CONDUCTIVITY AND STABILITY OF BISMUTH OXIDE-BASED ELECTROLYTES AND THEIR APPLICATIONS FOR IT-SOFCs

By

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To my loving family
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Cubic stabilized \(((\text{DyO}_{1.5})_x-(\text{WO}_3)_y-(\text{BiO}_{1.5})_{1-x-y})\) electrolytes (DWSB) having higher ionic conductivity than \((\text{ErO}_{1.5})_{0.2}(\text{BiO}_{1.5})_{0.8}\) (20ESB) were developed to achieve higher conductivity. An optimal 2:1 dopant content ratio \((\text{Dy}:\text{W})\) was determined based on the solid solubility limit, X-ray diffraction (XRD) pattern and Arrhenius behavior. Various compositions with the same 2:1 dopant content ratio were tested to obtain the conductivity dependence on total dopant concentration. With double doping, stabilization of the cubic phase was achieved with as little as 12 mol% total dopant concentration. Overall, DWSB has a closer inherent structure to pure \(\delta\)-\(\text{Bi}_2\text{O}_3\) than any singly doped compositions. Both lattice parameter and conductivity linearly extrapolate with total dopant concentration to that of pure \(\delta\)-\(\text{Bi}_2\text{O}_3\), resulting in the ability to stabilize \(\delta\)-phase at lower dopant concentration thus achieving higher conductivity.

However, this DWSB composition experienced conductivity degradation like other cubic stabilized bismuth oxides at intermediate temperatures (IT), i.e. \(500 \sim 700 ^\circ\text{C}\). Several DWSB compositions with the same 2:1 dopant content ratio \((\text{Dy}:\text{W})\) were annealed to observe isothermal conductivity behavior in the IT range with time. All DWSB compositions maintained their initial conductivity at \(700 ^\circ\text{C}\), but underwent conductivity degradation at \(\leq 600 ^\circ\text{C}\). The
effect of total dopant concentration on conductivity degradation behavior was investigated at 600 °C and 500 °C. Notably, the effect of dopant composition on conductivity behavior with time at 500 °C demonstrates that there is a trade-off between initial conductivity and long term stability at this temperature. Therefore, it is necessary to find an optimal total and relative concentration of dopants to provide the enhanced long term stability needed to make the DWSB electrolyte system feasible for 500 °C operation. To this end, it was found that (DyO1.5)0.25-(WO3)0.05-(BiO1.5)0.70, 25D5WSB, maintained a conductivity of 0.0068 S/cm without appreciable degradation after annealing at 500 °C for 500 hours.

Cathode performance can be improved by the introduction of a second ionic conducting phase with high conductivity due to increased triple phase boundary (TPB) lengths. In this study, bismuth oxide-based electrolytes were combined with La1-xSrxMnO3-δ (LSM) to obtain composite cathodes. This composite cathode had better performance on ESB ((Er2O3)0.20(Bi2O3)0.80) than on GDC (Gd0.1Ce0.9O2-δ).
CHAPTER 1
INTRODUCTION

1.1 Motivation

Fuel cells are energy conversion devices that produce electricity by electrochemical combination of a fuel with an oxidant. Particularly, solid oxide fuel cells (SOFCs) are potential alternative electric power generation systems because of their high electrical efficiency, fuel flexibility and minimal environmental impact [1, 2]. One of the major components of an electrochemical cell is the electrolyte, which is an ion-conducting membrane that separates the two electrodes. Solid oxide electrolytes should satisfy numerous requirements, including fast ionic transport, negligible electronic conduction and high mechanical and thermodynamic stability over a wide range of temperatures and oxygen partial pressures [3].

Yttria stabilized zirconia (YSZ) is the conventional electrolyte for SOFCs. YSZ exhibits ionic conductivity of about 0.1 S/cm at 1000 °C [4]. Unfortunately, electrolytes based on zirconia have to be operated at > 700 °C to obtain acceptable oxygen ion conductivity [5]. Such high operating temperatures demand the use of ceramics for interconnects and insulation, as well as time and energy to heat up to the operating temperature. Therefore, if SOFCs could be designed to give a reasonable power output in the IT range (500-700 °C), it becomes feasible to use low-cost, readily available metallic materials such as stainless steel for the interconnects and other balance-of-plant materials [2].

As shown in Figure 1-1, YSZ electrolyte exhibits considerably low ionic conductivity in the IT range [6]. For lower temperature cell operation to be achieved, the electrolyte resistance must be lowered. This lower electrolyte resistance can be achieved either by selecting new electrolyte materials that possess higher ionic conductivity or by decreasing the electrolyte thickness with better cell fabrication techniques [7-9]. In particular, the conductivity of $\delta$-$\text{Bi}_2\text{O}_3$
is one to two orders of magnitude higher than that of stabilized zirconia at corresponding temperatures [10]. Therefore, replacement of YSZ with an intermediate temperature oxide ion conductor may provide a significant reduction in the material and fabrication problems [11].

Cubic-stabilized bismuth oxides are known to exhibit the highest ionic conductivities [12-14]. However, the instability of the bismuth oxide-based electrolytes under a reducing atmosphere may limit their applications in fuel cell environments. Takahashi et al. showed that the oxygen partial pressure for the decomposition of Bi/Bi₂O₃ at 600 °C occurs at Po₂ = 10⁻¹³.1 atm [15]. A bilayered electrolyte concept has been developed to overcome this thermodynamic instability of cubic-stabilized bismuth oxides [16]. It has been also reported that cubic-stabilized bismuth oxides undergoes phase and structural changes in IT ranges [11]. Therefore, it is required to develop new bismuth oxide-based electrolytes which fulfills both criteria of conductivity and stability for SOFC applications.

1.2 Objective

Numerous studies have been carried out to develop new bismuth oxide-based electrolytes to achieve higher ionic conductivity. Single dopant systems have been mainly employed to stabilize the cubic fluorite structure of δ-Bi₂O₃. Recently, in the literature, it was found that a double doping strategy could increase the ionic conductivity of bismuth oxide-based electrolytes compared to the single dopant system. However, in previous studies, systematic criteria for selecting dopants were not well established.

In this work, we select prospective dopants based on their polarizability and ionic radius. After identifying the dopants, the effect of total dopant concentration and dopant ratio on the structure and conductivity of bismuth oxide based electrolytes will be investigated to obtain an optimum dopant concentration for maximum conductivity.
With respect to stability, it has been known that cubic-stabilized bismuth oxides experience conductivity degradation when annealed in the IT ranges for long periods of time. Therefore, it is necessary and meaningful to examine conductivity behavior of newly developed electrolyte materials. The conductivity behavior of several bismuth oxide-based electrolytes will be investigated as a function of temperature, time, total dopant concentration and dopant ratio. This study will provide an ideal dopant composition which takes into account stability as well as conductivity at a given operating temperatures. Conductivity degradation mechanisms will be examined to identify the reasons for the decrease in conductivity at intermediate temperatures. In addition, a new approach will be explored to enhance long term stability of bismuth oxide-based electrolytes.

Finally, a new composite cathode material containing bismuth oxide-based electrolytes will be fabricated. To compare cathode performance, Area Specific Resistance (ASR) will be measured using AC impedance spectroscopy.

### 1.3 Dissertation Organization

The contents of this work are categorized into eight chapters. Chapter 1 outlines the motivation and objectives of this work. Chapter 2 covers a brief introduction on principle of solid oxide fuel cell, solid oxide fuel cell electrolytes for IT-SOFCs and an overview of impedance spectroscopy. Chapter 3 introduces the novel bismuth oxide-based electrolyte with double dopants of Dy and W (DWSB). The effect of total dopant concentration and dopant ratio on structure and conductivity is investigated to obtain maximum conductivity. Chapter 4 discusses temperature- and time- dependent conductivity behavior of these DWSB compositions and also covers conductivity degradation mechanism at intermediate temperatures. In Chapter 5, the approach for enhancing the long term stability of DWSB electrolyte compositions at 500 °C are demonstrated. Chapter 6 introduces new doubly doped bismuth oxide-based electrolytes in
addition to DWSB. Chapter 7 presents the application of this bismuth oxide-based electrolyte in composite cathode materials. Finally, chapter 8 summarizes the obtained results.
Figure 1-1. Electrical conductivity of fluorite oxides [Reprinted from H. Inaba and H. Tagawa, Solid State Ionics 83 (1996) 1. with permission from Elsevier].
CHAPTER 2
BACKGROUND

2.1 Solid Oxide Fuel Cell

2.1.1 Principles of Solid Oxide Fuel Cell

Figure 2-1 is a schematic diagram to show how solid oxide fuel cells (SOFCs) work. SOFCs are solid state energy conversion devices that convert chemical energy into the electrical energy. Cells are composed of an anode, an electrolyte and a cathode. At the cathode side, oxygen molecules combine with electrons from an external circuit to form oxygen ions. The oxygen ions move to the anode side through the electrolyte. At the anode side, hydrogen molecules combine with oxygen ions to form water releasing electrons to the external circuit. The overall reaction is to form water as shown below. Therefore, these devices emit minimal pollution and provide efficient electricity.

The open circuit voltage (OCV) of the cell can be expressed by the Nernst equation as follows.

\[ E = E^o - \frac{RT}{2F} \ln \left( \frac{(P_{H_2O})_{anode}}{(P_{H_2})_{anode} \cdot (P_{O_2})_{cathode}^{1/2}} \right) \] \hspace{1cm} (2-1)

where \( E^o \) is standard voltage, \( F \) is Faraday’s constant. In addition, \((P_{H_2O})_{anode}, (P_{H_2})_{anode} \) are the partial pressure of water vapor and hydrogen at the anode, respectively. \((P_{O_2})_{cathode} \) is the oxygen partial pressure at the cathode.

Equilibrium constant \( K \) for overall reaction can be expressed by the following equation.

\[ K = \frac{(P_{H_2O})_{anode}}{(P_{H_2})_{anode} \cdot (P_{O_2})_{cathode}^{1/2}} \] \hspace{1cm} (2-2)

The standard Gibbs free energy change for this reaction is calculated using \( K \).

\[ \Delta G^o = -RT \ln K = -nFE^o \] \hspace{1cm} (2-3)
where \( n \) is the number of electrons participating in the reaction. By manipulating above equations, we can obtain the following equation.

\[
E = \frac{RT}{2F} \ln \left( K \cdot \frac{(P_{H_2})_{\text{anode}} \cdot (P_{O_2})_{\text{cathode}}^{1/2}}{(P_{H_2O})_{\text{anode}}} \right) \tag{2-4}
\]

Under reversible conditions, the dissociation equilibrium equation of water at the anode side is shown below.

\[
H_2O \leftrightarrow H_2 + \frac{1}{2}O_2 \tag{2-5}
\]

Therefore, the equilibrium constant for water dissociation is as follows.

\[
K_D = \frac{(P_{H_2})_{\text{anode}} \cdot (P_{O_2})_{\text{anode}}^{1/2}}{(P_{H_2O})_{\text{anode}}} = \frac{1}{K} \tag{2-6}
\]

\[
K \cdot (P_{H_2})_{\text{anode}} = \frac{1}{(P_{O_2})_{\text{anode}}^{1/2}} \tag{2-7}
\]

Inserting (2-7) to (2-4) gives the following equation.

\[
E = \frac{RT}{2F} \ln \left( \frac{(P_{O_2})_{\text{cathode}}^{1/2}}{(P_{O_2})_{\text{anode}}^{1/2}} \right) \tag{2-8}
\]

Finally, it is found that the open circuit voltage of an SOFC is dependent on the \( P_{O_2} \) difference between two electrodes.

**2.1.2 Actual Performance**

The actual cell potential is decreased from its ideal potential due to several types of irreversible losses. This loss is referred to as polarization or overpotential. Figure 2-2 shows a schematic diagram which explains multiple phenomena associated with irreversible losses in an actual fuel cell.
• Activation Polarization (activation) – This stems from the activation energy of the electrochemical reactions at the electrodes.

• Ohmic Polarization (ohmic) – Ohmic losses are caused by ionic resistance in the electrolyte and electrodes, electronic resistance in the electrodes and contact resistance.

• Concentration Polarization (concentration) – This type of polarization is due to finite mass transport limitation rates of the reactants and strongly depends on the current density, reactant activity and electrode structure.

Therefore, actual voltage can be expressed as the following equation.

\[ V = V_0 - \eta_{\text{activation}} - \eta_{\text{ohmic}} - \eta_{\text{concentration}} \]  

(2-9)

where \( V \) is the actual voltage, \( V_0 \) is the theoretical voltage, \( \eta_{\text{activation}} \) is activation polarization, \( \eta_{\text{ohmic}} \) is ohmic polarization and \( \eta_{\text{concentration}} \) is concentration polarization.

Among three polarization mechanisms, ohmic polarization occurs because of resistance to the flow of ions in the electrolyte and resistance to flow of electrons through the electrode. Ohmic losses can be expressed as the following equation because both the electrolyte and electrode obey Ohm’s law.

\[ \eta_{\text{ohmic}} = IR \]  

(2-10)

where \( I \) is the current flowing through the cell, and \( R \) is the total cell resistance, which includes electronic, ionic and contact resistance:

\[ R = R_{\text{electronic}} + R_{\text{ionic}} + R_{\text{contact}} \]  

(2-11)

Any of these components can dominate the ohmic resistance, depending on the cell type. We refer to the ohmic resistance normalized by the active cell area as the Area Specific Resistance (ASR). ASR has the dimension of \( \Omega \text{cm}^2 \). The ASR is a function of the cell design,
material choice and fabrication technique. The ohmic polarization can be explained by the following equation using ASR.

\[ \eta_{\text{ohmic}} = IR = i \cdot (\text{ASR}) = i \cdot \rho \cdot L = i \cdot (1/\sigma) \cdot L \]  

(2-12)

From Eq. 2-12, it is evident that ohmic polarization in the electrolyte is determined by its conductivity and thickness. Therefore, many efforts have been made to reduce ohmic polarization in two ways – from a fabrication aspect and from a material selection aspect. As discussed earlier, thin film technology using YSZ electrolytes has been rapidly developed and makes it feasible to produce cost-effective thin films for IT-SOFCs [7-9]. However, zirconia based SOFCs still requires high processing temperatures (1200 to 1700 °C) for fabrication and this may affect electrode performance, resulting in lower specific surface area and decreased catalytic activity. Therefore, an alternative electrolyte with higher ionic conductivity for IT-SOFCs has many advantages over fabricating thin YSZ films.

