MPD at 650 °C. While the OCPs of these cells (Fig. 4-4) shows a different trend and relatively trivial change (~0.03V), the resultant performance enhancement mostly comes from decreasing polarization with AFL, as shown in Fig. 4-5. This implies that the finer AFL structures (Fig. 4-2-c,d,e) effectively increased TPB density at the anode/electrolyte interface. In contrast, MPDs of cells with 40 and 80wt% NiO AFL compared to that of cell with no AFL were decreased. In this case, it is considered that although the AFLs formed very fine particulate structures (Fig. 4-2-b,f), excessively high content of NiO or GDC can reduce the connectivity of the TPBs (Ni, GDC, and pore) leading to inactive regions. Therefore, the AFL composition should be considered as an important factor in terms of SOFC performance.

As mentioned above, the highest MPD was obtained at the AFL with 60wt% of NiO (1147 mW/cm²) showing a 30% increase compared to no AFL cell (882 mW/cm²), while higher OCPs were observed at higher NiOwt% AFLs. Assuming full reduction of NiO into Ni during operation, the Ni to GDC volume ratio of this AFL is easily calculated with the densities of Ni, NiO and GDC. The results is 48.6vol% Ni to 51.4vol% GDC, that is almost 1:1 volume ratio. This result is in good agreement with a recent study of NiO-SDC (samarium-doped ceria) AFL system by Ai et al [12]. It was also predicted by
previous modeling work. Schnieder et al. conducted analytical modeling for estimating TPB length of composite electrode using the discrete element method and showed that the TPB length is maximized at 50vol% of the ionic conducting phase in the composite anode [61]. On the other hand, another recent study by Wilson and Barnett reported the lowest electrode ASR with the highest TPB length at 50wt% NiO in a NiO-YSZ(yttria-stabilized zirconia) active layer, which is a 1:2 volume ratio of Ni to YSZ [62]. However, it is reasonably considered that the ionic conductivity of stabilized zirconia is much lower than that of doped ceria at the IT range (500 °C ~ 800 °C). The NiO particle size (~2.5 μm) used in that study was much larger compared to this study’s NiO size (< 1 μm). Therefore, the lowest resistance with the highest TPB length can be achieved at lower GDC content and higher NiOwt%, leading to higher porosity. For further understanding, the quantification of microstructural properties will be needed to find relationship with electrochemical performances.

4.3.2.2 Temperature dependence

In order to verify the validity of the optimal AFL composition of 60wt% NiO at the IT range, a current-voltage measurement for each cell was conducted at various temperatures from 450 to 650 °C with a 50 °C interval. The resultant MPDs with AFL composition are plotted in Fig. 4-6, including the MPDs of the no AFL cell separately marked as open symbols. For all temperatures tested, cells with 60wt% NiO in the AFL shows highest MPDs with 1147, 626, 271, 118, and 45 mW/cm² at 650, 600, 550, 500, and 450 °C, respectively. This result shows that the effect of AFL optimal composition is valid through the intermediate to low temperature ranges.
4.3.2.3 Long term stability

To see the effect of optimal composition AFL on high performance, a potentiostatic test under an applied voltage where cells reached 98% of their MPD was done for each cell. The applied voltages were 0.379 V for the AFL cell and 0.380 V for the no AFL cell. Fig. 4-7 shows preliminary results of a 200 hrs long term stability test for the no AFL and 60wt% NiO AFL cells under the 90 sccm of H₂/Air condition. While the no AFL cell shows initial degradation of power density and stabilized behavior, the effect of the optimal composition AFL was retained for 200 hrs with high power density of ~1.1 W/cm². For practical application of this AFL, however, further long term testing under various temperatures and gas conditions should be conducted.

4.3.2.4 Effect of AFL composition on ASR

In order for further investigation, electrochemical impedance tests were carried out for all samples. Fig. 4-8-a shows the impedance spectra of each AFL composition at 650 °C for which an I-V test was conducted. From the high and low frequency complex-plane intercepts of the impedance spectrum with the real axis, the ohmic, electrode, and total ASR values were calculated while normalizing the resistance according to cathode area. The detailed values are tabulated in Table 4-1 and plotted in Fig. 4-8-b. As shown in the Table, in this study, total ASR values from electrochemical impedance (ASREIS) are within 4% deviation from the ASR at IV curves (ASRIV) in Fig. 4-5.

As expected from the previous section, total ASRs from AFL composition show a similar trend to the MPD. The lowest total ASR (0.188 Ωcm²) at 650 °C was achieved at 60wt% NiO AFL, which was decreased by 25.7% from that of the no AFL cell (0.253 Ω·cm²). The ohmic ASRs are similar for all samples because the samples tested in this study have similar thicknesses of electrolytes with similar densities as supported by
microstructures shown in Fig. 4-1. Therefore, most of the ASR drop comes from the electrode ASR drop, which is considered as anodic polarization reduction since the cathodes should be identical. From this result, it is expected that different AFL compositions directly influence a change in TPB density, affecting anodic polarization. Most likely the TPB density is the highest at 60wt% of NiO in AFL, which is at 1:1 volume ratio of Ni to GDC after reduction.

Based on these results, the relationship between electrode ASR and MPD with various AFL compositions are examined. As shown in Fig. 4-5, the performance enhancement of power density reflects the ASR trend. In Fig. 4-9, it is clearly shown that electrode ASR has an almost linear relationship with MPD. However, there are still some deviations from the linearity. At this point it is noted that the ASRs were measured at the open circuit condition, whereas the MPDs occurred at higher current densities which have complex contributions from various polarizations, such as activation, ohmic and concentration polarization as shown in I-V curves in Fig. 4-3. Therefore, for a more precise study, the ASRs measured under applied currents will be done in the future. In addition, to completely understand electrode ASR, comprehensive microstructural features should be considered, such as surface area, porosity, tortuosity and TPB density.

4.4 Conclusions

In this study, the effect of AFL composition on the electrochemical performance was investigated for IT SOFCs. For this, the various AFLs with composition from 40 to 80wt% NiO were fabricated. The fine and well-distributed AFL structures with different NiO amounts were confirmed by microstructural analysis. The optimal AFL composition was achieved at 1:1 volume ratio of Ni to GDC in the AFL, which is 60wt% NiO. The
effect of the optimal AFL composition on MPD was valid at intermediate to low
temperature ranges. In addition, a preliminary long-term stability test showed the
possibility of practical application of this optimal composition. The measured MPD and
ASR show a linear relationship implying that the performance enhancement greatly
depends on the AFL composition, which might be caused by microstructural features
such as TPB density, porosity, tortuosity of pores and surface area. For further
understanding of the AFL effect on electrochemical performances, the quantitative
analysis of AFL microstructures should be done.
Figure 4-1. Backscattered images showing a cross-sectional view of anode-supported SOFCs with different NiO content in the anode functional layers; no AFL(a), 40wt% (b), 50wt%(c), 60wt%(d), 65wt%(e), and 80wt%(f) NiO.
Figure 4-2. Magnified microstructures of the anode or AFLs with different NiO content. No AFL (a), 40wt% (b), 50wt% (c), 60wt% (d), 65wt% (e), and 80wt% (f) NiO. Backscattering mode provides better contrast to distinguish Ni (dark gray), GDC (white), and pore (black) phases.
Figure 4-3. I-V plots of fuel cells with various AFL compositions at 650°C; 40(●), 50(▲), 60(★), 65(●) and 80(▶)wt% of NiO in AFL, and no AFL(■). The gas condition was 90sccm of air and 3% of wet hydrogen on the anode and cathode side, respectively.
Figure 4-4. Open circuit potential of the fuel cells with various NiO contents in NiO-GDC AFL. Solid line (red) shows linear fit of the measured data (square)
Figure 4-5. MPD (Red square) and total $\text{ASR}_{\text{iv}}$ estimated from IV curves (blue star) are plotted with NiO contents in AFL. The open symbols represent no AFL cell.
Figure 4-6. Maximum power densities of fuel cells with various AFL compositions at the temperature range from 450 to 650 °C. Open symbols represent MPD of no AFL cell at each temperature.
Figure 4-7. Long term stability test of fuel cell with 60wt% of NiO in the AFL and the no AFL cell for 200 hrs at 650 °C. Potentiostatic tests were conducted with an applied voltage of 0.379 V for the NiO 60wt% AFL cell and 0.380 V for the no AFL cell, at which the cells showed 98% of MPD. The gas condition was 90sccm of air and 3% of wet hydrogen on the anode and cathode side, respectively.
Figure 4-8. Impedance spectra with various AFL compositions (a), and total, electrode, and ohmic ASRs of fuel cells with different NiO content (b) calculated from impedance spectra (a). Open symbols represent no AFL results.
Figure 4-9. MPD plots with electrode ASR shows a linear relationship. Red line is linear fitting of the measured data (black dots).
Table 4-1. Detailed ASR values of the testing cells with various NiO contents in AFL

<table>
<thead>
<tr>
<th>AFL</th>
<th>NiO (wt%)</th>
<th>Total ASR&lt;sub&gt;iv&lt;/sub&gt; (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Total ASR&lt;sub&gt;EIS&lt;/sub&gt; (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Ohmic ASR (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>Electrode ASR (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40:60</td>
<td>40</td>
<td>0.259</td>
<td>0.260</td>
<td>0.071</td>
<td>0.189</td>
</tr>
<tr>
<td>50:50</td>
<td>50</td>
<td>0.227</td>
<td>0.231</td>
<td>0.070</td>
<td>0.161</td>
</tr>
<tr>
<td>60:40</td>
<td>60</td>
<td>0.182</td>
<td>0.188</td>
<td>0.055</td>
<td>0.133</td>
</tr>
<tr>
<td>65:35</td>
<td>65</td>
<td>0.196</td>
<td>0.203</td>
<td>0.061</td>
<td>0.142</td>
</tr>
<tr>
<td>80:20</td>
<td>80</td>
<td>0.286</td>
<td>0.281</td>
<td>0.076</td>
<td>0.205</td>
</tr>
<tr>
<td>no AFL</td>
<td>65</td>
<td>0.253</td>
<td>0.253</td>
<td>0.074</td>
<td>0.179</td>
</tr>
</tbody>
</table>
CHAPTER 5
COMPREHENSIVE QUANTIFICATION OF NIO-GDC ANODE FUNCTIONAL LAYER
MICROSTRUCTURE BY THREE-DIMENSIONAL RECONSTRUCTION USING
FIB/SEM

5.1 Introduction

The inevitable demand on lowering solid oxide fuel cell (SOFC) operational
temperatures has been fueled by commercialization of SOFCs [3, 5, 7, 9, 63]. Currently
the anode supported SOFC design has been widely studied due to possible
accommodation of ultra thin electrolyte [8, 20, 55]. For this design, however, the anode
polarization is possibly dominant due to the anode having the largest volume fraction in
the SOFC. To solve this problem, the electrode polarization losses at the anode should
be effectively reduced. It has been well known that the microstructures of an electrode
greatly influence the electrochemical properties in a SOFC. For example, the volume
fraction of the each component in the electrode can modify microstructures in an anode
or cathode[62]. In previous work, it was shown that tailoring different compositions of
the anode functional layer changed the electrochemical performance and power density
of the SOFC [64]. In the work, 60wt% of NiO in NiO-GDC AFL, which is Ni-GDC AFL
after reduction, showed highest maximum power density with 1.15 W/cm² at 650 °C.
Reducing the electrode ASR is the major factor for increase performance, and the ASR
was found to have an optimal NiO composition (60wt%) of AFL. Moreover, the electrode
ASR and AFL composition change showed an inverse linear relation to maximum power
density. It was expected that at the optimal composition the number of reaction sites,
that is, triple phase boundaries (TPBs), which consisted of an electronic conductor (Ni),
ionic conductor (GDC), and gas diffusion path (pore), is highest. However, the
evaluation of TPB density is not easily achieved with the conventional two dimensional
(2D) SEM analysis. Some studies were conducted for estimating TPB length or density by stereological methods using analysis of 2D SEM images [62, 65]. However, accuracy of active TPB length estimation was limited due to phase interconnectivity issues, which is three-dimensional (3D) property. Recently, 3D reconstruction techniques were employed to deal with microstructural analysis of SOFCs using FIB/SEM dual beam system [66-72]. Using this technique, more accurate and realistic quantifications of the SOFC electrode microstructure has been available. Moreover, quantified microstructural features were attempted to link directly with electrochemical properties. For example, TPB density was linked to charge transfer and adsorption properties and the tortuosity was used to describe concentration polarization[68]. However, most of the studies were conducted for composite cathodes and Ni-YSZ anode for intermediate to high temperature (> ~700 °C) SOFC applications.