**2.2 Solid Oxide Fuel Cell Electrolytes for IT-SOFCs**

Doped ceria and stabilized bismuth oxides with fluorite-type crystal structures exhibit much higher ionic conductivities than YSZ. Therefore, these materials have obtained much of attentions for IT-SOFC applications. However, these fluorite type solid oxides have limited thermodynamic properties.

Even though aliovalent doped ceria is an excellent candidate to replace YSZ, it shows mixed conduction under reducing atmospheres. This will lower open circuit potential and consequently reduce powder density.

Cubic-stabilized bismuth oxides are known to have the highest ionic conductivity. However, their phase and structural stability in the IT range still needs to be examined. In this study, bismuth oxide-based electrolytes will be the primary focus.
2.2.1 Phases and Conductivity of Pure Bi$_2$O$_3$

Bi$_2$O$_3$ exhibits polymorphism and has $\alpha$, $\beta$, $\gamma$ and $\delta$ phases [18]. The structure of the various Bi$_2$O$_3$ phases was investigated systematically by Harwig [18, 19]. The high temperature fluorite-related $\delta$-phase of Bi$_2$O$_3$ was found to be an excellent oxide ion conductor [12-14]. This phase exists between 729 °C and the melting point of bismuth oxide at 824 °C. Below 729 °C the $\delta$-phase transforms to the low temperature monoclinic $\alpha$-phase [18]. When cooling the $\delta$-phase, one of two intermediate metastable phases may be formed; the tetragonal $\beta$-phase at 650 °C or the body centered cubic (bcc) $\gamma$-phase at 639 °C [18]. The structure data of all of the Bi$_2$O$_3$ phases are summarized in Table 2-1.

The ionic conductivities of $\alpha$, $\beta$, $\gamma$ and $\delta$-phases were systematically measured by Harwig et al. [20, 21]. According to their study, $\delta$-Bi$_2$O$_3$ exhibits high ionic conductivity as shown in Figure 2-3. Pure $\delta$-Bi$_2$O$_3$ exhibits high ionic conductivity due to its relatively open structure which can accommodate a high level of atomic disorder [6]. However, $\delta$-Bi$_2$O$_3$ transforms to monoclinic $\alpha$-phase on cooling below 730 °C. Therefore, the application of $\delta$-Bi$_2$O$_3$ is limited to the narrow temperature range of 730 °C-824 °C.

2.2.2 Structure of Pure $\delta$-Bi$_2$O$_3$

$\delta$-Bi$_2$O$_3$ has a defect fluorite structure where 25% of the sites in the oxygen sub-lattice are vacant. The high intrinsic defect concentration gives high ionic conductivity to this material. The unit cell of cubic bismuth oxide consists of four cations occupying the FCC positions and six anions occupying the eight tetrahedral positions. The nature of the arrangement of the six anions and the two anion vacancies has been a subject of controversy. Several contrasting models have been proposed to describe the high temperature cubic phase of pure $\delta$-Bi$_2$O$_3$ [22-24].

However, none of these models by itself is consistent with the experimental neutron diffraction results. Neutron diffraction studies of cubic bismuth oxides by Battle et al. [25] and
Wachsman et al. [26] showed that a significant fraction of oxygen ions occupy the 32f interstitial positions. Battle et al. [25] showed that δ-Bi₂O₃ has a defective fluorite structure in which 43% of the regular tetrahedral sites (8c) are randomly occupied with 3.44 oxygen ions and the remaining 2.56 oxygen ions per unit cell are displaced from their regular 8c positions along the <111> directions.

In addition, Yashima et al. [27, 28] carried out the maximum entropy method (MEM) [29, 30]-based pattern fitting combined with the Rietveld refinement [31] using neutron-powder-diffraction data to determine the accurate disorder in δ-Bi₂O₃. They firstly conducted Rietveld analysis about three structure models including the Gattow [23], Harwig [18] and Battle models [25] (Figure 2-4). They obtained the best fit with the observed neutron diffraction data through the Battle model, compared to other models.

The calculated profile with the Battle model was good agreement with the observed one. The refined crystal parameters based on the Battle model are given in Table 2-2. The structure parameters was fairly consistent with those in the literature [25].

Secondly, Yashima et al. [27] carried out the MEM analysis with the structural factors obtained by the Rietveld analysis using the Battle model. The MEM map provided much information on the complicated disorder of oxide ions in δ-Bi₂O₃ compared with previous models. This result demonstrates that the positional disorder of oxide ions in δ-Bi₂O₃ is not fully described by previous simple models consisting atom spheres. Figure 2-5 shows the MEM nuclear density distribution map on (110) plane which visualizes the structure disorder at 778 °C. It shows that the oxide ions are disordered over a wide area compared with Bi ions in δ-Bi₂O₃.

Recently, Aidhy et al. carried out molecular dynamics (MD) simulations to determine and characterize the defect structure of pure δ-Bi₂O₃ [32]. They identified the effect of ionic
polarizability on the structure and ionic diffusion of pure δ-Bi₂O₃ through MD simulations. They found that the polarizability of the ions is the key determinant of the oxygen diffusion behavior. They created polarizable δ-Bi₂O₃ and non-polarizable δ-Bi₂O₃ with MD simulation and observed the effect of polarizability on the oxygen diffusion of δ-Bi₂O₃. It was found that the polarizable δ-Bi₂O₃ shows a continuous increase in the mean-squared displacement (MSD), implying the presence of diffusion, while the non-polarizable δ-Bi₂O₃ only had a small amount of atomic motion for an initial period of time and ceased. It is believed that this cessation of oxygen diffusion is due to the formation of vacancy-ordered structure. They concluded that low polarizability results in a combined ordering of the vacancies in <110> and <111> direction, however, high polarizability allows δ-Bi₂O₃ to maintain the disordered state of oxygen sublattice with sustained diffusion. This MD result was also consistent with the experimental results obtained with dopants having different polarizability [33, 34].

2.2.3 Stabilized Bismuth Oxide

2.2.3.1 Structure and ionic conductivity of doped bismuth oxides

It is necessary that high temperature cubic phase be stabilized in order to use bismuth oxide-based electrolytes for IT-SOFCs. Numerous studies have shown that the high conductivity δ-phase in Bi₂O₃ can be stabilized at lower temperatures by the addition of several Lanthanide (Ln³⁺ or Y³⁺) dopants [35-37]. However, due to the mismatch in ionic radii between the host and dopant cations, structure stabilization has resulted in the reduction of ionic conductivity. Verkerk et al. assumed that the stabilization of relatively loose high temperature δ-phase of Bi₂O₃ occurs by a contraction of this structure due to the dopant [38]. An investigation was conducted regarding the development of a relationship between the ionic radius of the Ln³⁺ and Y³⁺ substituent ion and the minimum amount of Ln₂O₃ or Y₂O₃ (X_min) required to stabilize the fcc phase of Bi₂O₃ [38]. Figure 2-6 shows the relationship between the ionic radius of each
dopant and its corresponding $X_{\text{min}}$ for phase stabilization. Figure 2-7 also shows the effect of these factors on the conductivity. These results demonstrate that minimum dopant concentration for cubic-phase stabilization is more important than ionic radius to achieve maximum ionic conductivity. In this respect, maximum ionic conductivity is achieved by lowering $X_{\text{min}}$. In case of singly doped bismuth oxide system, the highest ionic conductivity was obtained by the fcc phase of $\text{Er}_2\text{O}_3$ stabilized $\text{Bi}_2\text{O}_3$ as shown in Figure 2-7.

2.2.3.2 Stabilization with double dopants

Besides the singly doped $\text{Bi}_2\text{O}_3$ system, several ternary $\text{Bi}_2\text{O}_3$-based oxides with double dopants have been synthesized and characterized [39, 40]. Meng et al. showed that the fcc structure in $\text{Bi}_2\text{O}_3$-based solid solutions could be stabilized down to room temperature using two rare-earth oxide dopants, with much lower total dopant concentration than that of a singly doped oxide [39]. This cooperative effect was attributed to the increase in entropy of the resulting ternary system as a consequence of mixing [39]. It was observed that the existence of second dopant in smaller concentration stabilized the fcc structure and led to an increase in conductivity, especially in the lower temperature regions. Hu et al. also reported the conductivity variation in $\text{Bi}_2\text{O}_3$-based oxides with different trivalent co-dopants [41].

2.2.3.3 The determination of dopant species

The effectiveness of prospective dopants depends on factors such as ionic radius and dopant polarizability. Shirao et al. investigated the correlation between the electronic polarizability of an ion and the effective ionic radius in lanthanide ions. They observed that the polarizability was approximately proportional to the cube of ionic radius [42]. Furthermore, Jiang et al. showed that dopant ionic radius affected the crystallographic structure and conductivity [33]. They carried out a systematic study of bismuth oxides which were stabilized with different rare earth oxides, $\text{RE}_2\text{O}_3$ ($\text{RE} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$, or $\text{Yb}$) as well as $\text{Y}_2\text{O}_3$. Most
samples were synthesized with the same composition of 25 mol% dopant, e.g. (RE\text{2}O\text{3})_{0.25}(Bi\text{2}O\text{3})_{0.75}. Among those dopants, the cubic structure was obtained with Dy\text{2}O\text{3}, Ho\text{2}O\text{3}, Y\text{2}O\text{3}, Er\text{2}O\text{3}, Tm\text{2}O\text{3} and Yb\text{2}O\text{3}. However, larger-radii rare-earth dopants (La\text{3}+ through Gd\text{3}+) resulted in formation of the rhombohedral structure. This result demonstrates that the structure of stabilized bismuth oxides is dependent on dopant ionic radius.

Wachsman et al. found that dopants used in stabilizing the cubic structure of Bi\text{2}O\text{3} are typically less polarizable than Bi\text{3}+ and their degree of polarizability affects the conductivity and stability of the disordered structure of δ-Bi\text{2}O\text{3} [34]. In order to better understand how the polarizability of dopant cation affects long term stability of conductivity, the respective electrolyte composition was annealed at 500 °C in air. Within the fcc phase-stability window, they found that the stability for the disordered oxygen sublattice was enhanced as dopant polarizability increased as shown in Figure 2-8. Due to its large radii and high polarizability, Dy provided the greatest stability at 500 °C [33, 34]. Further, recent simulation studies found that polarizability is more important than radii to determine oxygen diffusion in Bi\text{2}O\text{3} and high polarizability leads to a disordered lattice [32].

Time constant term was introduced to express time-dependent conductivity decay behavior [43]. Conductivity behavior with time can be represented by an empirical equation,

\[ \sigma(t) = \sigma(\infty) + (\sigma(0) - \sigma(\infty))\exp[-(t/\tau)^{\beta}] \]  

where \( t \) is time, \( \sigma(0) \) is the initial conductivity, \( \sigma(\infty) \) is the conductivity at infinite time, \( \tau \) is the pertinent time constant, and \( \beta \) is a dimensionless parameter. The time constant is an indicator of decay rate and therefore the kinetic stability of the disordered or the ordered structure can be explained by this time constant (\( \tau \)). A greater \( \tau \) indicates a greater degree of stability of the disordered structure. The correlation between the dopant polarizability and the time constant for
aging is shown in Figure 2-9. From this figure, it is clear that there is a strong linear dependence between the dopant polarizability and the kinetics of aging. Thus, highly polarizable cations can be incorporated as dopants into bismuth oxide to enhance conductivity stability.

### 2.2.4 Phase Stability

Datta et al. examined the \((\text{Y}_2\text{O}_3)_{\chi\text{-}}(\text{Bi}_2\text{O}_3)_{1-\chi}\) (xYSB) phase diagram [44] and they showed that the \(\delta\)-phase in 25YSB is stable down to low temperatures (~ 400 °C). However, recent work shows that the \(\delta\)-phase decomposes to a rhombohedral structure when samples of this composition are annealed at temperatures below 700 °C for long periods of time [45]. Phase destabilization was also observed by Takahashi et al. in 20YSB after annealing [36].

Watanabe indicated that all the stabilized \(\delta\) phases in the \(\text{Ln}^{3+}\) doped bismuth oxide (\(\text{Ln}^{3+}\) = rare earth trivalent cation) reported were the quenched high-temperature stable phases [46]. He emphasized that these quenched \(\delta\)-\(\text{Bi}_2\text{O}_3\) phases are metastable at lower temperatures (~ below 700 °C). Thus, on annealing at such temperatures these phases transform gradually into the low-temperature stable phases. Fung et al. also reported that the cubic phase in the \(\text{Ln}_2\text{O}_3\text{-Bi}_2\text{O}_3\) and \(\text{Y}_2\text{O}_3\text{-Bi}_2\text{O}_3\) systems has been found to be unstable below 700 °C and undergoes a transformation to a rhombohedral phase [47-49]. Thus, it was concluded that the transformation of the cubic phase into a lower-conductivity rhombohedral phase over some composition ranges may be a general feature of rare-earth oxide (or \(\text{Y}_2\text{O}_3\))-bismuth oxide systems. In addition, the high ionic conductivity cubic phase in fact may be a metastable phase below ~700 °C.

### 2.2.5 Structural Stability

Jiang et al. demonstrated that in the case of \(\text{Ln}_2\text{O}_3\text{-Bi}_2\text{O}_3\) (or \(\text{Y}_2\text{O}_3\text{-Bi}_2\text{O}_3\)) systems, the conductivity degradation can be caused by the formation of ordered structure as well as the cubic-to-rhombohedral transformation when the samples are annealed below a certain transition temperature [50]. Wachsman et al. extensively investigated this ordering phenomenon without
involving phase change using differential thermal analysis, XRD, TEM and neutron diffraction [14, 26, 34, 51-53]. Modeling of ordered structures based on TEM diffraction patterns indicates a \langle 111 \rangle\> vacancy ordering in the anion sublattice. In addition, neutron diffraction experiments [26, 53] demonstrate that the vacancy ordering is accompanied by the displacement of almost all the oxygen ions from 8c to 32 sites (positional ordering).

Jiang et al. investigated the trend in conductivity decay with Er$_2$O$_3$ concentration as shown in Figure 2-10 [50]. It is observed that the aging rate decreases as Er$_2$O$_3$ dopant concentration increases for 15ESB, 20ESB and 25ESB. These compositions still underwent large conductivity decay. However, the decay rate was considerably reduced for 30ESB, 35ESB and 40ESB. In addition, there is no significant difference in decay rate with composition at the higher doping concentrations.

Jiang et al. performed DSC experiments to measure the enthalpy change for relaxation of the aged sample with different Er$_2$O$_3$ concentrations as shown in Table 2-3 [50]. The largest measured enthalpy change was 7.79 kJ/mol for 15ESB. The enthalpy change for other compositions is even smaller than that of 15ESB. After the sample has been annealed for 100 hours, it was thought that the aging process was nearly complete. Earnest reported the enthalpy change associated with the $\alpha$-$\delta$ transition for pure Bi$_2$O$_3$ as 33.2 kJ/mol [54]. Since this value is much larger than the reverse-aging enthalpy change, Jiang et al. rationalized that the energy change for the aging process is much smaller than that for a phase transformation, implying that the two processes are completely distinct [50].

2.3 Impedance Spectroscopy

In order to measure the electrical conductivity of solid oxide electrolyte, A.C. impedance spectroscopy has been widely used. The equivalent circuit which is suitable for these impedance
spectra will be discussed. Impedance spectra of CeO$_2$–based electrolytes and Bi$_2$O$_3$-based electrolyte will be compared.

2.3.1 Impedance Spectra for Conventional Ceramics

It is generally reported that a capacitive double layer is formed at the interface between electrolyte and electrode when a potential gradient is applied to the both electrodes of the cell. The reason for the double layer is attributed to the fact that the electrochemical reaction of interfaces is dependent on time. The equivalent circuit and impedance spectra for interface reaction are given in Figure 2-11(a). The impedance can be expressed as follows.

$$ Y = Z^{-1} = Y' + jY'' \quad (2-14) $$

$Y$ is the admittance and is the reciprocal of impedance $Z$. $Y'$ and $Y''$ are the real part and imaginary part of admittance, respectively. Therefore, $Y'$ represents resistive component and $Y''$ represents capacitive component of the cell response.

$$ Y' = R^{-1} \quad (2-15) $$

$$ Y'' = X_{dl}^{-1} = \omega C_{dl} \quad (2-16) $$

$R$, $C_{dl}$ and $X_{dl}$ represent ohmic resistance, capacitance of the electrical double layer and reactance, respectively. In addition, $\omega$ represents angular frequency.

$$ Y = Z^{-1} = Y' + jY'' = R^{-1} + jX_{dl}^{-1} = \frac{X_{dl}^{-1} + jR}{R \cdot X_{dl}^{-1}} = \frac{1 + j\omega R C_{dl}}{R} \quad (2-17) $$

$$ Z = \frac{R}{1 + j\omega R C_{dl}} \quad (2-18) $$

When electrolyte resistance, $R_u$ is included, the equivalent circuit and impedance spectra are shown in Figure 2-11(b) and the impedance can be expressed as follows.

$$ Z = R_u + \frac{R}{1 + j\omega R C_{dl}} = R_u + \frac{R}{1 + \omega^2 R^2 C_{dl}^2} = j \frac{\omega C_{dl} R^2}{1 + \omega^2 R^2 C_{dl}^2} \quad (2-19) $$
From this equation, impedance Z can be separated into real ($Z'$) and imaginary ($Z''$) components.

\[ Z' = R_u + \frac{R}{1 + \omega^2 R^2 C_{dl}^2} \]  
\[ Z'' = -\frac{\omega C_{dl} R^2}{1 + \omega^2 R^2 C_{dl}^2} \]  

From this equation, the following relation between $Z'$ and $Z''$ is obtained.

\[ (Z' - R_u)^2 + (Z'')^2 = \frac{R^2}{1 + \omega^2 R^2 C_{dl}^2} = R(Z' - R_u) \]  
\[ (Z' - R_u)^2 - R(Z' - R_u) + (Z'')^2 = 0 \]  
\[ (Z' - R_u - \frac{R}{2})^2 + (Z'')^2 = \left(\frac{R}{2}\right)^2 \]  

Conductivity measurement was performed by electrochemical impedance spectroscopy (EIS). The impedance of a system can be calculated by the following equation,

\[ Z(\omega) = \frac{V(t)}{I(t)} \]  

where $I$ is current and $V$ is a.c. voltage. The equation can be rewritten in terms of real ($Z'$) and imaginary ($Z''$) components.

\[ Z = Z' + iZ'' \]  

By plotting $Z'$ vs. $Z''$, one acquires a semicircle where the magnitude of $Z'$ along the x-axis indicates the resistance R of the electrolyte sample. That is,

\[ Z' = R \]
Electrical conductivity of this electrolyte can be calculated from sample geometry and resistance.

\[ \sigma = \frac{d}{A \cdot R} \]  

(2-28)

where \( d \) is the specimen thickness and \( A \) is the cross-sectional area perpendicular to the current direction in the sample. Information about oxygen ion conduction can be obtained by plotting the conductivity as a function of temperature (Arrhenius equation below).

\[ \sigma T = A \exp\left(\frac{-E_a}{kT}\right) \]  

(2-29)

The pre-exponential factor \( A \) is a function of geometry, crystal lattice spacing, attempt frequency of ion hopping and entropy. The activation energy \( (E_a) \) is a function of vacancy mobility and vacancy distribution. The slope of this Arrhenius plot represents the activation energy of ionic conductivity for the system. This slope should be linear for single conduction processes.

**2.3.2 The Comparison of Impedance Response**

Impedance spectroscopy is often used to separate the bulk, grain boundary and electrode processes of polycrystalline ceramic materials with ionic or mixed conduction [56]. The high frequency component usually corresponds to the true bulk properties, as measured for single crystals [57], the intermediate frequency range is ascribed to resistive grain boundaries and the low frequency range corresponds to electrode processes or processes occurring at the material/electrode interface. The bulk relaxation frequency \( f_B \) is often at least two orders of magnitude higher than the grain boundary relaxation frequency \( f_{gb} \). The electrode relaxation frequency \( f_{el} \) is also much smaller than \( f_{gb} \). In these conditions, the Nyquist plot should show nearly separate semicircles for the bulk, grain boundary and electrode terms.
For example, in case of CeO₂-based electrolytes, we usually see three-arc responses which are related to the bulk, grain boundary and electrodes. If the frequency range is not limited, we may see every process which is related to this electrochemical reaction by impedance spectroscopy. However, due to experimental limitation, we only see some parts of the whole response depending on the temperature. For modeling of this impedance spectrum, an equivalent circuit was made which is suitable for this system. When we have a perfect semicircle, a capacitor can be used in the equivalent circuit model. However, in real circumstances, the arc is often depressed and this leads to the necessity of a constant phase element (CPE). In this case, a constant phase element (CPE) was used instead of a pure capacitor for modeling in order to apply this equivalent circuit to real impedance data. A constant phase element is equivalent to a distribution of capacitors in parallel and it arises due to the microstructural inhomogeneities within the sample [58, 59].

2.3.2.1 CeO₂-based electrolyte

Zhang et al. examined the ionic conductivity of ceria-based solid solutions as a function of silica contents [60]. To a large extent, the blocking behavior of grain boundaries is mainly attributed to the presence of thin siliceous films. The deleterious grain boundary behavior arising from SiO₂ impurities has been recognized in zirconia-based electrolytes for several decades and in ceria-based ceramics for over ten years. The impedance characteristics of the Ce₁₋ₓGdxO₂₋δ ceramics, with different levels of SiO₂, were investigated. Figure 2-12 shows the impedance spectra of the Ce₀.₈Gd₀.₂O₂₋δ (CGO20) ceramics with different levels of SiO₂, measured at 350 °C in air. It is found that the grain boundary impedance increases with SiO₂ content. Specifically, the sample CGO20 with ~ 3000 ppm SiO₂ has a very large grain boundary arc compared to the sample with relatively low SiO₂ content, indicating that SiO₂ impurity is extremely detrimental to the grain boundary conduction of ceria-based electrolytes.
2.3.2.2 Bi$_2$O$_3$-based electrolyte

Duran et al. developed Bi$_2$O$_3$-Y$_2$O$_3$ (or Er$_2$O$_3$) systems and examined the electrical properties of these oxygen ion conductors [61]. Concerning the AC impedance plane behavior they found for this material the absence of a grain boundary response. Two arc responses have been reported for bismuth oxides doped with Er$_2$O$_3$, Y$_2$O$_3$ and MoO$_3$ [61-63]. Figure 2-13 shows impedance plots of 20 mol% Er$_2$O$_3$ stabilized Bi$_2$O$_3$ (20ESB) at 350 °C and 500 °C obtained from Duran et al [61]. Based on this figure, in contrast to CeO$_2$-based electrolyte, bismuth oxide-based electrolytes show no evidence of a grain boundary contribution to their conductivity. This could be due to very small grain boundary impedance or to the similar time constants for both grain interior and grain boundary impedances. Unlike zirconia and ceria, bismuth oxide is very reactive and has considerable solid solubility with silica and alumina, two common constituents of grain boundary phases in ceramics. Thus it is possible that bismuth oxide segregated at grain boundaries has a “self-cleaning” effect [59]. Due to this property of bismuth oxide, the impedance response of bismuth oxide based electrolyte is clearly different from that of ceria based electrolyte. This can be considered a striking feature of bismuth oxide-based electrolyte.
Cathode: \( \frac{1}{2} O_2 + 2e^- \rightarrow O^{2-} \)

Anode: \( H_2 + O^{2-} \rightarrow H_2O + 2e^- \)

Cell: \( H_2 + \frac{1}{2} O_2 \rightarrow H_2O \)

Figure 2-1. Principle of operation of a solid oxide fuel cell with hydrogen as a fuel and oxygen as an oxidant.
Figure 2-2. Ideal and actual fuel cell voltage/current characteristic [17]
Figure 2-3. Electrical conductivity, log $\sigma$ versus temperature of Bi$_2$O$_3$ [Reprinted from N.M. Sammes, G.A. Tompsett, H. Nafe and F. Aldinger, J Eur Ceram Soc. 19 (1999) 1801. with permission from Elsevier].
Figure 2-4. Structural models for δ-Bi₂O₃. (a) Gattow model (b) Harwig model (c) Battle model and (d) Rietveld refinement and the MEM-based pattern fitting. Red and yellow spheres denote the bismuth and oxygen atom sites, respectively [Reprinted from M. Yashima and D. Ishimura, Chem Phys Lett 378 (2003) 395. with permission from Elsevier].
Figure 2-5. Scattering amplitude distribution on (110) plane of $\delta$-Bi$_2$O$_3$ at 778 °C with white contours in the range from at 0.3 to 4.0 fm/Å$^3$ (0.2 fm/Å$^3$ step). Oxide ions have a disorder along [111] directions. [Reprinted from M. Yashima and D. Ishimura, Chem Phys Lett 378 (2003) 395. with permission from Elsevier].
Figure 2-6. $X_{\text{min}}$, the minimum value of $x$ required to stabilize the fcc phase in $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Ln}_2\text{O}_3)_x$ as a function of the ionic radius ($R_{\text{ion}}$) of Ln$^{3+}$ [38].
Figure 2-7. Electrical conductivity, $\log \sigma$ of $(\text{Bi}_2\text{O}_3)_{1-x}(\text{Ln}_2\text{O}_3)x$ for $X_{\text{min}}$ as a function of the ionic radius of the substituted $\text{Ln}^{3+}$ [38].
Figure 2-8. Relative conductivity, as a function of time, at 500 °C, for different dopants [33].
Figure 2-9. Relationship between conductivity decay time constant and dopant polarizability [43].
Figure 2-10. Relative conductivity as a function of time, at 500 °C, for different Er$_2$O$_3$ concentrations [50].
Figure 2-11. Complex plane diagram (a) for a parallel RC circuit, and (b) in (a) with the addition of $R_u$, an uncompensated electrolyte resistance [55].
Figure 2-12. Impedance spectra of CGO20 with (○) 200 ppm, and (□) 3000 ppm SiO$_2$, measured at 350 °C in air [60].
Figure 2-13. Impedance complex plane plots of 20ESB [61].
Table 2-1. Structure data of the Bi₂O₃ phases [18]

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</tr>
<tr>
<td>β (°)</td>
<td>112.977</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* May persist to room temperature.
Table 2-2. Structure parameters of $\delta$-Bi$_2$O$_3$ measured at 778 °C [27]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>occupancy</th>
<th>Occupation number per unit cell</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>$U$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4$a$</td>
<td>1</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.078(2)</td>
</tr>
<tr>
<td>O1</td>
<td>8$c$</td>
<td>0.23(22)$^a$</td>
<td>1.84</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.08(5)</td>
</tr>
<tr>
<td>O2</td>
<td>32$f$</td>
<td>0.13(5)$^a$</td>
<td>4.16</td>
<td>0.335(21)</td>
<td>= x(O2)</td>
<td>= x(O2)</td>
<td>0.121$^b$</td>
</tr>
</tbody>
</table>
Table 2-3. Enthalpies of (Bi\textsubscript{2}O\textsubscript{3})\textsubscript{1-x}(Er\textsubscript{2}O\textsubscript{3})\textsubscript{x} \textsuperscript{†} [50]