In this study, the microstructural features of Ni-GDC AFLs, which is widely used for intermediate to low temperature (400 ~ 700 °C) SOFCs, with different NiO contents were investigated by 3D reconstruction technique using a FIB/SEM dual beam system. After reconstruction, the comprehensive quantification for various properties of the studied samples was conducted and the values were analyzed. Finally, the active TPB density was calculated and linked with electrochemical performances

5.2 Experimental

In the work four AFL samples were reconstructed and quantified, which include cells with 50, 60, 65, and 80wt% NiO AFL. As a reference, a sample without an AFL was also reconstructed. The detailed fabrication process and electrochemical performance test of the samples were described in previous work [64]. First of all, all samples were mounted in an epoxy supporter using a Struers EpoVac System. At the
same time, this epoxy infiltrates into the samples and fills open pores inside porous Ni-GDC anode/AFL structures, providing better contrast for SEM imaging. After the mounting process, the sample stub was grinded and polished using sandpaper and diamond paste down to 1μm roughness to obtain an even surface of the mount exposing anode-electrolyte interface.

The automated sectioning and imaging were carried out with a FIB/SEM duel beam system (FEI Strata DB 235). In this system, the electron beam pole (SEM) against the ion beam pole (FIB) leans at a 52° angle. (Fig. 5-1-a) The image at each slice was captured by SEM. To get better contrast difference among the phases, a through-lens-detector (TLD) in backscatter mode was utilized. The FIB was used to create a trench around the region of interest (ROI). The slicing distance (z-axis resolution) was 60 nm. To avoid charging effect during SEM process and protect from ion damage, protective platinum layers were deposited with an in-situ liquid metal-organic ion source (LMIS). This repeated imaging and slicing processes were automatically controlled using the Auto Slice and View software system (FEI Company).

After collecting the cross-sectional images for each sample, the alignment, segment, cropping and labeling for the three dimensional reconstruction were conducted by Amira software – ResolveRT™ (ver 4.0, Mercury Computer System Inc.). Fig. 5-1-b shows the schematic diagram of 3D reconstruction process. Amira was also utilized to quantify the various microstructural features from the 3D reconstructions of the samples, such as each phase (Ni, GDC, and pore) volume and surface area, phase gradient, and tortuosity of pores.
5.3 Results and Discussion

Fig. 5-2 shows the 3D reconstructions of the cells, which allows for direct qualitative comparisons between the anode/AFL structures. The z-axis dimension reconstructed for each sample was approximated at the distance of 8~10 μm from GDC electrolyte interface. Considering AFL thickness (~10μm) measured in previous study, the analyzed AFL depth in this study covers almost full cross-section of each AFL [64]. The detailed dimension for reconstructed samples are summarized in Table 5-1. Compared to the no AFL sample (Fig. 5-2-a), cells with AFLs (Fig. 5-2-b,c,d,e) show much smaller particulate structures. Among the AFLs, the change of amount of Ni (green in 3D reconstruction) and GDC (red in 3D reconstructions) is clear as NiOwt% increases. This result is in good agreement with 2D SEM image observation discussed in the previous section. Moreover, this 3D reconstruction allows the separation of each phase, or to combine only two phases. As illustrated in Fig. 5-3, each phase of GDC, Ni, pore, and combination of Ni-pore phases were reconstructed individually. From this phase separation, the quantification of the phase gradient, volume fraction, and surface area for each phase is possible. For the spatial distribution of each phase in AFLs, the phase gradient for each AFL sample was plotted in Fig. 5-4. It is evident in Fig. 5-4 that from b to e, the level of Ni and pore phase is getting higher, while the amount of GDC phase is decreased. In addition, the all AFLs (Fig. 5-4-b,c,d,e) have a very narrow transition zone (~ below 500nm) which is a region for significant increase of the GDC phase nearby GDC electrolyte, compared to over 2000 nm for bare anode (Fig. 5-4-a). This result indicates a very fine microstructure in the AFL and its features such as high surface area and large amount of reaction sites (TPBs) are well retained at the interface of the AFL/electrolyte. The anode without AFL lose many reaction sites and gas
diffusion paths due to penetration of the GDC electrolyte into large anode pores at the interfacial zone which is known to be the most important active reaction zone for the hydrogen oxidation.

For Ni, GDC and pore phases, the phase volume fractions were quantified using Amira™ tissue-statistics module. In this module, the number of voxels for each phase were counted and based on this result the numerical volume fraction for each phase is easily able to be calculated. This result can be one of the basic criteria for the practical confirmation of the credibility of the resultant 3D reconstructions. It is because there are theoretical values of Ni reduced from NiO, GDC, and pore volume fraction based on initial AFL composition, which can be calculated from the material properties such as Ni, NiO, and GDC densities when assuming full reduction of NiO into Ni. The theoretical and measured values of total volume fraction of each phase for different AFL are tabulated in Table 5-1 and plotted in Fig. 5-5-a. As observed in phase gradient graphs (Fig. 5-4), the Ni contents and porosity in AFL increases with increasing NiOwt%, while GDC is inversely proportional to initial NiOwt% in AFL. It is clearly shown that the Ni and GDC volume fractions extracted from the 3D reconstruction are well matched with theoretical values. For example, the volume fractions of Ni were 29.1 ± 1.0, 37.8 ± 5.9, 43.2 ± 6.7 and 51.1 ± 6.4vol% for 50, 60, 65, and 80wt% NiO AFL samples, respectively, which are very close to the theoretical values of 30.4, 36.3, 39.2, and 47.7vol%. However, porosity is little below the theoretical value, which might be an attributable to sampling resolution. In addition to the total volume fraction, the solid phase volume fraction between GDC and Ni was also calculated (Fig. 5-5-b). As expected from the theoretical value, at 60wt% NiO AFL the Ni to GDC volume ratio was
almost 1:1 with measured value of 48.1 ± 6.7 and 51.9 ± 6.7, at which ratio the highest performance among studied samples were shown in previous section. At this point, it is noted that these volume fraction results from the 3D reconstructions were based on around 150 slices of 2D SEM images and the graded phase plots in Fig. 5-4 showed the continuous fluctuation of each phase along the distance from the electrolyte. Therefore, to quantify the structural analysis of the composite SOFC anodes, the 3D reconstruction is more reliable and necessary compared to 2D SEM image analysis method.

The total surface area values of the AFL structures with different NiO contents were calculated using Amira tissue statistics module. The resultant values are normalized by the total volume of the region of interest (ROI) (Table 5-2).

The effective particle or pore diameters \( d \) for each AFL composition were calculated with a Brunauer-Emmett-Teller (BET) method using a general formula written as;

\[
d = 6 \frac{V}{S}
\]  

(5-1)

where \( V \) and \( S \) are the volume and surface area of the each phase, respectively. The Amira tissue statistics program was utilized for the calculation of the phase volume and surface area of Ni, GDC and pore in each sample. The effective diameters of Ni \( (d_{Ni}) \) phase in 50, 60, 65 and 80wt% NiO AFL correspond to 683, 771, 917, and 1120 nm, respectively, showing the expected trend. The complete data set is tabulated in Table 5-2 and plotted in Fig. 5-6. For all three phases, the linear relationship between effective diameter and AFL composition is shown, which is the proportionality for Ni and porosity, and an inverse proportionality for GDC. This result implies that the high NiO content in the AFL produce a structure with large Ni particles and very small GDC.
particles, which can cause poor connectivity of the smaller particle phase (GDC), increasing the deactivated TPB sites. In contrast, for low NiO AFL, same situation for Ni phase can occur but worse due to lower porosity, which interferes with the fast gas diffusion. Therefore, it is expected that at the medium point, around 55~60wt% NiO AFL can have optimal structure for highest TPB density. In this case, particle size control should be considered with other factors, such as composition and porosity.

The tortuosity was estimated using the moment of inertia module in the Amira software. Using this module, tracking of the center of the open pore phase through sample from the beginning of the AFL to the GDC electrolyte interface is possible, which allows us to measure the accumulated 3D Euclidian distance through the region. The accumulated Euclidean distance divided by AFL thickness yielded the tortuosity of the each sample (Table 5-2). For the 50, 60, 65, and 80wt% NiO AFL, the tortuosity values were 2.77, 1.91, 1.91, and 1.69, respectively. This result is in good agreement with the general theory that the higher porosity with larger pore diameter provides less complicated gas diffusion paths through the open pores, which means low tortuosity. This tortuosity concept can be combined with volume fraction of porosity to estimate effective diffusion coefficient, which is directly related to concentration polarization [68]. Therefore, for further analysis of this property and cell performance the deconvolution of the electrochemical impedance under applied current is in progress.

The TPB density for each AFL composition was quantified. The TPB site is where the three phases such as Ni, GDC, and pore meet at the same place. However, the TPB works only when these phases are properly connected. For example, the GDC phase of a TPB site should be connected to the GDC electrolyte to make a path for
oxygen ions from anode(AFL)/ GDC electrolyte interface to the active site. At the same
time, the Ni phase and pores should have percolation to the interconnect (or current
collector) and fuel side (outside anode), respectively. The reasons are to bring hydrogen
gas from the fuel source to TPB sites, to conduct charge transfer during hydrogen
oxidation at the TPB, and to complete the extraction of electrons from the reaction site
outside circuit. Therefore, counting the active TPB and removing the inactive (dead)
TPB from the total TPB measurement is a critical issue[70, 72]. In this study, the TPB
density was calculated based on the 3D reconstruction. For 3D reconstruction, every
voxel was label one of the phases including GDC, Ni, and pore. Generally one edge is
shared by 4 voxels and if an edge is shared by all 3 kinds of phases, then it is counted
as TPB length (Fig. 5-7). In order to estimate the actual working TPB density, the TPB
sites were classified into 3 categories, which are active, inactive, and unknown TPB. For
this, connectivity of each phase at the TPB was traced along xy, yz, and zx plane. If the
Ni, GDC and pores are connected across the AFL from GDC electrolyte to end of the
AFL, it was counted as ‘active’ TPB. If one of the phases connected to the TPB site was
isolated inside the reconstructed region, which was referred to ‘inactive TPB’. Other
cases are sorted as ‘unknown’ TPBs. The total TPB length (L_{TPB}) was estimated by
summation of the length of the voxel edges counted as the TPB. The TPB density (\rho_{TPB})
is calculated by

\[ \rho_{TPB} = \frac{L_{TPB}}{V_{total}} \]  

(5-2)

where the \( V_{total} \) is the total volume of ROI. The unit of TPB density is \( \mu m^{-2} \) (= \( \mu m/ \mu m^3 \)). For unknown TPBs, it was assumed that the same connectivity of the each phase
exists out of the ROI and the unknown TPBs might have the same portion of the active
and dead TPB in known region. Based on this assumption, the total active TPB density \( \rho_{TPB, \text{active, total}} \) was estimated by

\[
\rho_{TPB, \text{active, total}} = \frac{L_{TPB, \text{active}}}{V_{\text{total}}} \left( 1 + \frac{L_{TPB, \text{unknown}}}{L_{TPB, \text{active}} + L_{TPB, \text{dead}}} \right)
\] (5-3)

where the \( L_{TPB, \text{active}} \), \( L_{TPB, \text{dead}} \), and \( L_{TPB, \text{unknown}} \) are active, dead, and unknown TPB length in a measured volume, respectively. The calculated total active TPB densities were \( 8.5 \pm 1.4, 15.6 \pm 5.0, 14.2 \pm 3.4, \) and \( 6.3 \pm 2.3 \) \( \mu m^{-2} \), respectively (Table 5-2). As expected from total surface area and effective particle size analysis discussed above, the highest TPB density was achieved in AFL with 60wt% NiO, which is 1:1 volume ratio of Ni to GDC. Moreover this is in good agreement with the electrochemical impedance analysis in previous chapter. However, the standard deviation of TPB is greater for higher values. This result might reflect that the AFL with larger TPB density has higher randomness and complicity of the structure. This scattering of the TPB density can be reduced by introducing computational simulation method [72] or morphological correction factor [71]. Fig. 5-8 shows the TPB result compared to surface area. The surface area for each sample does not show any trend with AFL composition contrast to TPB density. It does not seem to be in agreement with results from other studies that the higher surface area produces higher probability of TPB density as previous shown previous studies [65, 67]. However, it should be considered that in this study the effective particle size and porosity was controlled by compositional change of AFL accompanying volume fraction change between phases, while other studies the phase composition of the electrodes were fixed. Fig. 5-9-a shows the TPB and electrode ASR with various AFL compositions. For the electrode ASR, the result was taken from the previous study [64]. In that study the electrode ASR measured from the AFL with
different NiO contents were presumable assumed that the cathode ASRs were the same value due to same process of the cathode fabrication for each cell. Therefore, the electrode ASR trend can show the anodic ASR change. As shown in Fig. 5-9-a, TPB density shows the inverse trend of electrode (anode) ASR change. Previously, Bieberie et. al reported that the main electrode process directly depends on the TPB length [73]. In that research, using a Ni pattern anode as a model electrode, they showed that the electrode conductivity under open circuit condition is correlated to TPB length, which is linear relationship between inverse resistance and TPB length. Fig. 5-9-b shows the plotting of one over ASR corresponds to TPB density, also showing the linear relationship. However, some deviation from the linearity is shown. This can be occurred by scattering of the TPB length from the 3D reconstruction accuracy or the different electrochemical mechanism dependence of compositional change of AFL on electrochemical polarization. Previously, Smith et. al reported that for the LSM-YSZ cathode the charge transfer and adsorption have a different dependence on TPB length, which was evaluated by deconvolution of impedance[68]. Therefore, further study about the effect of TPB density on anode polarization loss will be conducted through the deconvolution of anode impedance under applied current.