<table>
<thead>
<tr>
<th>X (%)</th>
<th>ΔH\textsubscript{R} (kJ/mol)</th>
<th>ΔH\textsubscript{σ(T&lt;600 °C)} (kJ/mol)</th>
<th>ΔH\textsubscript{σ(T&gt;600 °C)} (kJ/mol)</th>
<th>ΔH\textsubscript{σ(T&lt;600 °C)} - ΔH\textsubscript{σ(T&gt;600 °C)} (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>7.79(47)</td>
<td>121.(0)</td>
<td>21.(4)</td>
<td>99.(6)</td>
</tr>
<tr>
<td>20</td>
<td>5.80(46)</td>
<td>119.(6)</td>
<td>62.(8)</td>
<td>56.(8)</td>
</tr>
<tr>
<td>25</td>
<td>3.54(34)</td>
<td>117.(7)</td>
<td>75.(8)</td>
<td>41.(9)</td>
</tr>
<tr>
<td>30</td>
<td>0.700(2)</td>
<td>117.(5)</td>
<td>87.(7)</td>
<td>29.(8)</td>
</tr>
<tr>
<td>35</td>
<td>0.346(2)</td>
<td>115.(3)</td>
<td>100.(8)</td>
<td>14.(5)</td>
</tr>
<tr>
<td>40</td>
<td>0.214(1)</td>
<td>115.(5)</td>
<td>111.(1)</td>
<td>4.(4)</td>
</tr>
</tbody>
</table>

\textsuperscript{†}For relaxation of the order state (ΔH\textsubscript{R}), following a 500 °C anneal for 100 h; conductivity below ΔH\textsubscript{σ(T<600 °C)} and below ΔH\textsubscript{σ(T>600 °C)}, the order-disorder transition; and the difference between the two, ΔH\textsubscript{σ(T<600 °C)} - ΔH\textsubscript{σ(T>600 °C)}
CHAPTER 3
EFFECT OF TOTAL DOPANT CONCENTRATION AND DOPANT RATIO ON
CONDUCTIVITY OF DWSB COMPOSITIONS

3.1 Introduction

Cubic $\delta$-Bi$_2$O$_3$ exhibits the highest known oxygen-ion conductivity [12-14, 34]. The conductivity of $\delta$-Bi$_2$O$_3$ is two orders of magnitude higher than that of stabilized zirconia at corresponding temperatures [10]. $\delta$-Bi$_2$O$_3$ has high ionic conductivity due to its large number of highly mobile oxygen vacancies. The high mobility is attributed to the weak Bi-O bond and the high polarizability of Bi$^{3+}$ with its lone-pair 6$s^2$ electrons [34]. However, pure $\delta$-Bi$_2$O$_3$ transforms to monoclinic $\alpha$-phase on cooling below 730 °C, resulting in a greatly reduced conductivity and melts above 824 °C [64]. Therefore, the application of $\delta$-Bi$_2$O$_3$ is limited to the narrow temperature range of 730 °C-824 °C. Nevertheless, the high temperature phase of $\delta$-Bi$_2$O$_3$ can be stabilized down to room temperature by doping with other oxides [65]. However, due to the mismatch in ionic radii between the host and dopant cations, phase stabilization lowers the ionic conductivity.

Verkerk et al. found that, to stabilize the cubic phase of Bi$_2$O$_3$ to room temperature, it was necessary to dope Bi$_2$O$_3$ with cations with smaller ionic radii than Bi$^{3+}$. The stabilization occurs because such dopant cations induce a contraction of the open structure of $\delta$-Bi$_2$O$_3$ [38]. They obtained the highest ionic conductivity with (ErO$_{1.5}$)$_{0.2}$(BiO$_{1.5}$)$_{0.8}$ (20ESB) because doping with Er$^{3+}$ allowed for the lowest dopant concentration needed to stabilize the cubic structure in a single dopant system [38, 66].

In addition, several doubly doped Bi$_2$O$_3$ electrolyte systems have been synthesized and characterized to determine the optimal dopant concentration and the solid solution range [39, 40]. In one such study, Meng et al. showed that, with two dopants, the cubic phase of bismuth oxide could be stabilized with a lower total dopant concentration compared to the single dopant
system [39]. It is thermodynamically favorable to maintain its high-temperature fcc phase as long as the dopant concentration is sufficient because a large negative entropy change is accompanied when highly symmetric structure with random distribution of atoms at high temperatures transitions to a lower symmetric structure at lower temperatures. The use of two stabilizing dopants increases the entropies significantly. Therefore, double dopant strategy allows much lower dopant concentration to stabilize the fcc phase down to room temperature [39].

Among prospective dopants, Dy and W were selected for dopants to stabilize the structure and improve the conductivity. Based on the results obtained from Wachsman et al. [33, 34], Dy was chosen as a dopant. Other studies have shown that tungsten also stabilizes the fcc structure of Bi$_2$O$_3$ and has high polarizability [67-69]. Watanabe et al. also showed that Bi$_7$WO$_{13.5}$ (=7Bi$_2$O$_3$·2WO$_3$, 22.22 mol% WO$_3$) has high oxygen ion conductivity with a lower activation energy compared with other cubic stabilized bismuth oxides [69].

Accordingly, in our previous work [13, 70], we developed bismuth oxide electrolytes doubly doped with Dy$_2$O$_3$ and WO$_3$ (DWSB) that were found to have higher conductivity than 20ESB. However, the effect of total dopant concentration and dopant ratio on structure and conductivity of bismuth oxide based electrolytes was still not fully investigated. In this study, dopant ratio and total dopant concentration were systematically manipulated to obtain an optimum dopant concentration for maximum conductivity.

3.2 Experimental Procedure

3.2.1 Preparation of Electrolyte Samples

Figure 3-1 shows the flow chart of the typical powder synthesis. Disks of (DyO$_{1.5}$)$_x$-(WO$_3$)$_y$-(BiO$_{1.5}$)$_{1-x-y}$ (xDyWSB) composition were fabricated by solid state synthesis. Disks of (ErO$_{1.5}$)$_{0.2}$(BiO$_{1.5}$)$_{0.8}$ (20ESB) and (GdO$_{1.5}$)$_{0.1}$(CeO$_2$)$_{0.9}$ (10GDC) were also prepared for comparison of conductivity results. First, six different compositions were investigated;
(DyO\textsubscript{1.5})_{0.15-x}(WO\textsubscript{3})_x(BiO\textsubscript{1.5})_{0.85} (where \(x=0.05, 0.075, 0.10\)) and (DyO\textsubscript{1.5})_{0.10-x}(WO\textsubscript{3})_x(BiO\textsubscript{1.5})_{0.90}, (where \(x=0.03, 0.05, 0.07\)). The three former compositions, with a fixed 15 mol\% total dopant concentrations, are 10D5WSB, 7.5D7.5WSB and 5D10WSB. The latter three compositions, with a fixed 10 mol\% total dopant concentrations, are 7D3WSB, 5D5WSB and 3D7WSB.

Subsequently, various compositions with 2:1 mol dopant ratio between Dy and W were also prepared to determine the effect of total dopant concentration on conductivity:

(DyO\textsubscript{1.5})_{2x}(WO\textsubscript{3})_x(BiO\textsubscript{1.5})_{1-3x} (where \(x = 0.040, 0.045, 0.050, 0.055, 0.060\) and 0.070). These compositions are referred as 8D4WSB, 9D4.5WSB, 10D5WSB, 11D5.5WSB, 12D6WSB and 14D7WSB.

A stoichiometric mixture of Bi\textsubscript{2}O\textsubscript{3} (99.9995\% pure), Er\textsubscript{2}O\textsubscript{3} (99.99\% pure), Dy\textsubscript{2}O\textsubscript{3} (99.99\% pure) and WO\textsubscript{3} (99.8\% pure), from Alfa Aesar, were mixed and ball-milled with zirconia ball media in a high-density polyethylene bottle for 24 hours. Similarly a stoichiometric mixture of CeO\textsubscript{2} (99.9\% pure) and Gd\textsubscript{2}O\textsubscript{3} (99.99\% pure) from Alfa Aesar were used for 10GDC composition.

After drying, the mixed powders of DWSB or 20ESB were calcined at 800 °C for 16 hours. For 10GDC, the mixed powders were calcined at 1450 °C for 10 hours. Agglomerated powders were ground using mortar and pestle and sieved using a 325 \(\mu\)m mesh to get uniform particle sizes. The powders were pressed uniaxially into a disk-shaped 8 mm diameter die using 40 MPa to get disk-shaped pellets and pressed again to increase the density of the pellets through cold isostatic pressing at 200 MPa. The pellets of DWSB or 20ESB were subsequently sintered in air at 890 °C for 16 hours. For 10GDC, the pellets were sintered at 1550 °C for 10 hours.

The sintered pellets of bismuth oxide based electrolytes had densities 94\% \pm 2\% of theoretical densities and were polished to acquire an even surface and the desired thickness (3
Engelhard gold paste mixed with isopropanol was brushed onto both sides of the DWSB or 20ESB electrolytes and the organic additives were evaporated at 120 °C for 1 hour. Subsequently, the electrodes were sintered at 800 °C for 1 hour. For 10GDC, Pt paste (CL11-5349, Heraeus) was used as the electrode and sintered at 900 °C for 1 hour. Pt wires with circular Ag mesh were attached to the cells by mechanical contact.

3.2.2 X-Ray Diffraction Analysis

The lattice structure of the calcined powders was identified by means of X-ray diffraction analysis (XRD, Philips APD 3720). XRD pattern was obtained using CuK$_\alpha$ radiation at room temperature between 20° and 70° (2θ). Extrapolation method using Nelson-Riley function was performed to calculate the lattice parameter of cubic-stabilized DWSB compositions. Details on this method are given in Appendix B. CrystalMaker & CrystalDiffract Programs were used for better phase identification. Details on the use of this program are given in Appendix C.

In addition, High Temperature XRD (HT-XRD, Philips APD 3720 HT with heat supply under He gas condition) was used to obtain precise lattice parameter at 500 °C, 700 °C and 760 °C. The continuous scan was performed to obtain (111) peak of each composition between 26° and 30° (2θ) with step size of 0.01°. The ProFit For Windows program (Philips Profile Fit) was used to remove the contribution from K$_{\alpha2}$ radiation and lattice parameter was calculated with the wavelength of CuK$_{\alpha1}$.

3.2.3 Conductivity Measurements

Conductivity measurements were obtained from a two-point probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 over the frequency range of 0.1 Hz to 10 MHz. The frequency response analyzer was used in standalone mode for unbiased testing and interfaced to a computer using Zplot software. Due to the small sample impedances at high
temperature, a nulling technique was necessary to remove artifacts caused by inductive responses of the test leads and the equipment. This was achieved by measuring the impedance of the leads without a sample and then subtracting it from the sample measurements. The measurements were performed between 200 °C and 700 °C in air. For each composition, three different samples were used to determine the error for measured conductivity.

3.3 Results and Discussion

3.3.1 Structure

To find the ideal DWSB composition, total dopant concentration was varied according to three preset dopant content ratios of 2:1, 1:1 and 1:2. Figure 3-2 shows XRD patterns of various calcined DWSB compositions. Of these six compositions, single phase was obtained for 10D5WSB, 7.5D7.5WSB and 7D3WSB. Mixed phases were found for 5D10WSB, 5D5WSB and 3D7WSB. Figure 3-2 shows that total dopant concentration and dopant ratio affect phase purity of calcined DWSB compositions. It was analyzed that the secondary phases from 5D5WSB, 3D7WSB and 5D10WSB are the mixtures of a tetragonal phase (7Bi₂O₅•WO₃ ⇔ Bi₁₄WO₂₄, S.G. 88) and an orthorhombic (Bi₂O₅•WO₃ ⇔ Bi₂WO₆, S.G. 61) phase. Depending on the composition, relative amount of each secondary phase was different. There is a tendency to have single fcc phase as total dopant concentration and dopant ratio (Dy/W) increases as shown in Figure 3-2. This indicates that there exists a minimum dopant concentration necessary to stabilize the cubic structure of Bi₂O₃. It also shows that WO₃ has more limited solubility than Dy₂O₃ into Bi₂O₃.

Indeed, Verkerk et al. examined Dy₂O₃ doped Bi₂O₃ system (DSB) and obtained fcc structure with 28.5-50 mol% Dy₂O₃ [38], while Takahashi et al. investigated WO₃ doped Bi₂O₃ system (WSB) and attained fcc structure with 22-28 mol% WO₃ [67]. From a viewpoint of solid solution range, the WO₃ doped Bi₂O₃ system had a narrower range for fcc phase stabilization.
than the Dy$_2$O$_3$ doped Bi$_2$O$_3$ system [38, 67]. The XRD results confirm the literature finding. Therefore, it is expected that Dy content should be larger than the W content needed to attain a pure fcc phase in doubly-doped bismuth oxide.

Based on the XRD pattern of Figure 3-2, DWSB electrolytes with the same 2:1 mol dopant ratio between Dy and W were then prepared (6D3WSB, 7D3.5WSB, 8D4WSB, 9D4.5WSB, 10D5WSB, 11D5.5WSB, 12D6WSB and 14D7WSB). The total dopant concentration ranges from 9 mol% up to 21 mol%. Figure 3-3 shows XRD patterns of these DWSB electrolytes. All compositions were found to be pure fcc phase except for 6D3WSB and 7D3.5WSB.

Therefore, 8D4WSB is the composition which has the minimum dopant concentration for stabilizing fcc structure, with a 2:1 dopant content ratio. This result shows that the reduction of total dopant concentration needed to stabilize the cubic structure was achieved down to 12 mol% for DWSB compared with DSB (28.5 mol%), WSB (22 mol%) and ESB (20 mol%).