5.4 Conclusions

In this work, microstructural properties of Ni-GDC anode functional layers for IT-SOFCs were quantified by state-of-the-art 3D reconstruction technique. For 3D reconstruction, each sample was automatically sectioned and each sectional image was acquired using FIB/SEM dual beam system. After labeling of each image to give phase separation, the series of sectioned images were incorporated and reconstructed in 3D utilizing the Amira software. From this 3D reconstruction, the phase gradient through the
sample depth and volume fraction, effective diameter, surface area for each phases (Ni, GDC, and pore), and pore tortuosity were quantified. This result showed that the volume fraction was well matched with theoretical value showing each sample was well reduced. In addition to volume fraction, the graded phase plot showed that the actual AFL/ anode structure have some degree of deviation of the each phase volume fraction, so the accurate quantification microstructural properties could be achieved by bulk analysis. As one of the most important features in the anode microstructure, the active TPB density was evaluated with the algorithm of checking the connectivity of voxels for each phase. The highest TPB length was found at the 1:1 volume ratio of the Ni to GDC in AFL. Moreover, the TPB densities showed a linear relation to the inverse of electrode ASR. For the more accurate TPB estimation, the mathematical adjustment of rectangular voxel will be needed. In addition, the detailed analysis of anode reaction mechanism by deconvolution of impedance spectrum should be conducted for the direct relation to electrochemical properties with quantified microstructural features.
Figure 5-1. Schematic diagram of FIB/SEM dual beam system with sample (a) and 3D reconstruction process (b)
Figure 5-2. 3D reconstruction of Ni-GDC anode (a), and AFLs with initial composition of 50 (b), 60 (c), 65 (d), and 80 (e) wt% NiO nearby at anode(or AFL)/electrolyte interface.
Figure 5-3. Individually reconstructed phases from the 3D reconstruction of AFL with 65 wt% NiO; GDC (a), Ni (b), Pore (c), and combination of Ni and Pore phases.
Figure 5-4. Phase gradient of reconstructed samples with no AFL (a), 50 (b), 60 (c), 65 (d), and 80 (e) wt% NiO in Ni-GDC AFL
Figure 5-4. Continued
Figure 5-4. Continued
Figure 5-5. Volume fraction of Ni, GDC and pore phase in total volume (a), and volume fraction of Ni and GDC in solid volume of AFLs with various compositions. Open symbols represent theoretical values.
Figure 5-6. Effective particle diameters of Ni (rectangular), GDC (circle), and pore (triangle) phase of AFLs with various compositions.
Figure 5-7. Schematic diagram of TPB length calculation from 3D reconstruction. A rectangular parallelepiped represents a voxel in a 3D reconstruction and each one is labeled as one of phases; Ni, GDC, or Pore phase. A edge which is shared by all three phases is counted as a TPB length.
Figure 5-8. Plot of quantified surface area and TPB density of AFL with various NiO contents. Dotted lines are only for guide purpose.
Figure 5-9. (a) TPB density and electrode ASR with various AFL compositions (Dotted lines are only for guide purpose.) (b) plot of 1 over electrode ASR with TPB density. A red line represents linear fit for the plot showing inverse relationship between TPB and electrode ASR.
<table>
<thead>
<tr>
<th>Initial AFL Composition</th>
<th>NiO (wt%)</th>
<th>50</th>
<th>60</th>
<th>65</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDC (wt%)</td>
<td>50</td>
<td>40</td>
<td>35</td>
<td>20</td>
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</tbody>
</table>

<table>
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<tr>
<th>3D Reconstruction Dimension</th>
<th>X (μm)</th>
<th>Y(μm)</th>
<th>Z(μm)</th>
<th>Total Reconstructed volume (μm³)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>12.95</td>
<td>10.22</td>
<td>8.90</td>
<td>1177.91</td>
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</table>

<table>
<thead>
<tr>
<th>Phase Volume After Reduction</th>
<th>Ni in Total volume(%)</th>
<th>Theoretical</th>
<th>Measured(SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td></td>
<td>30.4</td>
<td>29.1(~1.0)</td>
</tr>
<tr>
<td>GDC</td>
<td></td>
<td>36.3</td>
<td>37.8(~5.9)</td>
</tr>
<tr>
<td>Pore</td>
<td></td>
<td>39.2</td>
<td>43.2(~6.7)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase Volume After Reduction</th>
<th>GDC in Total volume(%)</th>
<th>Theoretical</th>
<th>Measured(SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td></td>
<td>48.3</td>
<td>48.1(~6.7)</td>
</tr>
<tr>
<td>GDC</td>
<td></td>
<td>38.4</td>
<td>48.6</td>
</tr>
<tr>
<td>Pore</td>
<td></td>
<td>33.4</td>
<td>53.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase Volume After Reduction</th>
<th>Pore in Total volume(%)</th>
<th>Theoretical</th>
<th>Measured(SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td></td>
<td>21.2</td>
<td>16.3(~2.9)</td>
</tr>
<tr>
<td>GDC</td>
<td></td>
<td>25.3</td>
<td>21.6(~3.0)</td>
</tr>
<tr>
<td>Pore</td>
<td></td>
<td>27.4</td>
<td>21.8(~3.2)</td>
</tr>
</tbody>
</table>

| Phase Volume After Reduction | Ni in Solid volume(%) | Theoretical | Measured(SD) |
|------------------------------|                       |             |               |
| NiO                          |                       | 38.6        | 34.8(~1.0)    |
| GDC                          |                       | 48.6        | 48.1(~6.7)    |

| Phase Volume After Reduction | GDC in Solid volume(%) | Theoretical | Measured(SD) |
|------------------------------|                       |             |               |
| NiO                          |                       | 61.4        | 65.2(~1.0)    |
| GDC                          |                       | 51.4        | 51.9(~6.7)    |

Table 5-2. Summary of quantification of microstructural features of AFL with various compositions

<table>
<thead>
<tr>
<th>Initial NiO composition in AFL</th>
<th>wt%</th>
<th>50</th>
<th>60</th>
<th>65</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Ni diameter, d_{Ni}</td>
<td>nm</td>
<td>683</td>
<td>771</td>
<td>917</td>
<td>1120</td>
</tr>
<tr>
<td>Effective GDC diameter, d_{GDC}</td>
<td>nm</td>
<td>890</td>
<td>642</td>
<td>650</td>
<td>316</td>
</tr>
<tr>
<td>Effective Pore diameter, d_{pore}</td>
<td>nm</td>
<td>381</td>
<td>452</td>
<td>489</td>
<td>560</td>
</tr>
<tr>
<td>Surface area per volume, SA/V</td>
<td>μm⁻¹</td>
<td>2.4</td>
<td>2.9</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Tortuosity, τ</td>
<td>N/A</td>
<td>2.77</td>
<td>1.91</td>
<td>1.91</td>
<td>1.69</td>
</tr>
<tr>
<td>TPB density, ρ_{TPB}(SD)</td>
<td>μm²</td>
<td>8.5(~1.4)</td>
<td>15.6(~5.0)</td>
<td>14.2(~3.4)</td>
<td>6.3(~2.3)</td>
</tr>
<tr>
<td>*Electrode ASR at 650°C</td>
<td>Ω·cm²</td>
<td>0.161</td>
<td>0.133</td>
<td>0.142</td>
<td>0.205</td>
</tr>
</tbody>
</table>
CHAPTER 6
HIGH PERFORMANCE IT-SOFC WITH CERIA/BISMUTH OXIDE BILAYERED ELECTROLYTES FABRICATED BY A SIMPLE COLLOIDAL ROUTE USING NANO-SIZED ESB POWDER

6.1 Introduction

Solid oxide fuel cells (SOFCs) have been widely accepted and studied as a next-generation energy conversion device. They produce electricity by electrochemically combining fuel and oxidant across a ceramic ionic conductor, i.e., a solid state electrolyte [2]. The efficiency of SOFCs is not limited by theoretical Carnot efficiency, unlike that of combustion-type systems is limited. The fuel-to-electrical efficiency can reach approximately 45 to 60%. Considering utilization of the by-product heat in co-generation or bottoming cycles, the projected system efficiency can exceed 80%. In addition to high efficiency, SOFCs are attractive because of their reduced production of SOx and NOx, and significantly lower greenhouse gas emissions compared to combustion engines [3].

High system cost is one of the largest barriers to the commercialization of SOFC technology. Ionic conduction in the solid electrolytes is a thermally activated process, leading conventional SOFCs to operate in a temperature range from 900 °C to 1000 °C. Consequently, this high operation temperature requires the use of ceramic interconnects, high temperature seals, and super-alloy based balance-of-plant components, resulting in prohibitive system costs [9]. As Steele claimed, in lower temperature operation (500~700 °C), the system cost can be significantly reduced by allowing for the use of cheap stainless steel for the bipolar plates and the balance-of-plant, combined with the use of high temperature gaskets rather than rigid glass-based seals, which can also enhance its mechanical stability and lifetime [5].
Recent research efforts aim to develop alternative SOFC materials that operate in the 500 to 800 °C range. There are two major issues for lower temperature operation of SOFCs. The first is that the reduced oxygen ion conduction in ceramic electrolytes causes a significant increase in ohmic polarization at low and intermediate temperatures. The second is that electrode polarization is significant due to reduced cathode activity at the electrode and electrolyte interface. Therefore, development of electrolytes with high ionic conductivity in the IT range (500 ~ 700 °C) has been widely investigated by many researchers [5, 7].

Among the studied electrolyte materials, doped-ceria and stabilized bismuth oxide have been reported to have 1~2 orders of magnitude of higher ionic conductivity than conventional yttria stabilized zirconia electrolytes [74]. However, doped ceria shows lower open circuit potential (0.7~0.8 V) than the theoretical Nernst voltage due to its mixed ionic electronic conductivity (MIEC) causing electronic leakage and low power density [31]. Moreover, although stabilized bismuth oxide has very high oxygen ionic conductivity, its inherent thermodynamic instability under reducing conditions makes it a poor choice by itself as an electrolyte for SOFCs [37].

To overcome these problems, Wachsman et al. suggested a bismuth oxide/ceria bilayer electrolyte consisting of a layer of stabilized bismuth oxide on the oxidizing side and a layer of doped ceria on the reducing side [18]. In this arrangement, the ceria layer can improve the thermodynamic stability of the bismuth oxide layer by shielding it from very low Po2 and the bismuth oxide layer can serve to block electronic flux from doped ceria in reducing atmospheres, theoretically yielding high OCPs approaching the Nernst potential at the IT range. For over a decade, several researches have demonstrated
that the OCP can be effectively improved using the bismuth oxide/ceria bilayered electrolyte concept [18, 39-41]. However, high power density at low temperature was not readily achieved due to high ohmic losses from thick electrolyte-supported cell designs and the high reactivity of bismuth oxide with conventional perovskite cathodes, such as La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) due to weak metal-oxide bonds [75]. Therefore, recent research has focused on development of thin erbia stabilized bismuth oxide (ESB) / gadolinia doped ceria (GDC) bilayered electrolytes and ESB-compatible cathodes. Previously, Park and Wachsman reported that an ultra thin (~0.2 μm) and dense ESB layer can be deposited on Sm-doped ceria (SDC) pellets by pulsed laser deposition (PLD) [39, 40]. In addition, to overcome the reactivity of ESB with conventional perovskite cathodes, a bismuth ruthenate (Bi$_2$Ru$_2$O$_7$, BRO7)- ESB composite cathode was developed [76]. A recent optimization study by Camaratta et al. reported that BRO7-ESB composite cathodes exhibited very low ASR (0.73 and 0.03 Ω cm$^2$ at 500 and 700 °C, respectively) [77].

Based on these studies, we demonstrated an impressively high performance of ~1.94 W/cm$^2$ at 650 °C using a thin ESB/GDC electrolyte on an anode-supported cell with highly optimized BRO7-ESB cathodes [19, 20]. To accommodate dense and thin electrolytes on porous anode-supports, we integrated a recently developed a GDC anode functional layer (AFL) between the anode and GDC electrolyte by spreading of a precursor solution [14]. In this study thin (~4 μm) and relatively dense ESB was successfully deposited by PLD technique on 10 μm thick GDC film. The obtained total ASR was only 0.079 Ω-cm$^2$, showing a ~40% decrease compared to a cell with a single GDC electrolyte.
Up to now, these various studies have soundly proven that the bilayered electrolyte concept is highly encouraging in practical SOFC applications for low temperature operation. One of the key factors to fabricate ESB/GDC bilayered electrolytes is to obtain a dense and thin ESB layer on the sintered GDC electrolyte. Although PLD can be good for demonstration purposes in lab-scale experiments, a more cost-effective and practical fabrication process is necessary for future application of the ESB/GDC bilayered electrolyte.

In this study, we fabricated a thin and dense ESB/GDC bilayered electrolyte on anode-supported SOFCs by a simple and cost-effective colloidal deposition process. To obtain a dense ESB layer, nano-sized ESB particles used for the colloidal coating slurry were synthesized by a wet chemical co-precipitation method. In order to optimize the sintering conditions of the ESB layer on dense GDC, the evolution of the ESB microstructure with sintering temperature was investigated. To gauge the performance of the developed ESB/GDC electrolyte, current-voltage characteristics and electrochemical impedance tests were carried out.

6.2 Experimental Procedure

6.2.1 ESB Powder Fabrication

To synthesis very fine ESB powder, a coprecipitation route was employed. Pure Bi nitrate and Er nitrate were used as starting raw materials. They were weighed in stoichiometric proportions and dissolved in 70% nitric acid to produce a solution. An excess ammonia solution (Acros Organics, 28–30% of NH₃ solution in water) was added to the stirred solution to increase the pH value to 12. The addition of the ammonia solution resulted in the formation of a yellowish-brown color precipitate. The precipitate was filtered, and then subsequently dried at 80 °C for 12 hrs. The
agglomerated powder was then ground into fine particles using a mortar and pestle. The powder was then calcined at 900 °C for 10 hrs in air.

For comparison purpose, the ESB powder was synthesis by the conventional solid-state route. A stoichiometric mixture of Bi$_2$O$_3$ (99.9995% pure) and Er$_2$O$_3$ (99.99% pure), from Alfa Aesar, were mixed and ball-milled with zirconia ball media in a high-density polyethylene bottle for 24 hrs. After drying, the mixed powders of ESB were calcined at 800 °C for 16 hrs. Agglomerated powders were ground using mortar and pestle and sieved using a 325 µm mesh.

6.2.2 Fuel Cell Fabrication

The SOFC fabrication involved GDC spin coating on tape-cast anodes followed by ESB colloidal drop coating. The anode support was prepared by tapecasting 65 wt% of NiO (Alfa Aesar) and 35 wt% of GDC (Rhodia) with an appropriate amount of solvents and organic compounds. The anode tapes were presintered at 900 °C for 2 hrs. The GDC AFL was deposited by spraying GDC precursor solution on presintered anode surface. Subsequent heat treatment at 900 °C was carried out for the removal of the binder system. Detailed preparation and fabrication of GDC AFL on tape-cast anode were described the previous study [14].

Thin and uniform GDC electrolytes were deposited by spin coating with a GDC colloidal slurry. The Rhodia GDC powder was ball milled for 24 hrs with solsperse (dispersant) in ethanol. PVB (binder) and DBP (plasticizer) were added after the first ball-milling step and the solution was ball-milled for an additional 24 hrs. For spin coating, the anode substrates were fixed on the vacuum chuck of the spin coater. The thickness of the GDC electrolyte was controlled by the number of depositions with same spin speed. After deposition, samples were dried at room temperature for 10 hrs. After
drying, the multilayer anode/electrolyte structure was sintered at 1450 °C for 4 hrs using a ramp rate of 3 °C /m in air.

For the ESB/GDC bilayered electrolyte, the ESB layer was colloidally deposited by drop coating with co-precipitated ESB (cp-ESB) powder. To make a ESB colloidal slurry, co-precipitated ESB powder was mixed with a binder system which consisted of Solsperse, DBP and PVB as the dispersant, plasticizer, and binder, respectively. This mixture was ball-milled in ethanol for 24 hrs, and drop-coated onto the sintered GDC electrolyte surface. The drop-coating was repeated until a desired thickness was achieved. To see the effect of sintering temperature on formation of ESB layer on dense GDC electrolyte, as-deposited ESB/GDC bilayered cell was divided into several pieces by a diamond saw and each sample was sintered at 700, 800, and 900 °C for 4 hrs using a 400 °C 1 h binder burnout step, and a 5 °C/min ramp rate. For comparison, the same experiments were repeated using solid state ESB powder.

Two different composite cathodes were used for this study-- LSCF-GDC (50:50 wt%) on GDC electrolyte and A BRO7-ESB (50:50 wt%) on ESB/GDC bilayered electrolyte. The cathode development and cathoding procedure can be found earlier work [19, 77].

6.2.3 Characterization

The phase and size of the crystallites of as-calcined ESB powders were investigated by means of X-ray diffraction analysis (XRD, Philips APD 3720).

Microstructures of ESB powders and fuel cell structures with ESB/GDC bilayered electrolytes were observed using scanning electron microscopy (SEM, JEOL 6400 / 6335F). Qualitative elemental analysis of the fuel cell structure was conducted by energy-dispersive X-ray spectroscopy (EDX).
For electrochemical performance measurement, fuel cell samples were loaded in a fuel cell testing set-up. Current-voltage (I-V) characteristics were conducted by a Solartron 1287 potentiostat. The gas condition used was 30 sccm of dry air and 90 sccm of wet hydrogen to the cathode and anode side, respectively. To avoid gas leakage, the edge of cell and testing alumina tube were covered with ceramic sealant using the mixture of two part ceramabond-517 (liquid and power, Aremco). After the I-V measurement, two-point probe impedance analysis was carried out under open circuit condition using a Par-stat 2273 (Princeton Applied Research) over a frequency range of 100 KHz to 100 mHz.

6.3 Result and Discussion

6.3.1 Powder Characterization

Fig. 6-1 shows the XRD result of ESB powders synthesized by co-precipitation (cp) and solid-state (ss) route. For cp-ESB, the precursor powder was calcined at 500 °C for 4 hrs, while ss-ESB powder was synthesized by calcined at 800 °C for 16 hrs. As shown in Fig. 6-1-a, both cp-ESB and ss-ESB show a cubic-fluorite structure of doped-bismuth oxide without any other phases. This result indicates that the wet chemical co-precipitation method for synthesis of ESB powder is a greatly effective way to reduce the calcination temperature and processing time compared to the conventional solid-state route. Due to less thermal energy input during cubic-fluorite phase formation, we can expect lowered grain growth and significantly reduced crystallite size of cp-ESB powder. Generally the crystallite size of the material can be calculated by Scherrer equation [78];

\[ B(2\theta) = \frac{K\lambda}{L \cos \theta} \]  

(6-1)
where $K$ is the shape factor, $\lambda$ is the x-ray wavelength, typically 1.54 Å, $\beta$ is the line broadening at half the maximum intensity (FWHM) in radians, $\theta$ is the Bragg angle, and $L$ is the crystallite length. Fig. 6-1-b shows the magnified x-ray diffraction pattern of the (111) peak from Fig. 6-1-a at the theta range from 27 to 29 degree. Using this graph, we calculated the crystallite size of the both ESB powers by eq. (1) and they are summarized in Table 6-1. The crystallite size of cp-ESB was 1/3 the size of ss-ESB, indicating a high possibility of smaller particle sizes of cp-ESB powder.

The microstructural analysis by SEM was carried out to investigate the size and morphology of the ESB powder. Fig. 6-2 shows SEM images of the ESB prepared from different synthesis methods, that is, conventional solid state and wet-chemical route using co-precipitation. As shown in Fig. 6-2-a, the particle size of cp ESB powder is much less than 5 μm and each particle consists of soft agglomeration of nano-sized rod-shaped particulates with high aspect ratio. In contrast, the ss-ESB powder in Fig. 6-2-b shows particle size over ~5 μm and each particle appears to be hard-agglomerated. This result indicates that the co-precipitation process successfully reduced the resultant ESB particle size and significantly enlarged surface area, allowing for much higher sinterability.

6.3.2 Effect of Sintering Temperature on ESB/GDC Bilayered Electrolyte

In order to investigate the effect of particle size and sintering temperature on the formation of an ESB layer on a GDC electrolyte, ESB/GDC bilayered electrolytes were fabricated using cp-ESB and ss-ESB powder at various sintering temperatures (700, 800, and 900 °C).

The SEM images in Fig. 6-3 show cross-sectional views of the bilayered structures on anode supports fired at various temperatures. Using backscatter imagery, the
different phases-ESB (white), GDC (light gray), and NiO (dark gray)-are easily distinguished due to differences in elemental contrast. It should be noted that the SEM images for each ESB layer (Fig. 6-3-a, c, e, g for ss-ESB and b, d, f, h for cp-ESB) were taken at different magnifications. From these microstructures, it is clear that both cp- and ss-ESB layers increase in density with increasing sintering temperature. However, the ESB layer which was prepared from ss-ESB powder and fired at 900 °C is not fully dense. Instead, this ss-ESB electrolyte looks less dense when fired at 900 °C (Fig. 6-3-g) than when fired at 800 °C (Fig. 6-3-e) due to the formation of large pores. It is known that the bismuth oxide melting temperature is ~ 825 °C [79]. As Jiang and Wachsman reported, however, doped bismuth oxides have much higher melting temperature of over 2000 °C and differential thermal analysis (DTA) also found no melting endotherm for the stabilized bismuth oxide up to 1100 °C [80]. Therefore, we believe that this phenomenon is possibly caused by the sublimation of bismuth oxide phase over 825°C.

Moreover, the sintering of ESB layer is processed on a highly densified GDC substrate which was sintered at a much higher temperature (~1450 °C). In this case, the sintering mechanism of ESB powder is primarily dependent on vertical shrinkage without lateral shrinkage. Therefore, ss-ESB powder might not establish a dense layer below 800 °C due to its insufficient surface area leading low sinterability. Additionally, ss-ESB powder will be porous when fired above 900 °C due to the sublimation of bismuth oxide phase. This result indicates that micron-sized ESB powder prepared by conventional solid state synthesis is not appropriate for colloidal deposition of the ESB layer in ESB/GDC bilayered electrolytes.
On the other hand, as shown in Fig. 6-3-b, d, f, h, when cp-ESB powder was used, the ESB layer was highly dense when fired at 800 °C. SEM powder analysis (Fig. 6-3-a), of the cp-ESB powder shows that it has a very high surface area due to the nanosized nature of the particles. Therefore, it is possible for cp-ESB powder to produce sufficient surface energy at lower sintering temperatures for the particles to neck and densify by surface and lattice diffusion. Unlike the layer prepared from ss-ESB powder, the cp-ESB layer sintered at 900 °C (Fig. 6-3-h) looks very dense. However the ESB thickness was reduced compared to the same layer sintered at 800 °C (Fig. 6-3-f). Since 900 °C is above the pure bismuth oxide melting temperature, as discussed above, this indicates that partial sublimation of bismuth oxide phase or penetration of bismuth oxide into GDC layer have possibly occurred.

It should be noted that as seen in Fig 6-3-g, h, both ss- and cp- ESB layers sintered at 900 °C show diffusion of ESB phase into ceria layer and segregation of it into GDC grain boundaries. This is also clearly shown in Fig. 6-4 which is a magnified image of Fig. 6-3-g. It is considered that the over melting temperature of pure bismuth oxide (~825 °C) the partial pressure or fugacity of bismuth oxide might be high, which can cause higher activity of bismuth oxide or bismuth in ESB lattice. Therefore, this high activity can accelerate motion of bismuth oxide phase, leading diffusion of bismuth oxide phase along the GDC grain boundaries which generally has a high surface energy. It has also been reported that bismuth oxide can be soluble in CeO₂ forming a solid solution of Bi₁₋ₓCeₓO₂₋ₓO₂₋ₓ/₂ with a cubic fluorite structure [81]. Gil et al recently reported that the solid solubility limit of bismuth oxide in doped ceria is ~ 0.8wt% [82]. Park and Wachsman predicted the possible existence of solid solutioning at the
interface between the stabilized bismuth oxide and doped ceria bilayered electrolytes [40]. In this study, the conductivity of 2 mm thick Sm doped ceria (SDC) was lower than that of ESB (∼0.2 μm)/SDC (∼2 mm) bilayered electrolyte due to the high grain boundary conductivity of ESB/SDC. This phenomenon was explained as the formation of a solid solution of ESB into the grain boundary of SDC, which can lower the activation energy for oxygen ion transfer in SDC grain boundaries by a scavenging effect on impurity phases. Therefore, we can expect a positive effect on lowering ohmic polarization in the observed integrated ESB/GDC structure.

On the other hand, it is also shown that the fracture mode of GDC electrolyte with ESB sintered at 900 °C changed from inter-granular to intra-granular (Fig. 6-4), compared to GDC cross-sections near ESB layers sintered at lower temperature (Fig. 6-3-a ~ f). This might cause deterioration in the mechanical strength of the GDC electrolyte due to highly segregated bismuth oxide phase along the GDC grain boundary. Therefore, this phenomenon should be carefully controlled and further investigation will be needed.

Consequently, we could obtain dense ESB/GDC bilayered electrolytes by a simple colloidal deposition using fine ESB powders made by a co-precipitation method. The optimal sintering temperature for synthesizing dense ESB layers by colloidal deposition was ∼800 °C, which limited bismuth oxide sublimation and penetration into the GDC electrolyte.