The lattice parameters of various DWSB compositions with 2:1 mol dopant ratio were determined from the (111) peak position of XRD patterns at room temperature and high temperatures. Figure 3-4 shows the lattice parameters of various DWSB compositions measured at room temperature (RT) and 760 °C. At both temperatures, the lattice parameters decrease with increasing total dopant concentration because both dopants are smaller than the Bi$^{3+}$ radii [71, 72]. We also found that the decrease of lattice parameter was linear with dopant concentration, obeying Vegard’s law, within the fcc stability window.

The lattice parameters of DWSB compositions were also compared with those of other singly doped Bi$_2$O$_3$ compositions at room temperature in Figure 3-4. For single dopant compositions, (DyO$_{1.5}$)$_{0.285}$(BiO$_{1.5}$)$_{0.715}$ (28.5DSB) and (WO$_3$)$_{0.22}$(BiO$_{1.5}$)$_{0.78}$ (22WSB) have the minimum amount of dopant to stabilize the fluorite structure, respectively. From the literature,
the lattice parameter of 28.5DSB is about 5.49 Å [38], while the lattice parameter of 22WSB is about 5.50 Å at room temperature [73]. Extrapolating the lattice parameter of DWSB to the same total dopant concentrations, it is clear that the double dopant results in a significantly larger lattice parameter than is obtained from either of these dopants when they are singularly doped.

The lattice parameters of various ESB compositions (15ESB, 20ESB, 25ESB and 30ESB) at room temperature were also added for comparison [33]. It is interesting to note that the slope of the linear fit is the same for the DWSB compositions and the ESB compositions at room temperature. However, again we can see that the double doping results in a structure with a larger lattice parameter than singly doped Bi₂O₃, resulting in a larger intercept when the dopant concentration is extrapolated to zero (δ-Bi₂O₃).

In addition, the lattice parameters were then determined at a temperature where δ-Bi₂O₃ is thermodynamically stable (760 °C) through High Temperature XRD (HT-XRD) for 8D4WSB, 10D5WSB, 12D6WSB and 14D7WSB compositions. The slope of the linear fit at 760 °C is comparable to, but slightly higher than that of the linear fit at room temperature for DWSB compositions. This may result from a larger thermal expansion of the structure with decreasing total dopant concentration at 760 °C. When this linear fit was extrapolated to pure δ-Bi₂O₃ (dopant concentration = 0) at 760 °C, the calculated lattice parameter was 5.660 Å. This value is comparable to the lattice parameter of pure δ-Bi₂O₃ ( = 5.654 Å) obtained from Yashima et al. at 760 °C [74]. Therefore, this indicates that the doubly doped DWSB more closely matches the inherent structure of δ-Bi₂O₃ than any of the singly doped compositions.

3.3.2 Conductivity

Figure 3-5 shows the typical impedance spectra for 8D4WSB at (a) 200 °C and (b) 500 °C. The conductivities were calculated from bulk resistance values measured at the frequency corresponding to the appropriate minima in the Nyquist plots. Figure 3-5(a) shows the typical
bulk impedance consisting of a single semicircle and the electrode impedance at lower frequency. As the temperature increased, the high frequency semicircle attributable to the bulk resistance was no longer resolvable as shown in Figure 3-5(b). The bulk resistance values were then taken from the high frequency intercept. Electrolyte conductivity of each composition was converted from the bulk resistance measured and sample dimensions. It is worthwhile to note that two different current ranges are used when conductivity was measured using a Solatron over the entire frequency range. Above the transition frequency, the high frequency current range is used, while below the transition frequency, the low frequency range is used. In general, if the current range is set to Auto, the equipment will determine the correct current range based on the actual current present in the cell. The scattering of data can sometimes be seen at a certain frequency because of integration failure with Auto default setup. By selecting the adequate current range manually in both high frequency region and low frequency region, we could obtain better impedance spectra without scattering of data.

The bulk conductivities of three DWSB electrolytes (10D5WSB, 7.5D7.5WSB and 7D3WSB) are plotted in Figure 3-6. Of these compositions, 10D5WSB showed the highest conductivity. The conductivity of 10D5WSB was 0.487, 0.066 and 2.23×10⁻⁴ S/cm at 700, 500 and 300 °C, respectively.

Table 3-1 shows the conductivity activation energy and lattice parameter of 10D5WSB, 7.5D7.5WSB and 7D3WSB. It is reported that cubic stabilized bismuth oxides go through an order-disorder transition, which is reflected by a change in conductivity activation energy, at a temperature in the neighborhood of 600 °C [12-14, 34, 66]. That is, above the order-disorder transition temperature, the disordered state of oxygen sublattice is maintained. On the other hand, below this transition temperature, the oxygen sublattice becomes ordered. Even though
10D5WSB and 7.5D7.5WSB have the same total dopant concentrations, the 10D5WSB has a higher conductivity than 7.5D7.5WSB throughout the entire temperature range. On the other hand, 10D5WSB had a slightly larger disparity between the two activation energies than 7.5D7.5WSB. This may be attributed to the relatively smaller lattice parameter of 7.5D7.5WSB composition and difference in bond strength between Dy-O and W-O. This observation demonstrates that the dopant ratio plays an important role in determining ionic conductivity.

Figure 3-6 shows that 7D3WSB experienced an abrupt change in conductivity and activation energy. Above 600 °C, the conductivity is closer to 10D5WSB and below 600 °C, the conductivity is closer to 7.5D7.5WSB. This implies that 7D3WSB is not stable in the lower temperature range due to the small total dopant concentration. Therefore, from the XRD pattern and conductivity behavior, we concluded that it was necessary to have >10 mol% total dopant concentration in order to obtain DWSB stabilized in the fcc structure.

Figure 3-7 shows the conductivity values of various DWSB compositions with 2:1 mol dopant ratio as a function of total dopant concentration at (a) 700 °C and (b) 500 °C. Both figures show a trend wherein the highest conductivity is achieved with the lowest total dopant concentration. In addition, it is apparent that conductivity increases linearly as total dopant concentration decreases with fixed dopant ratio for both temperatures. When this linear fit of the data in Figure 3-7(a) was extrapolated to pure δ-Bi₂O₃ at 700 °C, the calculated conductivity value was 1.1 S/cm. Harwig et al. measured the conductivities of α, β, γ and δ phases of Bi₂O₃ [21]. From his plot, the conductivity of pure δ-Bi₂O₃ at 700 °C is about 1 S/cm which is very comparable to our calculated value from extrapolation. However, extrapolation at 500 °C is not possible because the conductivity of pure δ-Bi₂O₃ is not available at that temperature due to the cubic to monoclinic phase transition.
Among DWSB formulations tested in this study, 8D4WSB is the composition with minimum total dopant concentration for stabilizing the fcc Bi\(_2\)O\(_3\) phase down to room temperature. Single dopant systems of (Dy\(_2\)O\(_3\))-(Bi\(_2\)O\(_3\)) and (WO\(_3\))-(Bi\(_2\)O\(_3\)) have also been studied and the highest conductivity was achieved with the lowest dopant concentration for cubic structure stabilization in either case [38, 67]. The conductivity of 28.5DSB is 0.144 S/cm and 0.0071 S/cm at 700 and 500 °C, respectively [38]. Likewise, the conductivity of 22WSB is 0.062 S/cm and 0.01 S/cm at 700 and 500 °C, respectively [67].

Figure 3-8 shows the conductivity dependence of DWSB compositions on lattice parameter at 700 °C and 500 °C for both room temperature and HT XRD. The lattice parameters of 8D4WSB, 10D5WSB, 12D6WSB and 14D7WSB compositions were obtained at 700 °C and 500 °C through HT-XRD. The conductivity at 700 °C increases linearly as the lattice parameter at 700 °C and room temperature increases. Similarly the conductivity at 500 °C increases linearly as the lattice parameter increases at 500 °C. In order to compare DWSB with δ-Bi\(_2\)O\(_3\) we compared these results with that of Yashima et al. [74] and Harwig et al. [21] at 700 °C.

Harwig measured the conductivity of pure Bi\(_2\)O\(_3\) in the temperature range 300 - 800 °C in the heating and cooling directions. In the heating direction, due to the monoclinic to cubic phase transition at 729 °C, the conductivity of pure δ-Bi\(_2\)O\(_3\) was not available at 700 °C. However, in the cooling direction, due to the temperature delay of the cubic to monoclinic phase transition, the conductivity of pure δ-Bi\(_2\)O\(_3\) was obtained at 700 °C.

Yashima determined the lattice parameter as a function of temperature for pure δ-Bi\(_2\)O\(_3\) from 778 °C to 740 °C. Extrapolating Yashima’s data to 700 °C results in a lattice parameter of 5.648 Å. Extrapolating our DWSB conductivity relationship to a lattice parameter of 5.648 Å results in a calculated conductivity of 1.02 S/cm at 700 °C. This compares very favorably with
Harwig’s conductivity of 0.99 S/cm at 700 °C and demonstrates that the conductivity of DWSB linearly approaches that of δ-Bi₂O₃ as the lattice parameter increases, without a shift in the intercept.

The bulk conductivities of various DWSB electrolytes are plotted as log σ vs. 1000/T in Figure 3-9. Note the conductivity of 8D4WSB is two times higher than we previously reported (See Appendix A for details). For comparison we prepared 20ESB and 10GDC by a similar solid state synthesis route and measured their conductivities as described earlier. The conductivity of (YO₁.₅)₀.₁(ZrO₂)₀.₉ (10YSZ) [75] was also added to Figure 3-9 as a contextual reference. Figure 3-9 shows that above 400 °C DWSB compositions with the same 2:1 mol dopant ratio have higher conductivities than 20ESB, 10GDC and 10YSZ.

20ESB in this work had comparable conductivities as those reported by Verkerk et al. [66] and, 10GDC in this work also had similar grain ionic conductivity as those reported by Omar et al. [58]. This not only indicates that the conductivity values of 20ESB and 10GDC prepared in this work are comparable to literature value but also validates our experimental results for DWSB.

The conductivities of 8D4WSB, the highest conductivity composition, are 0.569, 0.098 and 2.50×10⁻⁴ S/cm at 700, 500 and 300 °C, respectively. At 500 °C, 8D4WSB is 4 times more conductive than 20ESB, 10 times more conductive than 10GDC and 100 times more conductive than 10YSZ. These results could allow significant reduction in SOFC operation temperature thereby making this DWSB composition a very promising electrolyte for low temperature applications.

The temperature dependence of ionic conductivity can be expressed by the following empirical equation.
\[
\sigma T = A \exp(-\frac{E_a}{kT})
\]

(3-1)

where \( \sigma \) is the oxygen ion conductivity, \( A \) is a pre-exponential constant, \( T \) is the absolute temperature, \( k \) is the Boltzmann constant and \( E_a \) is the activation energy for oxygen migration. Therefore, activation energy and pre-exponential terms are crucial determinants of the ionic conductivity of a solid. As mentioned earlier, cubic stabilized bismuth oxides undergo a change in conductivity activation energy at \( \sim 600 \, ^\circ\text{C} [34, 66] \). DWSB compositions also show a change in conductivity activation energy. In this study, activation energy was calculated in two temperature regions at \( \geq 600 \, ^\circ\text{C} \) and at \( \leq 600 \, ^\circ\text{C} \). Some studies for singly doped bismuth oxides have calculated two different activation energies at \( \geq 600 \, ^\circ\text{C} \) and \( \leq 550 \, ^\circ\text{C} [38, 66] \). Order-disorder transition temperature in Arrhenius plot could be slightly different around \( 600 \, ^\circ\text{C} \) depending on dopant composition. It could be meaningful to obtain the activation energy at \( \geq 600 \, ^\circ\text{C} \) and \( \leq 550 \, ^\circ\text{C} \) and to identify the effect of dopant concentration on the activation energy for these DWSB compositions.

Table 3-2 shows the values of activation energy measured below and above \( 600 \, ^\circ\text{C} \). The conductivity activation energy was plotted as a function of total dopant concentration in Figure 3-10. The conductivity activation energy in the high temperature region exhibits both an opposite trend and an order of magnitude greater effect as a function of dopant concentration compared with that in the low temperature region. The disparity between these two activation energies below and above \( 600 \, ^\circ\text{C} \) decreases when the total dopant concentration increases. When the data in the high and low temperature regions are extrapolated to higher dopant concentration, we find that DWSB should have a single activation energy of \( 1.035 \, \text{eV} \) at \( 30.8 \, \text{mol\%} \). Extrapolation of the high temperature region data (12 mol\% – 18 mol\%) to 0 mol\% dopant concentration (pure \( \delta-\text{Bi}_2\text{O}_3 \)) results in a calculated conductivity activation energy value of \( 0.29 \, \text{eV} \). This value is
comparable to the activation energy of pure $\delta$-Bi$_2$O$_3$ ($\approx 0.3$ eV) measured by Harwig et al. [21]. Thus, at high temperature when the anion sublattice is disordered the conductivity activation is due primarily to migration and as the dopant concentration decreases to 0 mol% the conductivity activation energy approaches that of pure $\delta$-Bi$_2$O$_3$.

Verkerk et al. showed that the activation energy of stabilized bismuth oxides is influenced by the dopant type and dopant concentration [76] and believed this was because the Ln-O (Ln = rare earth or Y) bond is much stronger than the Bi-O bond. However, Figure 3-8 also shows that the conductivity increases with lattice parameter and that the conductivity in the high temperature region extrapolates to that of $\delta$-Bi$_2$O$_3$. Therefore, in this temperature region it may be that lattice strain plays a larger role than bond strength. In contrast, the lower temperature region exhibits different trends and is also the region where defect ordering occurs [26, 52]. Therefore, the bond strength issues pointed out by Verkerk et al. [76] may be more prevalent in this region.