6.3.3 Microstructure of a Full Button Cell with ESB/GDC Bilayered Electrolyte

For comparison of electrochemical performance, two kinds of button cells were prepared - a single GDC electrolyte cell and an ESB/GDC bilayered electrolyte cell based on above study. To obtain similar electrolyte thickness, the colloidal deposition
process for each layer was repeated. For microstructural analysis before electrochemical performance, another button cell with ESB/GDC bilayered electrolyte was fabricated with the similar process. An ESB layer was deposited using colloidal slurry containing cp-ESB powder and sintered at 800 °C for 4 hours. Fig. 6-5 shows the cross-sectional SEM image of NiO-GDC anode/ ESB-GDC bilayered electrolyte/ BRO7-ESB composite cathode. As shown in this figure, a dense ESB/GDC layer was obtained and every layer is clearly distinguishable with good interfacial contact. To examine the possible interdiffusion between layers, an energy dispersed x-ray (EDX) line scan analysis was conducted along the base line (yellow) in Fig. 6-5. Three elements were traced along the line, which includes Bi (red line), Ce (blue line), and Ni (white line). The resultant data are overlapped in Fig. 6-5 and no solid state reaction or interdiffusion between layers was observed.

Fig. 6-6 shows the microstructures of cross section and surface of anode supported cells with a single GDC electrolyte and an ESB/GDC electrolyte after electrochemical performance test. Both cross-section and surface view of the GDC layer (Fig. 6-6-a,c) shows very high density without pores. In contrast, the ESB surface (Fig. 6-6-d) shows some porosity and lower density compared to the GDC surface, while the cross-section of ESB (Fig. 6-6-b) looks dense. For further densification, it needs to be optimized. As shown in Fig. 6-6, each electrolyte thickness was measured from the SEM image. The GDC electrolyte thickness was identical, ~9 μm for each cells. The ESB electrolyte thickness was ~4 μm.

6.3.4 Performance of a Button Cell with ESB/GDC Bilayered Electrolyte

Fig. 6-7-a shows the I-V characteristics of cells with GDC single layer and ESB/GDC bilayered electrolyte at 650 °C. The measurement was conducted under 90
sccm of 3% wet hydrogen to anode side and 30 sccm of dry air to cathode side. The maximum power density (MPD) of the ESB/GDC electrolyte reached ~1.47 W/cm² with a 69% increase in MPD compared to a GDC single layer (~ 0.87 W/cm²). The OCPs of the single GDC electrolyte cell and ESB/GDC bilayered electrolyte cell were 0.75 and 0.80 V, respectively. This OCP improvement with bilayered electrolyte can be evidence that the ESB layer in ESB/GDC bilayered electrolyte may effectively block the electronic conduction from the GDC due to reduction of Ce⁴⁺ to Ce³⁺ at low Po₂ region. Moreover, we previously reported similar OCP enhancement with a thin ESB/GDC bilayered electrolyte. At that time we fabricated a dense ESB layer of ~ 4 μm by PLD technique on ~ 10 μm thick GDC electrolyte by spray coating method, resulting OCP increase from 0.72 to 0.77 V [20]. It is noted that in this study we obtained higher OCP for both single and bilayered electrolyte cells compared to previous research results. We believe that this is caused by higher GDC density due to spin coating method instead spraying coating for GDC electrolyte in the previous study. Therefore, this result demonstrates that thin and dense ESB/GDC bilayered electrolytes can be achieved by conventional colloidal process by control of initial powder morphology and sintering condition. Although the ~ 0.05 V increase in OCP was achieved in a dense bilayered electrolyte, the major contribution of this outstanding enhancement in MPD came from ASR drop. The estimated total ASRs from IV curves near OCP region were 0.084 Ωcm² and 0.164 Ωcm² for cells with ESB/GDC bilayer and GDC single layer, respectively.

For the further analysis electrochemical impedance test was conducted and the result is shown in Fig. 6-7-b. In these Nyquist plots the total and ohmic ASR were extracted from the low and high frequency intercepts of the impedance spectra with the
real axis, respectively, and the electrode ASR was calculated from the difference between these two ASR values. The detailed values are tabulated in Table 6-2. The total ASR of ESB/GDC bilayered cell (0.088 $\Omega \cdot \text{cm}^2$) was decreased by 47.6% compared to that of cell with GDC single layer (0.168 $\Omega \cdot \text{cm}^2$). In addition, in this study the total ASRs from this AC impedance tests are identical to the ASRs from the I-V curves (DC impedances) within 5% deviation showing the good validity of the results. The electrode ASR of the bilayered electrolyte cell was decreased by 62.6% compared to that of GDC single cell. This ASR drop (0.062 $\Omega \cdot \text{cm}^2$) is expected to mostly come from the cathodic polarization reduction at the interface between high catalytic BRO7-ESB cathode and ESB electrolyte, considering the both cells utilized the same anode material using identical procedures. This result has been also well-supported by the former studies [19, 77]. The ohmic ASR was also decreased (26.1%, 0.018 $\Omega \cdot \text{cm}^2$) at 650 °C. Previously, it was shown that the ohmic ASR ($\text{ASR}_{\text{electrolyte}}$) of a billyared electrolyte can be estimated by a simple modeling for two series resistors written as

$$\text{ASR}_{\text{electrolyte}} = L_{\text{GDC}} \left( \frac{r}{\sigma_{\text{ESB}}} + \frac{1}{\sigma_{\text{GDC}}} \right)$$ (6-2)

where $L_{\text{GDC}}$ is thickness of GDC electrolyte, $r$ is thickness ration of ESB to GDC, and $\sigma_{\text{ESB}}$ and $\sigma_{\text{GDC}}$ are the conductivities of ESB and GDC, respectively [19, 42]. Based on known ESB and GDC conductivities [83], a similar or slightly higher ohmic ASR of the ESB (~4 $\mu\text{m}$)/GDC (~9 $\mu\text{m}$) bilayered electrolyte than that of ~a single 9$\mu\text{m}$ thick GDC can be expected by eq. (2) due to much higher conductivity of ESB than GDC at IT ranges. However, previous studies repeatedly showed that bilayer electrolyte can effectively reduce the electrolyte ASR even when we used same GDC thickness with a single GDC layer and an additional ESB layer was deposited [19, 20, 39]. Therefore, we
believe that this phenomenon is related to penetration and segregation of bismuth oxide phase at the GDC grain boundary, even though it was not defective in EDX analysis. Further discussion about ASR reduction of ESB/GDC bilayered electrolyte was exposited elsewhere [19, 20].

However, this MPD result was somewhat lower compared to the previous highest MPD with thin ESB by PLD and GDC bilayered electrolyte cell (~1.95 W/cm²) [20]. As ohmic ASR results suggested, the density of cp-ESB layer might be still less dense compared to PLD-ESB. Moreover, in this study, we used both solid state BRO7 and ESB powder for the cathode, while in the previous study microstructurally optimized BRO7-ESB cathode was used. Optimization of BRO7-ESB was described in detail by Camaratta et al [77]. Therefore, we can expect even higher MPD result by further improvement of ESB density and cathode performance.

6.4 Conclusions

We fabricated thin and dense ESB/GDC bilayered electrolytes by a simple colloidal deposition process. For producing highly sinterable ESB particles, a wet chemical co-precipitation route was introduced. Using this nano-scale ESB powder with high surface area, a dense and very thin (~ 4 μm) ESB layer was established on a GDC electrolyte by simple colloidal drop coating. The optimal sintering temperature of the ESB layer was found to be ~800 °C due to its poor densification at lower temperatures and evaporation at higher temperatures. Finally, an anode-supported SOFC with the thin and dense ESB/GDC bilayered electrolyte coupled to a BRO7-ESB cathode produced a very high maximum power density of ~ 1.5 W/cm² at 650 °C. This was possible due to the effect of the bilayered electrolyte on significantly decreasing electrode ASR as well as ohmic ASR. This study demonstrated that the high performance of
ESB/GDC bilayered electrolyte can be reproducible by the cost-effective and practical colloidal deposition. Based on this study, fabrication of large-scale planar cells with bilayered electrolytes for stack cell application is underway.
Figure 6-1. XRD diffraction pattern of ESB powders synthesized by coprecipitation route (red line) and solid state route (black line) (a). The magnified XRD diffraction pattern of the (111) peak is shown at the $2\theta$ range from 27 to 29° (b).
Figure 6-2. SEM of ESB powders synthesized by wet-chemical co-precipitation method (a) and solid-state route (b).
Figure 6-3. Evolution of ESB layers on GDC electrolyte at various sintering temperatures using ss-ESB (a,c,e,g) and cp-ESB (b,d,f,h). It is noted that the magnification of images for ESB electrolyte using cp-ESB powder is higher than that of ss-ESB powder.
Figure 6-4. Cross-sectional view of GDC electrolyte under ss-ESB layer after sintering at 900 °C, which is the magnified image from Fig. 5-3g. In backscattering mode, ESB (white), GDC (light gray), and NiO (dark gray) phases are well-distinguishable, showing ESB penetration into GDC grain boundaries.

Figure 6-5. Cross-sectional SEM image of a full button cell with ESB/GDC bilayered electrolyte. EDX line scan was conducted along the straight base line (yellow) and the intensity of each elements are presented as red (Bi), blue (Ce), and white (Ni) lines.
Figure 6-6. SEM image of cross-sectional view of a single GDC electrolyte cell (a) and ESB/GDC bilayered cell (b). Surface views of GDC electrolyte (c) and ESB electrolyte (d) are shown.
Figure 6-6. Continued
Figure 6-7. IV-Characteristics (a) and impedance spectra (b) of ESB/GDC bilayer (red square) and GDC single layer (blue triangle) cell.
Table 6-1. Calcination condition and crystallite size of ESB powders synthesis by co-precipitation and solid state route.

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>Calcine condition</th>
<th>FWHM ($^\circ$2θ)</th>
<th>Crystallite size (Å)</th>
</tr>
</thead>
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<tr>
<td>Co-precipitation</td>
<td>500°C for 4 h</td>
<td>0.48</td>
<td>171</td>
</tr>
<tr>
<td>Solid State</td>
<td>800°C for 16h</td>
<td>0.16</td>
<td>512</td>
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Table 6-2. Comparison of specification and electrochemical performance of the studied cells.

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>GDC thickness μm</th>
<th>ESB thickness μm</th>
<th>OCP V</th>
<th>MPD W/cm²</th>
<th>Total ASR$_{IV}$ Ω·cm²</th>
<th>Total ASR$_{EIS}$ Ω·cm²</th>
<th>Ohmic ASR Ω·cm²</th>
<th>Electrode ASR Ω·cm²</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>GDC</td>
<td>9</td>
<td>-</td>
<td>0.75</td>
<td>0.87</td>
<td>0.164</td>
<td>0.168</td>
<td>0.069</td>
<td>0.099</td>
<td>this study</td>
</tr>
<tr>
<td>cp-ESB/GDC</td>
<td>9</td>
<td>4</td>
<td>0.80</td>
<td>1.47</td>
<td>0.084</td>
<td>0.088</td>
<td>0.051</td>
<td>0.037</td>
<td>this study</td>
</tr>
<tr>
<td>PLD-ESB/GDC</td>
<td>10</td>
<td>4</td>
<td>0.77</td>
<td>1.94</td>
<td>0.075</td>
<td>0.079</td>
<td>0.046</td>
<td>0.033</td>
<td>[20]</td>
</tr>
</tbody>
</table>
CHAPTER 7
HIGH PERFORMANCE LSM-BASED CATHODE BOOSTED BY STABILIZED BISMUTH OXIDE FOR LOW TO INTERMEDIATE TEMPERATURE SOFCs

7.1 Introduction

La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ (LSM) –based cathodes are some of the most widely used cathodes for high temperature (over 800 °C) solid oxide fuel cells (SOFCs) due to their high thermal and chemical stability, electrical conductivity, as well as their catalytic activity for oxygen reduction. In addition, LSM-based cathodes exhibit good compatibility with conventional electrolyte materials, such as stabilized zirconia and doped ceria [2, 84-86]. However, despite these advantages, LSM-based cathodes are not a popular choice for reduced temperature SOFCs. This is due to the fact that LSM has negligible ionic conductivity and a high activation energy for oxygen reduction due to slow oxygen incorporation reaction into the solid lattice, leading to significantly deteriorated electrochemical catalytic effect at low temperatures [7, 63, 87, 88]. To overcome this problem, dual-phase composite cathode systems have been explored. Conventional ionic conducting phases such as yttria-stabilized zirconia (YSZ) and godolia-doped ceria (GDC) have been mixed with LSM leading to significantly enhanced electrochemical performance [84, 89-94]. For instance, Murray and Barnett reported that the area specific resistance (ASR) of pure LSM was lowered from 51.03 $\Omega$-cm$^2$ to 11.37 $\Omega$-cm$^2$ for LSM-YSZ and 6.81 $\Omega$-cm$^2$ for LSM-GDC [90]. The improved performance is a result of the increased number of three phase boundary (TPB) reaction sites between gas, electronic and ionic conducting phases, and by the addition of a pathway for ionic species to be transported thru the cathode. Thus it is expected that dual phase cathodes which incorporate materials with an ionic conductivity will yield further improvements in performance.
Stabilized bismuth oxide has been reported to have one of the highest known ionic conductivities—one or two orders of magnitude higher than the conventional material YSZ at intermediate temperatures (IT) [17, 95]. In addition to its high ionic conductivity, bismuth-oxide enhances surface oxygen exchange rate as well as charge transfer and oxygen dissociation, which is believed to be the rate-limiting step in the oxygen reduction reaction at the cathode [96-100]. Therefore, stabilized bismuth oxide is a good candidate for the ionic conducting phase in composite cathodes. For example, the addition of yttria or erbia stabilized bismuth oxide (YSB or ESB) into a metallic cathode silver (Ag) improved the performance of the cathode both by increasing TPBs and forming an ionic conduction path to the electrolyte [101-103]. However, the long term stability of Ag-based cathodes is poor [103]. Recently, we developed a bismuth-ruthenate Bi$_2$Ru$_2$O$_7$ (BRO7)-ESB composite cathode [76, 77]. Using this cathode on an ESB/GDC bilayered electrolyte, we demonstrated exceptionally high power density (~1.94 W/cm$^2$ at 650 °C) [19, 20]. It was suggested in the above study that cathode performance can be promoted not only by the addition of ESB into the cathode but also by using an ESB electrolyte at the cathode interface due to effect of ESB on improvement of oxygen dissociation followed by reduction of cathode polarization losses.

Recently, in order to overcome limitations of LSM-based cathodes, the utilization of stabilized bismuth oxides as the ionic conducting phase has received much attention [104-113]. Jiang et al. reported the performance of LSM-YSB composite cathodes, showing an interfacial resistance of ~1.0 Ω·cm$^2$ at 600 °C, which is 11 times lower than reported for LSM-YSZ cathodes [106]. Moreover, various fabrication techniques were
used in order to obtain increased TPB lengths by microstructural evolution [106, 107, 112]. Although these efforts progressively reduced the cathode ASR, the reported power densities of SOFCs utilizing LSM-bismuth oxide cathodes are still relatively low at IT (~600 mW/cm² at 650°C) [107]. To date, most of the studies of LSM-bismuth oxide composite cathodes have been conducted on zirconia-based electrolytes which exhibit significant ohmic resistance at intermediate temperatures due to its high activation energy for ionic conduction. Even though ultra thin YSZ electrolytes successfully reduce total ohmic polarization losses at reduced temperature [8], significant deterioration of ionic conduction and oxygen dissociation rate at the cathode/electrolyte interface is inevitable due to the abrupt change in ionic conduction phase from bismuth oxide in the cathode bulk to the zirconia electrolyte. Therefore, modification of the interface between the LSM-bismuth oxide cathode and the electrolyte is needed in order to achieve high performance at lower temperatures.

In this study, to overcome this, we introduced an (Er₂O₃)₀.₂₀(Bi₂O₃)₀.₈₀ (ESB) electrolyte layer coupled to the (La₀.₈₀Sr₀.₂₀)MnO₃₋₅ (LSM)-ESB composite cathode. To gauge the effect of the ESB electrolyte on the cathode performance, the interfacial resistance of the cathode on ESB and on GDC was measured on symmetric cells. The actual performance improvement of the LSM-ESB cathode on an ESB electrolyte layer was evaluated on anode-supported cells by I-V characterization.

7.2 Experimental

7.2.1 Sample Fabrication

The LSM-ESB composite electrode was prepared by simple powder mixing. Commercial LSM powder with a surface area of 5.6 m²/g was purchased from Fuel Cell Materials. The ESB powder for the cathode was synthesis by the conventional solid-
state method. A stoichiometric mixture of Bi$_2$O$_3$ (99.9995% pure), and Er$_2$O$_3$ (99.99% pure), from Alfa Aesar, were mixed and ball-milled with zirconia ball media in a high-density polyethylene bottle for 24 hrs. After drying, the mixed powders of ESB were calcined at 800 °C for 16 hrs. Agglomerated powders were ground using a mortar and pestle and sieved using a 325 µm mesh to get uniform particle sizes. For the LSM-ESB electrode ink, LSM powder and ESB powder of the same weight ratio (50:50wt%) were mixed with a binder system, which consists of alpha terpineol (Alfa Aesar), Di-n-butyl phthalate (DBP) and ethanol as binder, plasticizer and solvent, respectively. To make symmetric cells, we prepared both ESB and GDC electrolyte pellets by uniaxial pressing and sintering at 890 °C for 16 hrs and 1500 °C for 10 hrs, respectively. Once an appropriate viscosity was reached, the electrode slurry was applied to both sides of the electrolyte substrates by brush painting. After drying the symmetric cells at 120 °C for 1 hrs, a second coat of electrode slurry was applied to the electrolyte substrates. The doubly-coated cells were then sintered at 800 °C for 2 hrs in air. After sintering the electrode, silver mesh current collectors and platinum lead wires were pressed against the samples in a quartz reactor using a ceramic screw-and-bolt assembly.

For full button cell fabrication, the anode-supported cell structures with thin electrolytes were employed. NiO-YSZ (65:35wt%) anode-supports and anode functional layers (AFLs) consisting of NiO-GDC (65:35wt%) were tape-casted and attached to each other by uniaxial press on heating substrate and presintered at 900 °C. Thin and uniform GDC electrolytes were prepared by spin coating. In order to investigate the effect of the ESB electrolyte on LSM-ESB cathode, ESB/GDC bilayered electrolyte was prepared. To fabricate a thin and dense ESB layer on a GDC electrolyte, nano-sized
ESB powder was synthesized by wet chemical coprecipitation method. Using a colloidal solution containing nano-sized ESB particles, the ESB layer was deposited by spin coating. A detailed fabrication and discussion of ESB/GDC bilayered electrolytes was described in the previous work [19]. The multilayer of ESB/GDC/AFL/NiO-GDC anode structures is co-sintered at 1450 °C at 4 hrs. After sintering, the LSM-ESB cathode was applied in two coats on both ESB and GDC electrolyte surfaces by brush painting and sintered at 800 °C for 2hrs.

7.2.2 Characterization

The phase identification of LSM, ESB, and LSM-ESB composite cathodes were investigated by means of X-ray diffraction analysis (XRD, Philips APD 3720).

Microstructures of fuel cells with LSM-ESB cathodes were obtaining by scanning electron microscopy (SEM, JEOL 6400 / 6335F).

The interfacial polarization resistance of the LSM-ESB electrodes on symmetric cells was conducted through two-point probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260. The measurement condition of impedance was an AC voltage amplitude of 50 mV over the frequency range of 0.1 MHz to 0.1 Hz in air. The frequency response analyzer was used in standalone mode and interfaced to a computer using Zplot software. Measurements were made from 500 to 700 °C with an interval of 50 °C.

For electrochemical performance of the button cells, samples were loaded in the testing setup and sealed with cerambond sealant system. Current-voltage (I-V) characteristics were conducted by a Solartron 1407E under 90 sccm of dry air and 3% wet hydrogen to the cathode and anode side, respectively.
7.3 Result and Discussion

7.3.1 Impedance Spectroscopy for Symmetric Cells

In order to confirm the compatibility of ESB with LSM, a LSM and ESB powder mixture (50 to 50wt%) was annealed at 900°C for 50 hrs. Fig. 7-1 shows the resultant X-ray diffraction (XRD) patterns of LSM, ESB powder and mixtures of both powders before and after heat-treatment. After annealing, the XRD pattern of LSM and ESB mixture contains only the peaks of cubic fluorite structure from ESB and perovskite structure from LSM without any other peaks. This result indicates no inter-phase formation, suggesting that LSM and ESB are chemically stable even at 900 °C. This result of compatibility between LSM and ESB is in good agreement with previously reported results [106, 108, 113]. In contrast, it has been known that the pervoskite La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$ (LSCF)-based cathode, which is widely used as the conventional cathode for IT SOFCs, is highly reactive with ESB electrolyte due to weak metal-oxygen bond of bismuth oxide [19, 77].

Fig. 7-2 shows a cross-sectional view of the symmetric cells with LSM-ESB cathodes on ESB and GDC electrolyte pellets. In both cases, the composite cathodes show good adhesion to electrolyte substrates at the cathode/electrolyte interface. In order to distinguish each phase, backscattered SEM images were also observed, which are shown as insets in Fig. 7-2. It is clearly shown that relatively large ESB particles are well-distributed in a very fine LSM particle matrix. However, the majority in LSM-ESB cathode seems to be LSM particles, even though we mixed 50: 50wt% of LSM to ESB powders. It is noted that in this study the ESB powder in the composite cathode is large (1~5 μm) and agglomerated due to solid state synthesis, while commercial LSM powder is much smaller (< 1 μm) than ESB powder. As many studies reported, microstructural
optimization, such as particle size and spatial distribution can modify the connectivity and increase the surface area of the composite cathodes to produce more active TPB sites. Therefore, at this point, the performance of LSM-ESB composite cathode might not be optimal.

Fig. 7-3 is the resultant impedance spectra measured under open circuit condition from 500 to 700 °C with 50 °C interval for LSM-ESB/ESB/LSM-ESB and LSM-ESB/GDC/LSM-ESB symmetric cells. For direct comparison of electrode ASR on the different electrolytes, all of the impedance spectra have been ohmic resistance-corrected. That is, the high frequency intercept at the real axis of each spectrum, which corresponds to bulk electrolyte, electrode-sheet, and lead-contact resistance, has been subtracted from each data point. The electrode ASRs of the LSM-ESB cathode on GDC at 500, 550, 600, 650, and 700 °C were 10.56, 3.31, 1.11, 0.44, and 0.19 Ω-cm\(^2\), respectively. This result is very comparable with the ASRs of the LSM-YSB cathode on Sm-doped ceria (SDC) electrolytes reported by Li et al. In their study, the electrode ASRs were ~ 1.08 and 0.15 Ω-cm\(^2\) at 600 and 700 °C, respectively. This suggests that the performance of the LSM-ESB cathode in this study is reasonable. It should be noted, however, that despite the fact that ESB has higher ionic conductivity than YSB [114], the ASR of LSM-ESB on GDC in the present study is slightly higher than for LSM-YSB on SDC. This might be due to microstructural features associated with infiltrated nano-scale YSB particles into LSM backbones, while in this study, LSM-ESB cathode was fabricated by a simple mechanical mixing method with micron-sized ESB powders. As mentioned above, further improvements in electrochemical performance of this LSM-ESB system can be expected by microstructural optimization. On the other hand, the
electrode ASRs of the LSM-ESB on ESB substrate were substantially lower—4.18, 1.29, 0.43, 0.19, and 0.08 at 500, 550, 600, 650, and 700 °C, respectively.

In Fig. 7-4, the electrode ASR values from the impedance spectra in Fig. 7-3 are plotted with various temperatures (right Y-axis). In addition, the percent electrode ASR reduction on ESB relative to that on GDC was calculated at each temperature (left Y-axis in Fig. 7-4), and a ~ 60% reduction in ASR was retained for all testing temperatures. This result indicates that the reduced interfacial resistance of LSM-ESB cathode on the ESB electrolyte remained in effect throughout the IT range. We believe that this dramatic electrode ASR drop using the ESB electrolyte is caused by the high oxygen dissociation rate of the bismuth oxide and the continuous fast ionic conduction pathways from the cathode to the electrolyte without an abrupt change at the LSM-ESB cathode and ESB electrolyte interface.

As illustrated in Fig. 7-5, the measured cathodic resistances of LSM-ESB on both ESB and GDC electrolyte are compared to that of LSM-GDC and LSM-bismuth oxide composite cathodes on various electrolytes in recent literature studies. As expected, all LSM-bismuth oxide cathodes including the results in this study showed lower electrode polarization losses than those of LSM-GDC cathodes which were reported by Murray et al [90]. This result indicates that bismuth oxide phase integrated into LSM based-cathodes increases the effective TPB length due to its higher ionic conduction. However, even though doped ceria such as GDC and SDC has higher ionic conductivity than YSZ (or ScSZ) electrolytes at IT, the reported LSM-bismuth oxide cathodes (and the LSM-ESB cathode in this study) on GDC or SDC show a similar level of electrode ASRs compared to cathodes using zirconia-based electrolytes, while LSM-GDC
cathodes have shown lower ASR on GDC electrolytes compared to YSZ electrolytes. It is considered that due to the superior ionic conductivity of ESB or YSB in the composite cathode, the effect of the GDC electrolyte at the cathode/electrolyte interface against the YSZ electrolyte can be negligible. Instead, the performance of the LSM-bismuth oxide cathode on GDC or YSZ seems to depend on bismuth oxide phase fraction and cathode microstructures as shown in previous studies.