The relation between pre-exponential terms and total dopant concentration was also investigated. Table 3-3 shows pre-exponential terms measured for the low and high temperature regions. The pre-exponential term is also plotted as a function of total dopant concentration in Figure 3-11. What is surprising is that even though the conductivity is higher in the high temperature region, the pre-exponential term is in fact lower in this temperature region for all compositions investigated.

As with the conductivity activation energy, the trend with dopant concentration is opposite for the low and high temperature regions. The pre-exponential term decreases with increasing total dopant concentration in the low temperature region, while it increases in the high temperature region. For both regions the conductivity decreases with increasing dopant
concentration. Therefore, in the high temperature region the increase in pre-exponential term with dopant concentration is overshadowed by the increase in conductivity activation energy with dopant concentration. In contrast, in the low temperature region the small decrease in conductivity activation energy with dopant concentration is overshadowed by the much larger decrease in pre-exponential term with dopant concentration.
Figure 3-1. Flow chart for the powder synthesis using conventional solid state reaction.
Figure 3-2. X-ray diffraction patterns of DWSB (a) with a fixed 10 mol% and (b) with a fixed 15 mol% total dopant concentration.
Figure 3-3. X-ray diffraction patterns of DWSB with 2:1 mol dopant ratio between Dy and W.
Figure 3-4. Lattice parameters of various DWSB compositions with 2:1 mol dopant ratio measured at room temperature (RT) and 760 °C as a function of total dopant concentration; the lattice parameters of 22WSB, 28.5DSB and various ESB compositions at room temperature (RT) are added for comparison [33, 38, 73].
Figure 3-5. Typical impedance spectra of 8D4WSB composition in air (a) 200 °C and (b) 500 °C.
Figure 3-6. Arrhenius plot of conductivities for 10D5WSB, 7.5D7.5WSB and 7D3WSB.
Figure 3-7. Conductivity versus total dopant concentration of DWSB electrolyte with 2:1 mol dopant ratio at (a) 700 °C; inset represents the extrapolation to pure $\delta$-Bi$_2$O$_3$ and (b) 500 °C. If not shown, error bars are smaller than the data points.
Figure 3-8. Conductivity versus lattice parameter of DWSB compositions with 2:1 mol dopant ratio at (a) 700 °C for both room temperature (RT) and 700 °C XRD and (b) 500 °C.
Figure 3-9. Arrhenius plot of conductivities for 8D4WSB, 9D4.5WSB, 10D5WSB, 11D5.5WSB, 12D6WSB, 14D7WSB, 20ESB and 10GDC; the dashed line represents the conductivity of 10YSZ [75].
Figure 3-10. The conductivity activation energy for low temperature region ($\leq 600 \, ^\circ C$) and for high temperature region ($\geq 600 \, ^\circ C$) for DWSB systems as a function of total dopant concentration of DWSB compositions.
Figure 3-11. The pre-exponential term for low temperature region (≤600 °C) and for high temperature region (≥600 °C) as a function of total dopant concentration of DWSB compositions.
Table 3-1. Conductivity activation energy and lattice parameter of 10D5WSB, 7.5D7.5WSB and
7D3WSB.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ea (eV) (≤600 °C)</th>
<th>Ea (eV) (≥600 °C)</th>
<th>ΔEa (eV)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10D5WSB</td>
<td>1.077±0.007</td>
<td>0.626±0.018</td>
<td>0.451±0.016</td>
<td>5.554±0.001</td>
</tr>
<tr>
<td>7.5D7.5WSB</td>
<td>1.040±0.007</td>
<td>0.764±0.042</td>
<td>0.276±0.046</td>
<td>5.549±0.001</td>
</tr>
<tr>
<td>7D3WSB</td>
<td>1.427±0.003</td>
<td>0.571±0.019</td>
<td>0.856±0.018</td>
<td>5.534±0.002</td>
</tr>
</tbody>
</table>
Table 3-2. Conductivity activation energies of various DWSB compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_a$ (eV) ($\leq$600 °C)</th>
<th>$E_a$ (eV) ($\geq$600 °C)</th>
<th>$\Delta E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8D4WSB</td>
<td>1.108</td>
<td>0.544</td>
<td>0.564</td>
</tr>
<tr>
<td>9D4.5WSB</td>
<td>1.086</td>
<td>0.583</td>
<td>0.503</td>
</tr>
<tr>
<td>10D5WSB</td>
<td>1.077</td>
<td>0.626</td>
<td>0.451</td>
</tr>
<tr>
<td>11D5.5WSB</td>
<td>1.084</td>
<td>0.637</td>
<td>0.447</td>
</tr>
<tr>
<td>12D6WSB</td>
<td>1.082</td>
<td>0.677</td>
<td>0.405</td>
</tr>
<tr>
<td>14D7WSB</td>
<td>1.069</td>
<td>0.796</td>
<td>0.273</td>
</tr>
</tbody>
</table>
Table 3-3. Pre-exponential terms of various DWSB compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ln A (S cm⁻¹ K) (≤600 °C)</th>
<th>Ln A (S cm⁻¹ K) (≥600 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8D4WSB</td>
<td>20.70</td>
<td>12.81</td>
</tr>
<tr>
<td>9D4.5WSB</td>
<td>20.33</td>
<td>13.28</td>
</tr>
<tr>
<td>10D5WSB</td>
<td>19.90</td>
<td>13.64</td>
</tr>
<tr>
<td>11D5.5WSB</td>
<td>19.88</td>
<td>13.67</td>
</tr>
<tr>
<td>12D6WSB</td>
<td>19.74</td>
<td>14.11</td>
</tr>
<tr>
<td>14D7WSB</td>
<td>18.43</td>
<td>14.72</td>
</tr>
</tbody>
</table>
CHAPTER 4
TEMPERATURE- AND TIME- DEPENDENT CONDUCTIVITY BEHAVIOR OF DWSB ELECTROLYTE SYSTEMS

4.1 Introduction

Cubic stabilized bismuth oxides exhibit high conductivity through structure stabilization over a wide temperature range [37, 66, 67]. However, due to an order-disorder transition, a change in conductivity activation energy is observed at ~ 600 °C [12, 14, 34]. Previous reports have shown that the polarizability of the dopant cations, which are typically less polarizable than Bi$^{3+}$, affects the conductivity and the stability of the disordered fluorite structure [34].

Cubic stabilized bismuth oxides experience conductivity degradation when annealed in intermediate temperature (IT) ranges, i.e. 500 ~ 700 °C for long periods of time [26, 38, 47-49, 52, 77]. Many studies have been conducted to investigate the factors influencing this conductivity degradation of cubic-stabilized bismuth oxides with time in IT ranges, and it has been reported that both phase transformation [47-49] and aging effects [26, 33, 52] might contribute to conductivity degradation of cubic stabilized bismuth oxides. However, there is still uncertainty about the temperature regime and the kinetics of each process.

Fung et al. and Watanabe et al. reported that the cubic phase in the Ln$_2$O$_3$-Bi$_2$O$_3$ ($\text{Ln}^{3+}$ = rare earth trivalent cation) and Y$_2$O$_3$-Bi$_2$O$_3$ systems are unstable ≤ 700 °C and undergoes a phase transformation from cubic to rhombohedral phase [47-49, 77]. The phase change and the concomitant lattice restructuring resulted in conductivity degradation. Likewise, Verkerk et al. observed that 25 mol% Dy$_2$O$_3$ doped Bi$_2$O$_3$ transformed almost completely from the cubic structure to a rhombohedral structure after annealing at 607 °C for 2000 hours [38], again accompanied by conductivity degradation.

Indeed, Watanabe reports that all the stabilized $\delta$ phases in the Ln$^{3+}$-doped bismuth oxide series ($\text{Ln}^{3+}$ = rare earth trivalent cation) reported are quenched high temperature phases and
thereby metastable at temperatures, below ~700 °C [77]. Moreover, Watanabe indicates that there exists a critical transformation temperature which varies with composition and dopant type below which the cubic-phase transforms gradually into a stable non-cubic phase [77].

In addition to phase transformation, ordered structure of oxygen sublattice has also been shown to play a crucial role in conductivity degradation. Wachsman and co-workers have shown that cubic-stabilized bismuth oxides undergo an order-disorder transition of the oxygen sublattice without phase transformation at about 600 °C [12, 14, 26, 33, 34, 51, 52, 78]. This phenomenon leads to a non-linear decay in conductivity (aging effect) below this temperature with time.

Jiang et al. indicated that although phase transformation and aging lead to conductivity degradation, the kinetics of these two processes are different [33]. They showed that each process dominates in one of two different temperature regimes. To find the time-dependence of the conductivity degradation, they compared the relative conductivity of (YO\textsubscript{1.5})\textsubscript{0.25}(BiO\textsubscript{1.5})\textsubscript{0.75} (25YSB) annealed at 500 °C and 650 °C. The conductivity of 25YSB at 500 °C decreased monotonically with time, without apparent phase change. In contrast, the conductivity of this composition at 650 °C was maintained for about 50 hours and then decreased abruptly afterwards due to a cubic-to-rhombohedral phase transformation which they observed using X-ray diffraction. Based on these results, they demonstrated that the fcc-rhombohedral phase transformation was most rapid at ~ 650 °C, while the aging phenomenon toward an ordered structure was most rapid at ~ 500 °C.

In Chapter 3, we developed cubic-stabilized DWSB electrolytes having higher conductivity than 20ESB [79]. Through double doping with Dy and W, a reduction of total dopant concentration needed to stabilize the cubic structure was achieved at 12 mol% and it resulted in higher conductivity than 20ESB, the most conductive of the cubic-stabilized bismuth
oxides reported [79]. However, due to the long term stability issues outlined above, it is crucial to assess the performance of this DWSB composition with respect to temperature and time.

Hence, the objectives of this chapter are to examine conductivity behavior of the DWSB system as a function of temperature, time, dopant ratio and total dopant concentration. This study provides insight into the steps needed to obtain optimal dopant composition at a given operating temperature by considering both initial conductivity and long term stability at various temperatures.

4.2 Experimental Procedure

4.2.1 Sample Preparation

In Chapter 3, flow chart of the powder synthesis was demonstrated. In the same way, the electrolyte pellets were prepared for conductivity measurements. In order to investigate temperature- and time- dependent conductivity behavior, four DWSB compositions of the preferred (highest conductivity) 2:1 mol dopant ratio were selected for long-term stability tests: $(\text{DyO}_{1.5})_{2x}(\text{WO}_3)_x(\text{BiO}_{1.5})_{1-3x}$ (where $x = 0.04, 0.05, 0.06$ and $0.07$); these compositions are referred as 8D4WSB, 10D5WSB, 12D6WSB and 14D7WSB, respectively.

4.2.2 Temperature Dependent Conductivity Behavior

Conductivity measurements were performed through two-point probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 over the frequency range of 0.1 Hz to 10 MHz. Details on conductivity measurements were explained in Chapter 3. For the long term stability test, each composition was annealed at a given temperature to observe conductivity behavior with time. The measurements were performed between 300 °C and 700 °C in air for duration of 100 hours. Each electrolyte pellet was only used for one temperature measurements to identify conductivity mechanism through post-analysis.
4.2.3 Characterization

The crystal phase of as-sintered and annealed samples was identified by means of X-ray diffraction analysis (XRD, Philips APD 3720). After we observe conductivity behavior of each composition at a given temperature for 100 hour annealing, X-ray diffraction (XRD) patterns were obtained at room temperature to check phase stability. XRD pattern was obtained using CuK$_\alpha$ radiation at room temperature between 20° and 80° (2θ). In order to obtain phase identification and the relative amount of each phase in mixtures, CrystalMaker & CrystalDiffract Programs were used. CrystalDiffract program can generate the calculated diffraction patterns using the structure parameters which include the types and positions of atoms in a unit cell of a crystal. This program also provides the way to work with observed and calculated data. By comparing an observed diffraction pattern with a number of calculated patterns, we can identify an unknown substance and further know the relative amount of each phase in case of mixtures. Details on the use of this program are given in Appendix C.

The microstructures of as-sintered and annealed samples were observed by scanning electron microscopy (SEM, JEOL JSM 6400). Thermal etching was not conducted for sample preparation in order to maintain internal structure obtained from long term annealing.

To confirm the conductivity mechanism, differential thermal analysis (DTA) was performed with TGA/SDTA851e from Mettler Toledo using alumina crucible as sample holders from room temperature to 820 °C. As-sintered and annealed pellets were ground using mortar and pestle to get fine powders for DTA measurements. The heating rate was 10 °C/min. Nitrogen gas was used as the purging gas, with a flow rate of 45 cm$^3$/min.
4.3 Results and Discussion

4.3.1 Conductivity

Figure 4-2 shows the bulk conductivities of selected DWSB compositions with 2:1 mol dopant ratio, 20ESB and 10GDC as log \( \sigma \) vs. 1000/T. As this figure shows, 8D4WSB exhibits the highest conductivity of all compositions over the temperature range shown.

As described in Chapter 3, cubic-stabilized bismuth oxides go through an order-disorder transition, which is reflected by a change in \( E_a \) at ~ 600 °C [12, 14, 34, 66]. It has been reported that the size of the change in the activation energy is related to the aging rate of cubic-stabilized bismuth oxides [33].

Table 4-1 shows conductivity activation energy of selected DWSB compositions and 20ESB in both low and high temperature regions. Each of the DWSB compositions shows a change in conductivity activation energy, and we will explore the relationship between this change and stability in the following sections.

4.3.2 Stability

4.3.2.1 Conductivity behavior of DWSB in the IT ranges

In order to observe the effect of annealing temperature on conductivity behavior with time, various DWSB compositions were annealed between 500 and 700 °C for 100 hours. The effect of total dopant concentration on conductivity at each annealing temperature was examined.