On the other hand, it is clearly shown that the LSM-ESB cathode on an ESB electrolyte exhibits significantly lower electrode polarization losses than that of any other LSM-based cathode in all measured temperature ranges from 500 to 700 °C. This outstanding result can be explained that the synergetic effect of the ESB phases both in cathode bulk and at the electrolyte/cathode interface on enhancing oxygen dissociation rate and accelerating ionic conduction leading to a dramatic reduction of activation polarization for oxygen reduction in the cathode. Previously we reported a similar effect of the ESB electrolyte on reducing electrode ASR for BRO7-ESB composite cathode on ESB, showing 26% reduction of the ASR relative to that on GDC electrolyte [19]. Therefore, this study again demonstrates that the ESB electrolyte has a highly significant effect on boosting the SOFC cathode reaction rate at the IT range.

Meanwhile, the activation energy of LSM-ESB cathodes on GDC and ESB was estimated from ASR plots in Fig. 7-5 using an Arrhenius relationship. The calculated activation energies for both cells were the same, ~1.24 eV, which is in good agreement with low end of other reported values for LSM-bismuth oxide cathodes (1.23 ~ 1.5 eV), which depend on microstructure and composition of the composite cathodes [104, 106, 108, 112]. In addition, it is been reported that the activation energy for the pure LSM on
SDC electrolyte is ~ 1.5 eV [106]. This result shows that the addition of ESB phase into the cathode bulk or at the electrode/electrolyte interface might change the mechanism of the oxygen reduction at cathode. In addition, this estimated activation energy implies that the surface oxygen exchange reaction of which activation energy is known to ~ 1.25 eV at low temperature might be a rate-limiting step for the cathode reaction, providing a good reason for use of ESB with high oxygen surface exchange rate to reduce the electrode polarization [45].

In order to gauge the long-term stability of the LSM-ESB cathode, the electrode ASR of the LSM-ESB cathode on an ESB electrolyte pellet was measured at 700 °C. Fig. 7-6 is the resultant plot of the electrode ASR at 700°C for 100 hrs. The ASR of the LSM-ESB cathode maintained a constant value for 100 hrs of 0.08 ± 0.001 Ω-cm², indicating no initial degradation in electrode performance. To verify the stability of the LSM-ESB system for IT SOFCs, however, further long term testing in the lower temperature ranges and under various applied current conditions should be carried out.

7.3.2 I-V Characterization for Button Cells

To further investigate the effect of LSM-ESB cathodes coupled to an ESB electrolyte on the actual IT-SOFC performance, current-voltage measurements were conducted on anode-supported button cells. In order to obtain an ESB electrolyte, an ESB-GDC bilayered electrolyte cell design was utilized due to the thermodynamic instability of the ESB electrolyte at low Po2 conditions [16, 18]. Further details regarding the ESB-GDC bilayered electrolyte are available in the recent studies [19]. In this study two cells were fabricated, which included LSM-ESB (cathode) / GDC (electrolyte) /Ni-GDC and LSM-ESB/ESB-GDC/Ni-GDC.
Fig. 7-7 shows SEM images of the two cells after testing. As shown in the cross-sectional views (Fig. 7-7-a,b), the structure of two cells are identical except a thin (~ 3 μm) ESB electrolyte is observed in ESB/GDC bilayer cell between the LSM-ESB cathode and GDC electrolyte (Fig. 7-7-b). Fig. 7-7-c,d show the surface views of the GDC and ESB electrolyte for the GDC single electrolyte cell and GDC/ESB bilayered electrolyte cell, respectively, and some cracks and pores can be observed. This indicates that the densities of both electrolytes were not optimal. This issue will be discussed later in this section.

The current-voltage measurement results of both cells at 650°C are plotted in Fig. 7-8-a. The maximum power densities (MPDs) obtained were 658 and 836 mW/cm² for LSM-ESB on GDC and LSM-ESB on ESB/GDC, respectively. Even though the OCP of the cell with LSM-ESB on ESB/GDC is slightly lower than that of LSM-ESB on GDC, the MPD of LSM-ESB on ESB/GDC was increased by 27% compared to that of GDC single layer cell. The increased power density is due to the significant reduction in the total ASR calculated from the IV curves in Fig. 7-8-a, which were reduced by ~ 54% from 0.566 Ω-cm² for cell-1 to 0.263 Ω-cm² for LSM-ESB on ESB/GDC. In this study we used the same fabrication procedure and confirmed identical microstructures for the two cells with the exception of the ESB interlayer in ESB/GDC bilayer structure, as shown in Fig. 7-7-a,b. Thus, we believe that MPD enhancement of the LSM-ESB on ESB/GDC cell mostly came from the effect of ESB electrolyte on reducing the electrode (cathodic) ASR at the LSM-ESB cathode/ESB electrolyte interface.

For further analysis, two points probe impedance tests were conducted. Fig. 7-8-b illustrates the resultant nyquist plots for each cell under open circuit condition with the
same gas condition for I-V test at 650 °C. From the high frequency intercepts ($R_H$) and low frequency intercepts ($R_L$) at the real axis of the complex plane, the ohmic and total ASR values were estimated, respectively. The electrode ASR including anode and cathode polarization resistance was calculated using the equation written as:

$$\text{ASR}_{\text{electrode}} = R_L - R_H$$  \hspace{1cm} (7-1)

The detailed values are tabulated in Table 7-1. In this study, the total ASR values obtained using DC measurement from IV (ASR$_{IV}$) and electrochemical impedance (ASR$_{EIS}$) showed less than 1% deviation indicating high reliability of the resultant data. As expected from symmetric cell measurements, the electrode ASR was significantly reduced for the bilayered electrolyte cell (0.164 Ω-cm$^2$), showing ~ 64% reduction compared to single layer cell (0.450 Ω-cm$^2$). This result is quite consistent with the cathodic ASR change for the symmetric cell measurement in the previous section. These I-V and impedance results demonstrate that the effect of the ESB electrolyte on LSM-ESB cathode polarization losses directly influences the SOFCs performance at IT, showing reasonably high maximum power density of over 850 mW/cm$^2$ at 650 °C. At this point it is noted that the GDC electrolyte densities in the testing cells were not high and have many small pores and the ESB layer also showed poor density affected by GDC layer as shown in Fig. 7-7. It is well known that the density and thickness of the electrolyte strongly influence ohmic resistance and SOFC performance [14]. Therefore, the MPD of the LSM-ESB cathode can be much higher if denser and thinner GDC and ESB electrolytes are used.

Fig. 7-9 shows IV-curves of both cells at various temperature ranging from 450 to 650 °C. The MPDs of the cell with LSM-ESB on GDC were 25, 72, 182, 389, and 658
mW/cm² at 450, 500, 550, 600, and 650 °C, respectively. In case of the bilayered cell, higher MPDs were exhibited and are reported to be 50, 124, 275, 533, and 836 mW/cm² at 450, 500, 550, 600, and 650 °C, respectively. The improvement in MPD from the cell with LSM-ESB on GDC to the cell with LSM-ESB on ESB at each temperature was calculated and plotted with actual MPD values for each cell in Fig. 7-10. It is noted that in order to give better visualization of the MPDs at low temperature, a log scale was used for the power density (left axis in Fig. 7-10). In this plot, it is clearly shown that the enhancement in MPD linearly increases as temperature decreases. For instance, the MPD of ESB/GDC bilayered cell compared to that of GDC single layer increased by less than 30% at 650 °C but 51 and 100% at 550 and 450 °C, respectively. This indicates that the effect of the ESB electrolyte on LSM-ESB performance is valid and even greater at low temperature. It is believed that the portion of cathodic polarization losses is larger at lower temperature due to its thermally activated nature [7]. Therefore, the beneficial effect of the ESB electrolyte layer on cathode performance should be emphasized on using LSM-ESB cathodes for low temperature SOFC application.

Fig. 7-11 shows a comparison of MPDs for SOFCs with various LSM-bismuth oxide cathodes at low to intermediate temperatures. For all temperatures, the LSM-ESB cathode coupled to ESB electrolyte shows highest MPD. To my knowledge, the MPDs (LSM-ESB on ESB/GDC electrolyte) in this study are the highest for any SOFCs using LSM-bismuth oxide composite cathodes reported to date. Furthermore, this LSM-ESB cathode on an ESB electrolyte can be expected to produce much higher power density at intermediate and even lower temperatures through microstructural tailoring, including cathode structure as well as electrolyte density and thickness control.
7.4 Conclusions

Conventional LSM cathodes for high temperature SOFCs were prepared for low temperature SOFC application by pairing it with ESB in a composite cathode. Due to the inherent high conductivity and fast oxygen exchange rate of ESB, the LSM-ESB composite cathode showed much lower cathodic polarization losses than any other LSM-based cathode at the IT range. Moreover, when ESB was used as an electrolyte, the electrode ASR was reduced further (by ~60%) compared to that of the same LSM-ESB cathode on a GDC electrolyte. Using the LSM-ESB cathode on a ESB-GDC bilayered electrolyte, the MPD produced at 650 °C was ~ 865 mW/cm², which is the highest reported MPD to date for SOFCs using LSM-bismuth oxide cathodes. This study demonstrated that the performance of LSM-ESB cathodes can be effectively boosted when using ESB electrolytes. This is a very promising finding for development of SOFCs which operate at low to intermediate temperatures.
Figure 7-1. XRD pattern of LSM, ESB, and LSM+ESB (50:50wt%) powers before and after annealing at 900 °C 50 hrs
Figure 7-2. SEM images of LSM-ESB cathode on GDC electrolyte (a) and ESB electrolyte (b). The insets are backscattered images.
Figure 7-3. Impedance spectra of the LSM-ESB cathode on ESB and GDC pellets at the temperature ranges from 500 to 700 °C
Figure 7-4. Electrode ASRs of LSM-ESB cathode on GDC (blue circles) and ESB (red squares) electrolytes, and ASR reduction rate (black stars).
Figure 7-5. Comparison of the electrode polarization resistance of LSM-bismuth oxide cathodes at IT ranges. LBSM is short for La$_{0.74}$Bi$_{0.10}$Sr$_{0.16}$MnO$_{3-δ}$.

Ref: a,b-[90], c-[111], d-[104], e-[108], f-[109], g-[106], h-[112]
Figure 7-6. Long term stability test of LSM-ESB cathode on ESB electrolyte at 700 °C for 100 hours.
Figure 7-7. SEM images of cross-sectional views for cell-1(a) and cell-2(b), and surface views for cell-1 (c) and cell-2 (d)
Figure 7-7. Continued
Figure 7-8. I-V characteristics (a) and impedance spectroscopy (b) of cell-1 and cell-2 at 650 °C.
Figure 7-9. I-V characteristics at various temperature for cell-1 (a) and cell-2 (b)
Figure 7-10. Maximum power density improvement (black stars) of cell-2 (red squares) at various temperatures compared to cell-1 (blue circles)
Figure 7-11. Comparison of maximum power density of SOFCs using LSM-bismuth oxide composite cathodes at IT ranges.

Ref: a-[107], b-[106], c-[112], d-[108], e-[111], f-[109]
Table 7-1. Detailed total, ohmic, and electrode ASR values for Cell-1 and Cell-2 at 650 °C

<table>
<thead>
<tr>
<th></th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Total ASR&lt;sub&gt;T&lt;/sub&gt;</th>
<th>Total ASR&lt;sub&gt;EIS&lt;/sub&gt;</th>
<th>Ohmic ASR</th>
<th>Electrode ASR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-1</td>
<td>LSM-ESB</td>
<td>GDC</td>
<td>0.566</td>
<td>0.569</td>
<td>0.119</td>
<td>0.450</td>
</tr>
<tr>
<td>Cell-2</td>
<td>LSM-ESB</td>
<td>ESB-GDC</td>
<td>0.263</td>
<td>0.261</td>
<td>0.097</td>
<td>0.164</td>
</tr>
</tbody>
</table>
CHAPTER 8
CONCLUSIONS

In this dissertation, several works have been conducted to reduce polarization losses for the anode, electrolyte and cathode at reduced temperatures. In all, the goal was to develop high performance solid oxide fuel cells running at low to intermediate temperatures.

A novel AFL was developed to dramatically improve SOFC performance (Chapter 3). The bimodally integrated nano-/micron- composite AFL was fabricated by simply spray coating a precursor solution into a conventional submicron Ni-GDC functional layer. The composition used for the anode substrate, the colloidal AFL (C-AFL), and the precursor-integrated AFL (N+C-AFL) was Ni-GDC. The electrolyte composition was GDC, a system that has received much attention for its potential for use in IT-SOFCs. A systematic study comparing cells using no AFL, a C-AFL, and the newly-developed N+C-AFL was conducted. It showed that the N+C-AFL sample exhibited a maximum power density of 1160 mW/cm² at 600 °C—a 287% increase compared to the sample with no AFL and a 70% increase compared to the sample using a conventional AFL. Both ohmic and non-ohmic losses were lowered, suggesting that the 2D interfacial region between the anode and the electrolyte was enhanced as well as TBP lengths. Additionally, it was shown that the fractional improvement in power increases with decreasing temperature, a critical point for reduced operating temperatures. These findings are very encouraging not only based on dramatic improvement in performance, but also in the simplicity of the technique itself. It is further believed that this N+C-AFL technique is versatile enough to be applied to other SOFC systems for similar gains in performance, and will be a milestone in the field of reduced temperature SOFCs.
In addition to the effect of particle size in AFL, the effect of AFL composition on the electrochemical performance was investigated using submicron-sized Ni-GDC AFL (Chapter 4). For this, AFLs with composition ranging from 40 to 80 wt% NiO were fabricated. Microstructural analysis confirmed these functional layers to have phases which are fine and well-distributed. The optimal AFL composition was achieved at 1:1 volume ratio of Ni to GDC, which corresponds to 60 wt% NiO. This composition exhibited the highest MPD over the intermediate to low temperature range. In addition, a preliminary long-term stability test showed the possibility of using this system in practical SOFC applications. The measured MPD and ASR show an inverse linear relationship implying that the performance enhancement greatly depends on AFL composition.

To better understand the relationship between microstructure and electrochemical performance, the effect composition on the microstructures of Ni-GDC AFLs was investigated (Chapter 5). AFLs with various Ni-GDC compositions (50 – 80 wt% NiO before reduction) were quantified by a three dimensional (3D) reconstruction technique using a FIB/SEM dual beam system. Each AFL sample was automatically sectioned into 150 slices with 60 nm intervals. The Amira software package allowed for alignment, segmentation, and reconstruction of the 2D images to a 3D image. From these reconstructions, the volume fraction, effective particle size, phase gradient, and surface area for Ni, GDC, and pore phases as well as pore tortuosity for each sample were quantified. The estimated phase volume fraction was well matched to the theoretically calculated value. The optimal effective particle size and phase fraction were seen at 60 wt% NiO. The active TPB densities were calculated based on the connectivity of voxels
labeled with each phase. The highest TPB density achieved was ~ 15.6 μm² and corresponded to 60wt% NiO. The TPB density showed an inverse proportionality to electrode ASR. This result implies that the quantified microstructural values, which are controllable, can be directly applied to predict the electrochemical performance of SOFCs.

In Chapter 6, a discussion was given on the fabrication of a thin and dense bilayer electrolyte consisting of erbium stabilized bismuth oxide (ESB) and gadolinium-doped ceria (GDC) applied on a tape-cast anode-supported SOFC using a practical and cost-effective colloidal deposition process. Using a wet chemical co-precipitation method, nano-sized ESB particles were successfully synthesized at temperatures as low as ~ 500 °C, which is much lower than those needed for powders prepared by the conventional solid state route (~ 800 °C). Due to the high sinterability of this powder, a dense erbia stabilized bismuth oxide (ESB) layer was successfully formed on a gadolinia doped ceria (GDC) electrolyte by a simple colloidal coating method. A systematic study on the sintering behavior of ESB revealed that at higher sintering temperatures, bismuth oxide can sublime or penetrate into the GDC sublayer. SEM and EDX analysis of a full button cell with an ESB/GDC bilayer sintered at 800 °C showed no visible interfacial diffusion between each layer. I-V measurement of the cell showed high power density (~ 1.5 W/cm²) at 650 °C due to an enhancement in OCP and a significant reduction in ASR when compared to a GDC single cell. This result demonstrates that this ESB/GDC bilayer electrolyte is practical for high performance SOFCs at low operational temperature.
In Chapter 7, an alternative high performance composite cathode for low to intermediate temperature SOFCs was described. Using a highly conductive ESB phase, the performance of conventional (La$_{0.80}$Sr$_{0.20}$)MnO$_{3-δ}$ (LSM) cathodes was dramatically improved. The ESB phase was utilized not only as the ion-conducting phase in the LSM-ESB composite cathode, but also as an electrolyte coupled to LSM-ESB cathode. The electrode ASR measured from a symmetric cell consisting LSM-ESB electrodes on an ESB electrolyte was only 0.08 Ω-cm$^2$ at 700°C, which is ~60% lower than that of LSM-ESB on GDC electrolytes (0.19 Ω-cm$^2$). This exemplifies the synergetic effect the ESB phase has both in the cathode bulk and at the electrolyte/electrode interface. The ESB phase is presumed to increase the effective TPB length as well as enhance the oxygen surface exchange reaction. This effect was shown to occur at all temperatures tested, from 500 to 700 °C. The MPDs of the anode-supported SOFCs with LSM-ESB cathodes on ESB/GDC bilayered electrolytes were 50, 124, 275, 533, and 836 mW/cm$^2$ at 450, 500, 550, 600, and 650 °C, respectively. These are to date the highest reported MPDs for SOFCs using LSM-bismuth oxide composite cathodes and demonstrate that the LSM-ESB composite cathode boosted by an ESB electrolyte is very promising for low-to-intermediate SOFC applications.
APPENDIX A
DEPENDENCE OF OCP ON GDC ELECTROLYTE THICKNESS

In this dissertation, the GDC electrolyte has been used for all works. Contrast to the conventional YSZ electrolyte with pure ionic conductivity, SOFCs with doped ceria electrolyte have shown lower OCP from theoretical Nernst voltage due to electronic leakage current and oxygen permeation of GDC [60]. It has been also reported that these leakage current and oxygen permeation properties are function of the electrolyte thickness [59, 60]. In this appendix, the dependence of the OCP on GDC electrolyte thickness on Ni-GDC anode-supported SOFCs was briefly studied.

In order to gauge the effect of GDC electrolyte thickness on OCP of SOFCs in the IT range, eight anode-supported SOFCs with different electrolyte thicknesses were fabricated. The NiO-GDC anode supports were made by a tape-casting process. For the better electrolyte deposition, submicron-sized Ni-GDC AFL (50wt% NiO) was colloidally deposited. Next, GDC electrolyte was coated on the AFL surface by a spin coating method. Thickness of the electrolyte was controlled by the number of repeated coating process in the fixed spin speed and time condition. Detailed fabrication process of SOFCs with thin GDC electrolyte on the anode-support was described on Chapter 4.

Fig. A-1 shows the SEM images of the cross-sectional microstructures of the tested samples. From these micrographs, it was observed that different GDC electrolyte thicknesses of the prepared samples were obtained using the control of spin coating process. The measured electrolyte thicknesses were varied from 6.2 to 32.9 μm. The detailed values of electrolyte thickness measured were tabulated in Table A-1.

The OCP was measured under 90 sccm of hydrogen with 3% water as a fuel at the anode side and 30 sccm of dry air as an oxidant at the cathode side in the
temperature range from 500 to 650 °C. The resultant OCP values at 500, 600, and 650 °C for each sample with electrolyte thickness were plotted in Fig. A-2, and summarized in Table A-1. At all temperatures, the OCP was decreased as electrolyte thickness decreased. These experimental results demonstrate the theory that the electronic leakage current and oxygen permeation in GDC electrolyte is greater at thinner electrolyte thickness [59, 60].

Recently this experiment result was verified by continuum-level electrochemical model developed Duncan and Wachsman [60]. Fig. A-3 shows the resultant modeling fit with author’s experimental data by Duncan. For this modeling, the OCP model equation is given as

\[
\Phi_{oc} = \Phi_{th} - \eta_{oc} - \frac{k_B T}{q} \ln \left( \frac{c_{v,0}}{c_{v,L}} \right) + \frac{D_v - D_e}{z_v D_v - z_e D_e} \ln \left( \frac{u_e - u_v}{c_{v,0} - c_{e,a}} \right)
\]  

(A-1)

Detailed explanation and derivation of this model equation are in the previous work by Duncan et. al [60].
Figure A-1. Microstructures of Ni-GDC anode/GDC electrolyte/LSCF cathode SOFCs with various electrolyte thicknesses.
Figure A-2. Experimental OCP values from electrochemical test at 500, 600, and 650 °C as a function of GDC electrolyte thickness.
Figure A-3. Fit of the OCP model (eq. A-1) to experimental data for OCP as a function of electrolyte thickness.
<table>
<thead>
<tr>
<th>Sample#</th>
<th>GDC Electrolyte Thickness(μm)</th>
<th>OCP at 650(°C)</th>
<th>OCP at 600(°C)</th>
<th>OCP at 500(°C)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>6.2</td>
<td>0.648</td>
<td>0.664</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>9.0</td>
<td>0.749</td>
<td>-</td>
<td>0.838</td>
</tr>
<tr>
<td>3</td>
<td>9.4</td>
<td>0.790</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>11.3</td>
<td>0.801</td>
<td>0.847</td>
<td>0.890</td>
</tr>
<tr>
<td>5</td>
<td>12.6</td>
<td>0.822</td>
<td>0.855</td>
<td>0.913</td>
</tr>
<tr>
<td>6</td>
<td>19.7</td>
<td>0.843</td>
<td>0.860</td>
<td>0.920</td>
</tr>
<tr>
<td>7</td>
<td>26.3</td>
<td>0.876</td>
<td>0.914</td>
<td>0.961</td>
</tr>
<tr>
<td>8</td>
<td>32.9</td>
<td>0.895</td>
<td>0.935</td>
<td>0.990</td>
</tr>
</tbody>
</table>
In this section, the result of the long term stability test of a SOFC with 60wt% NiO in Ni-GDC AFL is described. This result is extended long term stability test data from chapter 4. To see the effect of AFL on the SOFC performance of the function of time, a potentiostatic test was conducted for 600 hrs at 650 °C. As a testing condition, a voltage of 0.379V where cell reached 98% of their MPD at initial I-V test was applied. The test was carried out under the gas condition of the 90 sccm of H₂ with 3% of H₂O as a fuel and 90 sccm of dry air as an oxidant at anode and cathode sides, respectively. Figure B-1 shows the result of a 600 hours long term stability test for the 60 wt% NiO AFL cell. Up to 200 hours, the effect of the AFL was retained with high power density of ~1.1 W/cm². However, over 200 hours, the power density decreased with time. The degradation rate was quite linear with time and measured at the time period from 250 to 600 hours with a linear fitting method. The estimated degradation rate was ~1.03 mW/cm²/hour.

To further investigate, current-voltage curves were measured before and after long term test at the various intermediate temperature ranges. In figure B-2, the I-V characteristics before and after long term tests compared in the temperature ranges from 500 to 650 °C with 50 °C interval. The maximum power densities before long term testing were 1.11, 0.63, 0.27, 0.12 W/cm² at 650, 600, 550, and 500 °C, respectively. However, after the potentiostatic test for 600 hours the MPDs measured were decreased as 0.78, 0.47, 0.21, 0.08 W/cm² at 650, 600, 550, and 500 °C, respectively. It is clearly shown that the degradation of power densities mainly came from lower OCP after long term test. It might be explained as the decreasing effective thickness of GDC.
electrolyte due to gradual reduction of Ce⁴⁺ into Ce³⁺ under low Po₂ condition, causing increase of electronic current leakage through the electrolyte. In addition to leakage current issue, this degradation is possibly explained that this performance degradation phenomenon with time might come from the changing of microstructures of the anode and cathode with time under applied current. For further investigation, electrochemical impedance spectroscopy can be analyzed and the microstructural analysis of the long term tested sample with SEM or 3D reconstruction using FIB/SEM dual beam system will be required.
Figure B-1. Long term stability test of a SOFC with 60wt% NiO in Ni-GDC AFL. The potentiostatic test was conducted at 650 °C for 600 hours under an applied voltage of 0.379 V.
Figure B-2. Comparison of I-V plots of the testing sample between before long term test and after long term test for 600 hours at 650°C (a), 600°C (b), 550°C (c), 500°C (d).
Figure B-2. Continued
Figure C-1. Schematic SOFC testing setup – a button cell testing setup configuration and I-V and EIS testing equipment.

- Furnace
- Anode Supported Button Cell
- Ceramabond (Sealant)
- Alumina Tube
- Fuel (H₂)
- Air (O₂)
- Current-voltage (Solartron 1287)
- Temperature Controller
- Electrochemical Impedance (Parstat 2273) (100 kHz ~ 100mHz)
Figure C-2. Illustration of symmetric cell configuration for EIS test (top) and EIS testing setup (bottom)
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Kang Taek Lee was born in Seoul Korea in 1976. After graduating from Saehwa High School in Seoul, Korea, He started his campus life at Yonsei University in Korea with Ceramic Engineering major. During his studies, he was enlisted in the Republic of Korea Army for a general soldier in the department of biological and chemical weapon. After that, he came back to the Yonsei University and finished his course work and received his Bachelor of Science degree, in August 2002. His enthusiasm for materials science drove him to enter the graduate school at Korea Institute of Advanced Science and Engineering (KAIST) in Korea. After 2 years, he received the master’s degree and worked at LG electronics for one and half years. In 2006, he moved to the U.S. and entered University of Florida at the department of materials science and engineering. He joined in Dr. Wachsman’s group, and finally received his Ph.D in August of 2010.