Figure 4-3 shows the conductivity behavior of three different DWSB compositions annealed at 700 °C with time. When the samples were annealed at 700 °C, which is significantly higher than the expected order-disorder transition temperature of ~ 600 °C, each DWSB composition maintained its initial conductivity. Also, 8D4WSB with a lower total dopant concentration maintained higher conductivity than 10D5WSB and 12D6WSB. This observation demonstrates that all DWSB compositions under consideration are stable at 700 °C.
However, these DWSB compositions experienced a decrease in conductivity when annealed ≤ 600 °C. Figure 4-4 shows time-dependent conductivity behavior for various DWSB compositions annealed at (a) 600 °C and (b) 500 °C. 20ESB was also annealed at 500 °C for comparison with the DWSB compositions.

Although conductivity degradation was observed in the DWSB compositions at ≤ 600 °C, the conductivity degradation trend with respect to total dopant concentration was different at 600 °C versus 500 °C. Of these DWSB compositions, 8D4WSB maintained the highest conductivity of 0.10 S/cm after 100 hour annealing at 600 °C. On the other hand, of all DWSB compositions as well as 20ESB, 10D5WSB had the highest conductivity of 0.0051 S/cm after 100 hour annealing at 500 °C due to its relatively high initial conductivity and low degradation rate.

The relative conductivity (σ/σ₀) was plotted on a semi-log scale in order to clearly observe the time-dependent conductivity degradation trend at both temperatures. Figure 4-5(a) shows the relative conductivity versus time for various DWSB compositions annealed at 600 °C. This figure shows that conductivity degradation is observed in all compositions and increases as total dopant concentration increases (with a fixed dopant ratio). Conversely, when these DWSB compositions are annealed at 500 °C, the trend reverses as shown in Figure 4-5(b) and the conductivity degradation lessens as total dopant concentration increases.

To compare the relative amount of conductivity decrease after 100 hours, log (σ₁₀₀/σ₀) was plotted at 600 °C and 500 °C as a function of total dopant concentration as shown in Figure 4-6. Log (σ₀/σ₀) was chosen as a baseline for the initial conductivity at both temperatures. From these plots, it is obvious that conductivity degradation exhibits an opposite trend as a function of total dopant concentration at 600 °C versus 500 °C. In addition, DWSB compositions experienced a
relatively larger conductivity decrease at 500 °C compared to 600 °C except for 14D7WSB (total dopant concentration = 21 mol%), which has the highest total dopant concentration in this study.

Clearly this shows 2 different phenomena. At 500 °C, it is ordering and higher total dopant concentration decreases activation energy difference and rate of ordering. At 600 °C, it is phase stability which is observed for some (not all dopants) singly doped bismuth oxides. It is believed that increasing W concentration makes it less phase stable at 600 °C. Details on the phase stability of these DWSB compositions will be discussed in the following section.

4.3.2.2 Conductivity degradation mechanism

SEM was carried out to compare their microstructures between as-sintered sample and annealed sample. Figure 4-7 shows SEM images of fractured 8D4WSB pellets. As shown in Figure 4-7(a), as-sintered 8D4WSB has well-sintered grains and many pores are trapped within the grains. However, Figure 4-7(b) and Figure 4-7(c) show that the 8D4WSB annealed at 600 °C (or 500 °C) for 100 hours has the distortion of the lattice grain. This could be due to the phase decomposition while annealing at 600 °C and 500 °C.

In order to investigate phase stability during annealing, the structure of each composition was characterized using X-ray diffraction analysis after each stability test. Figure 4-8 shows XRD patterns of various DWSB compositions annealed at 600 °C for 100 hours. This figure shows that all DWSB compositions tested at this temperature experienced varying amounts of phase change with the conductivity degradation. Figure 4-8(b) shows the magnified version of XRD patterns which are composed of the main peak of each phase between 26 ~ 30° (θ). It appears that the amount of secondary phase tends to increase as total dopant concentration increases.

Many studies have shown that some singly doped bismuth oxides undergo a phase transformation from cubic to rhombohedral phase at 600 °C [47-49]. However, the secondary
phase which is observed from DWSB compositions in this study was not identified as a rhombohedral phase. Instead, the secondary phases of Figure 4-8 were well matched with a (Bi rich) tetragonal phase \(7\text{Bi}_2\text{O}_3\cdot\text{WO}_3 \equiv \text{Bi}_{14}\text{WO}_{24}, \text{S.G. 88}\) and an (W rich) orthorhombic \(\text{Bi}_2\text{O}_3\cdot\text{WO}_3 \equiv \text{Bi}_2\text{WO}_6, \text{S.G. 61}\) phase. CrystalDiffract program was used to obtain phase identification and the relative amount each phase in mixtures. First, the calculated mixture pattern of cubic [27], tetragonal \((\text{Bi}_{14}\text{WO}_{24})\) [80] and orthorhombic \((\text{Bi}_2\text{WO}_6)\) [81] were generated using respective structure parameter. By manipulating the relative amount of each phase in calculated mixtures, it was analyzed that the observed pattern of 14D7WSB annealed at 600 °C for 100 hours is approximately composed of 45% cubic phase, 30% orthorhombic phase and 25% tetragonal phase.

Indeed, Watanabe et al. found that \(\text{Bi}_7\text{WO}_{13.5}\) (22.22 mol% \text{WO}_3) decomposed gradually into the tetragonal and orthorhombic phases below 670 °C [69]. They measured the electrical conductivity for \((\text{Bi}_2\text{O}_3)_{1-x}(\text{WO}_3)_x\) electrolyte compositions. Figure 4-9 shows the electrical conductivities of for \((\text{Bi}_2\text{O}_3)_{1-x}(\text{WO}_3)_x\), where \(x = 0.125\) (tetragonal), 0.25 (cubic) and 0.50 (orthorhombic) obtained by Watanabe et al. [69]. This figure demonstrates that the neighboring phases, \(\text{Bi}_{14}\text{WO}_{24}\) (12.5 mol% \text{WO}_3) and \(\text{Bi}_2\text{WO}_6\) (50 mol% \text{WO}_3) had far lower conductivity than \(\text{Bi}_7\text{WO}_{13.5}\) (22.22 mol% \text{WO}_3), which has a cubic structure [69]. Therefore, we deduce that secondary phase formation is likely a strong component of isothermal conductivity degradation of DWSB at 600 °C. It is also believed that W concentration as a second dopant should be minimized since the secondary phase formation is due to a decomposition of \((\text{WO}_3)-(\text{Bi}_2\text{O}_3)\) cubic phase.

On the other hand, when these DWSB compositions were annealed at 500 °C for 100 hours, the trend of conductivity degradation and phase change according to total dopant
concentration was different. Unlike annealing at 600 °C, at 500 °C the conductivity degradation rate of the DWSB compositions lessens as total dopant concentration increases as shown in Figure 4-5(b) and Figure 4-6.

Figure 4-10 shows XRD patterns of various DWSB compositions including 20ESB annealed at 500 °C for 100 hours. Figure 4-10(b) clearly shows that the amount of secondary phase tends to decrease as the total dopant concentration increases. Although secondary phases still exist at the lowest dopant concentration, the amount of secondary phase diminished considerably as total dopant concentration increases. Especially, 14D7WSB maintained a cubic structure after the 100 hour annealing at 500 °C.

It is interesting to note that 20ESB did not undergo a phase transformation even with large conductivity decay as shown in Figure 4-10. The stability observed for 20ESB is consistent with literature findings [33]. Specifically, Wachsman et al. found that this conductivity decay without a phase change was due to the ordering of the oxygen sublattice [26, 33, 51, 52, 78]. For DWSB compositions, conductivity degradation was still observed for 12D6WSB and 14D7WSB at 500 °C although the phase change was negligible, which indicates that this conductivity degradation at 500 °C is due to anion ordering. This assertion is further supported by the fact that each DWSB composition undergoes a larger conductivity degradation at 500 °C than at 600 °C in spite of the reduced secondary phase formation at 500 °C.

To confirm the difference in conductivity degradation mechanism at 600 °C vs. at 500 °C, differential thermal analysis (DTA) was performed to investigate the effect of thermal history on the samples from room temperature to 820 °C. Figure 4-11 shows the DTA results of 8D4WSB which was (a) as-sintered, (b) annealed at 600 °C for 100 hours and (c) annealed at 500 °C for
100 hours. The as-sintered 8D4WSB sample did not exhibit a peak, while the 8D4WSB samples annealed at 600 °C and 500 °C exhibited endothermic peaks.

Watanabe et al. also used DTA to characterize (Y$_2$O$_3$)$_{0.225}$(Bi$_2$O$_3$)$_{0.775}$ (22.5YSB) with rhombohedral phase and observed a drastic endothermic peak at 720 °C [82]. They demonstrated that the endothermic peak which corresponds from rhombohedral to cubic phase transformation occurs near 720 °C in the (Y$_2$O$_3$)$_x$(Bi$_2$O$_3$)$_{1-x}$ series [82]. In our study, we observed an endothermic peak at ~ 767 °C for 8D4WSB composition annealed at 600 °C. Therefore, it is believed that the endothermic peak at ~ 767 °C corresponds to the transformation from secondary phase formed during annealing at 600 °C to high-temperature cubic phase. The temperature difference for the endothermic peak position between 22.5YSB and 8D4WSB could be attributed to the nature of the different structure of secondary phases.

For 8D4WSB composition annealed at 500 °C, two endothermic peaks at ~ 630 °C and at ~ 750 °C were observed. The first endothermic peak at ~ 630 °C is consistent with previous DTA results of 20ESB reported by Wachsman et al. [51] and previous differential scanning calorimetry (DSC) results of 20ESB reported by N. Jiang et al. [33] They report that the ordered structure of oxygen sublattice is relaxed to a disordered state at ~ 630 °C with absorption of energy upon heating.

Therefore, this result clearly demonstrates 8D4WSB undergoes the ordering of the oxygen sublattice as well as secondary phase formation when annealed at 500 °C for 100 hours and that this anion ordering contributed to a larger decrease in conductivity at 500 °C. The second endothermic peak temperature (~ 750 °C), associated with phase transformation, for 8D4WSB annealed at 500 °C, was relatively lower than the endothermic peak temperature (~ 767 °C) of 8D4WSB annealed at 600 °C. This fact provides further evidence that 8D4WSB experience less
secondary phase formation at 500 °C than at 600 °C. Therefore, the DTA results confirm that anion ordering played a dominant role in conductivity degradation at 500 °C for the 8D4WSB composition.

For 8D4WSB annealed at 500 °C for 100 hours, XRD patterns were obtained before and after DTA measurement as shown in Figure 4-12. This result also identifies that cubic fluorite structure with disordered oxygen sublattice can be achieved upon heating to ~ 800 °C, supporting the DTA results.

Therefore, it can be concluded that the disordered state of the oxygen sublattice for DWSB compositions is maintained at 700 °C, which is significantly higher than order-disorder transition temperature. Hence, conductivity degradation was not observed while annealing at this temperature. Conversely, phase destabilization and/or ordering of oxygen sublattice occur at temperatures ≤ 600 °C, resulting in conductivity degradation. Especially, anion ordering is a dominant source for conductivity degradation at 500 °C, while phase transformation is dominant at 600 °C. The effects of the difference in bond character between Bi-O and dopant (Dy or W)-O may be obscured at 700 °C due to the higher thermal energies. However, the differences in bond character which are caused by the dopant type and dopant concentration starts to influence the structure and therefore the conductivity as temperature decreases.

4.3.2.3 Conductivity behavior of 8D4WSB

Figure 4-2 shows that 8D4WSB is the highest conductivity composition, but experienced the most rapid conductivity degradation at 500 °C as shown in Figure 4-4. Indeed, the conductivity of 8D4WSB after 100 hour annealing at 500 °C was less than that of other DWSB compositions. It is believed that 8D4WSB has the highest initial conductivity since it has more open structure with larger lattice parameter [79], but its stability decreases when there is insufficient thermal energy to maintain the high oxygen vacancy concentration. Therefore,
though the double dopant strategy using Dy and W was successful in achieving high initial conductivity, it struggled to deliver phase and structural stability between 500 and 600 °C.

To obtain a clearer picture of the long term stability of 8D4WSB, additional anneals were conducted at 400 °C, 300 °C and 650 °C to observe the conductivity degradation. Figure 4-13(a) shows the conductivity behavior of 8D4WSB annealed at each different temperature including previous 500 ~ 700 °C temperature ranges. The relative conductivity (σt/σo) of 8D4WSB was plotted as a function of time at various temperatures in Figure 4-13(b).

In contrast to 500 °C operation, conductivity degradation was greatly reduced at 400 °C and 300 °C. Figure 4-13(b) clearly shows that the degradation rate at 300 °C was much smaller than that at 400 °C. This suggests that exponentially slower kinetics at decreased temperatures influence the conductivity degradation rate. That is, slow kinetics, for phase transformation or anion ordering, retard the conductivity degradation rate as temperatures decreases below 500 °C.

X-ray diffraction analysis was used to identify the phase stability in the samples after a 100 hour anneal at various temperatures. Figure 4-14 shows the XRD patterns of 8D4WSB annealed at 300 ~ 700 °C for 100 hours as well as a reference pattern for an as-sintered pellet. This figure also includes the XRD pattern of cubic Bi$_2$O$_3$ which has Fm$\bar{3}$m space group (225).

The cubic fluorite structure was maintained when 8D4WSB was annealed at ≥ 650 °C and ≤ 400 °C. On the other hand, secondary phases were formed between 500 and 600 °C. That is, 8D4WSB is phase stable at temperatures ≥ 650 °C and ≤ 400 °C. Yaremchenko et al. have also reported that Bi$_2$O$_3$-ZrO$_2$-Y$_2$O$_3$ and Bi$_2$O$_3$-Nb$_2$O$_5$-Ho$_2$O$_3$ solid solutions experienced phase instability at 600 °C and 500 °C [83]. Moreover, they reported that the new secondary phase could not be assigned as rhombohedral phase. This result is consistent with our findings for the Bi$_2$O$_3$-Dy$_2$O$_3$-WO$_3$ system (DWSB).
Figure 4-13 and Figure 4-14 show that the small degradation of conductivity is still observed below 500 °C without phase change. Since there was no observed phase change below 500 °C, we believe that the slight conductivity degradation below this temperature is due to ordering of oxygen sublattice [26, 33, 52].

Practically, 8D4WSB, which is the highest initial conductivity composition, can be a promising electrolyte composition when operated above 650 °C. There is a possibility that this composition could be also used for low temperature (≤ 400 °C) applications if electrode kinetics is fast enough, since it undergoes only slight conductivity degradation without phase change. Lowering the total dopant concentration to obtain higher conductivity is reasonable above the order-disorder transition temperature (~ 600 °C) or below 500 °C for DWSB compositions in this study, but further study will be necessary to enhance the long term stability of this DWSB electrolyte composition between 500 and 600 °C.
Figure 4-1. Comparison of conductivity decay of 25YSB at 500 °C and 650 °C [33].
Figure 4-2. Arrhenius plot of conductivities for 8D4WSB, 10D5WSB, 12D6WSB, 14D7WSB, 20ESB and 10GDC.
Figure 4-3. Conductivity behavior of 8D4WSB, 10D5WSB and 12D6WSB annealed at 700 °C as a function of time.
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Figure 4-14. XRD patterns of 8D4WSB annealed at various temperatures for 100 hours.
Table 4-1. Conductivity activation energies of 8D4WSB, 10D5WSB, 12D6WSB, 14D7WSB and 20ESB.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$E_a$ (eV) ($\leq 600 , ^\circ$C)</th>
<th>$E_a$ (eV) ($\geq 600 , ^\circ$C)</th>
<th>$\Delta E_a$ (eV)</th>
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<td>0.564</td>
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<td>10D5WSB</td>
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<td>12D6WSB</td>
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<td>14D7WSB</td>
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<td>0.273</td>
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<td>20ESB</td>
<td>1.235</td>
<td>0.733</td>
<td>0.502</td>
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CHAPTER 5
ENHANCED LONG TERM STABILITY OF BISMUTH OXIDE BASED ELECTROLYTES
FOR IT-SOFC OPERATION AT 500 °C

5.1 Introduction

The popular yttria stabilized zirconia (YSZ) electrolyte is known to be quite stable in Solid
Oxide Fuel Cells (SOFCs) due to its thermodynamic stability in both oxidizing and reducing
atmospheres [11]. However, YSZ requires an operation temperature of > 700 °C to obtain
acceptable ohmic resistance [1, 2]. Lower temperature operation allows a wider choice of
interconnect materials and improvement in cell reliability during prolonged operation [10, 11].
Therefore, it would be of great benefit if SOFCs could be designed to give a reasonable power
output in IT ranges (500 ~ 700 °C) [84].

In the last few decades, cubic-stabilized bismuth oxide has received attention as an
alternative electrolyte material to conventional YSZ. Cubic-stabilized bismuth oxides exhibit the
highest known oxide ion conductivity over a wide temperature range [66, 79]. In the IT range, its
ionic conductivity is two orders of magnitude higher than that of YSZ at corresponding
temperatures [66, 79]. Therefore, it is expected that a replacement of YSZ by cubic-stabilized
bismuth oxide would allow significant reduction in SOFC operation temperature. On the other
hand, when annealed in the IT range for long periods of time, cubic-stabilized bismuth oxides are
known to experience conductivity degradation due to phase and structural instability [33, 48].

In Chapter 3 and Chapter 4, it was found that (DyO$_{1.5}$)$_{0.08}$-(WO$_3$)$_{0.04}$-(BiO$_{1.5}$)$_{0.88}$, 8D4WSB,
had the highest conductivity due to the reduction of total dopant concentration and concomitant
larger lattice parameter [79] and showed good long term stability when it was annealed above ~
650 °C [85]. However, 8D4WSB had the greatest decrease in conductivity at 500 °C, resulting
from the phase change and ordering of the oxygen sublattice [85]. It was also found that
conductivity degradation decreased as total dopant concentration increased for DWSB
compositions [85]. This result demonstrates that more stable DWSB compositions can be achieved at 500 °C by increasing total dopant concentration. Enhancing the long term stability is crucial for making stabilized bismuth oxides amenable to SOFC operation over time periods in excess of several hundred hours, in the IT range.

The objectives of this Chapter 5 are to examine the effect of dopant concentration on conductivity behavior of various DWSB compositions with time at 500 °C, and to obtain an optimal dopant composition which has enhanced long term stability at this temperature. Phase stability was investigated for each DWSB composition before and after annealing at 500 °C, to determine the factors contributing to conductivity degradation.

5.2 Experimental Procedure

5.2.1 Sample Preparation

All samples were synthesized by the solid state reaction of a stoichiometric mixture of oxides. In this study, four (DyO$_{1.5}$)$_x$(WO$_3$)$_{0.05}$(BiO$_{1.5}$)$_{1-x}$ (where x = 0.10, 0.15, 0.20 and 0.25) (DWSB) compositions with the same 5 mol% W concentration were prepared. These compositions are referred as 10D5WSB, 15D5WSB, 20D5WSB and 25D5WSB. (DyO$_{1.5}$)$_{0.25}$(BiO$_{1.5}$)$_{0.75}$ (25DSB) and (GdO$_{1.5}$)$_{0.1}$(CeO$_2$)$_{0.9}$ (10GDC) were also prepared for conductivity comparison.

5.2.2 Time Dependent Conductivity Behavior

Conductivity measurements were performed through two-point probe electrochemical impedance spectroscopy (EIS) using a Solartron 1260 over the frequency range of 0.1 Hz to 10 MHz. Conductivity measurements were performed for each composition at 500 °C for 300 ~ 500 hours to observe conductivity behavior with time. The conductivity measurements were carried out on an hourly basis at this temperature in air.
5.2.3 Phase Analysis

The phase analysis of as-sintered and annealed samples was identified by means of X-ray diffraction analysis (XRD, Philips APD 3720). XRD pattern was obtained using CuK$_\alpha$ radiation at room temperature between 20° to 80° (2θ). Extrapolation method using Nelson-Riley function was carried out to estimate the lattice parameter of cubic-stabilized bismuth oxides at room temperature. In addition, in order to obtain phase identification and the relative amount of each phase in mixtures, CrystalMaker & CrystalDiffract Programs were used.

5.3 Results and Discussion

5.3.1 Conductivity

In our previous work [85], although all DWSB compositions experienced large conductivity degradation at 500 °C, (DyO$_{1.5}$)$_{0.10}$-(WO$_3$)$_{0.05}$-(BiO$_{1.5}$)$_{0.85}$, 10D5WSB, maintained the highest conductivity after 100 hour anneal at this temperature including 20ESB. It has been shown that ordering decrease with increasing dopant concentration at this temperature [33, 85]. Hence higher dopant concentrations are required to achieve a stable DWSB composition, even though this results in a lower initial conductivity.

It was also determined that W concentration should be minimized since the secondary phase formation is due to a decomposition of (WO$_3$)-(Bi$_2$O$_3$) cubic phase. Therefore, considering both phase stability and electrical properties, we increased the Dy dopant concentration with a fixed 5 mol% W dopant concentration in order to attain improved conductivity stability.

Figure 5-1 shows XRD patterns of various DWSB compositions, each with the same 5 mol% W content. It was found that initially all DWSB compositions had single cubic structure. The lattice parameters of these compositions were determined from XRD patterns using Nelson-Riley function at room temperature. Figure 5-2 shows that the lattice parameter measured at room temperature linearly decreases with increasing Dy concentration, obeying Vegard’s law.
When this linear fit is extrapolated to pure $\delta$-Bi2O3 (dopant concentration = 0), the calculated lattice parameter is 5.609 Å and is very comparable to that of our previous work [79].

The bulk conductivities of various DWSB compositions with different Dy concentration (10D5WSB, 15D5WSB, 20D5WSB and 25D5WSB) are plotted in Figure 5-3. We observed that the conductivity decreased as Dy dopant concentration increased.

Table 5-1 shows the activation energy values for these DWSB compositions in the low and high temperature regions. The change in activation energy slope of plot below and above 600 °C decreases with increasing Dy dopant concentration. This behavior is consistent with our previous findings [79]. It has been known that the observed change in conductivity activation energy is generally consistent with the trend in aging rate of cubic stabilized bismuth oxides at 500 °C [33, 79]. Of those DWSB compositions, 25D5WSB has considerably lower activation energy difference below and above 600 °C.

5.3.2 Stability

5.3.2.1 Long term conductivity behavior

Long term stability tests were performed for 15D5WSB, 20D5WSB, 25D5WSB and 25DSB at 500 °C for about 300 hours. Particularly 25D5WSB was annealed at 500 °C for 500 hours. Figure 5-4(a) shows time-dependent conductivity behavior for these compositions as well as, for comparison, 10D5WSB at 500 °C. This figure shows that as the total dopant concentration (Dy concentration in this case) increased, the long term stability was greatly enhanced although the initial conductivity decreased as the total dopant concentration increased.

In order to examine the time-dependent conductivity behavior in more detail, the relative conductivity ($\sigma(t)/\sigma(t=0)$), was plotted. Figure 5-4(b) shows relative conductivity behavior for various DWSB compositions and 25DSB as a function of time at 500 °C.
DWSB compositions usually showed slight conductivity degradation in the initial period of time and underwent large conductivity degradation afterwards except for 25D5WSB. Figure 5-4 shows that the onset time of large degradation in conductivity is delayed and the overall degradation rate decreases as dopant concentration increases. Consequently, we observed that conductivity degradation at 500 °C was significantly minimized by increasing the total dopant concentration while retaining a constant 5 mol% W concentration for DWSB compositions. Therefore, this result demonstrates that higher dopant concentrations provide better stability at this temperature.

Table 5-2 shows the conductivity of various DWSB compositions and 25DSB before and after annealing at 500 °C for various time periods. In particular, for 25D5WSB, no appreciable degradation was observed for 500 hours other than a small depression of conductivity in the initial period of time from 0.0081 S/cm to 0.0070 S/cm.

The conductivity (0.0068 S/cm at t = 500 hours) of 25D5WSB after 500 hour annealing was even higher than that (0.0051 S/cm at t = 100 hours) of 10D5WSB after 100 hour annealing and comparable to the initial grain conductivity of 10GDC (0.0068 S/cm). Figure 5-5 shows impedance spectra of 25D5WSB vs. 10GDC measured at 500 °C in air. This figure clearly shows that grain boundary resistance of 25D5WSB is negligible, but 10GDC has a large grain boundary resistance.

Duran et al. developed Bi$_2$O$_3$-Y$_2$O$_3$ (or Er$_2$O$_3$) systems and examined the electrical properties of these oxygen ion conductors [61]. Concerning the AC impedance plane behavior, they observed the absence of a grain boundary response for this material. Two arc responses consisted of bulk and electrodes also have been reported for bismuth oxides doped with Er$_2$O$_3$, Y$_2$O$_3$ and MoO$_3$ [61-63]. Based on these results, bismuth oxide-based electrolytes show no
evidence of a grain boundary contribution to their conductivity. This could be due to very small 
grain boundary impedance or to the similar time constants for both grain interior and grain 
boundary impedances. Unlike zirconia- and ceria-based electrolytes, it is well known that 
bismuth oxide-based electrolytes have negligible grain boundary resistances because bismuth 
oxide has considerable solid solubility with silica and alumina, two common impurity 
constituents of grain boundary phases in ceramics [59]. This can be considered a striking feature 
of bismuth oxide-based electrolyte.

On the other hand, Zhang et al. examined the ionic conductivity of ceria-based electrolytes 
as a function of silica contents [60]. They reported that SiO₂ impurity is extremely detrimental to 
the grain boundary conduction in ceria-based electrolytes [60]. This impedance spectrum of 
10GDC is comparable to that of Omar et al. [58, 86]. It is believed that large grain boundary 
resistance of 10GDC is due to the SiO₂ impurity content in this study. Therefore, with respect to 
total conductivity, 25D5WSB has 84 times greatly higher conductivity than 10GDC even after 
500 hour annealing at 500 °C.

To verify the phase stability of these DWSB compositions after annealing at 500 °C, X-ray 
 diffraction analysis was performed. Figure 5-6 shows XRD patterns of various DWSB 
compositions annealed at 500 °C. This figure also includes the JCPDS pattern of δ-Bi₂O₃ which 
has a space group of Fm\(\bar{3}\)m (225). In order to compare the intensity of the secondary phase, all 
XRD patterns were normalized based on the intensity of (111) main peak of fcc structure.

10D5WSB and 15D5WSB had mixed phases of tetragonal and orthorhombic from the 
decomposition of (WO₃)-(Bi₂O₃) cubic phase, similar to that found in 8D4WSB. Using 
CrystalDiffract program, it was analyzed that annealed 10D5WSB composition is approximately 
composed of 61% cubic phase, 31% orthohombic phase and 8% tetragonal phase. Details on this
analysis are given in Appendix C. We also observed that the secondary phases in 15D5WSB were reduced, even after a 300 hour annealing. In particular, 20D5WSB and 25D5WSB maintained cubic fluorite structure throughout the anneal time.

Of the two compositions, 20D5WSB had a small depression in conductivity initially and then maintained its conductivity until a gradual decrease in conductivity began after ~ 100 hour annealing. When we compare the XRD patterns between 20D5WSB and 25D5WSB in Figure 5-6, it was observed that the crystallinity of 20D5WSB was reduced as revealed by peak broadening, although the fcc structure was maintained. This observation provides clues that phase destabilization begins occurring gradually after ~ 100 hour and consequently results in conductivity degradation for 20D5WSB. However, 25D5WSB maintained its conductivity even after 500 hour annealing and we did not observe any indication of phase instability for this composition. Therefore, this result demonstrates that 25D5WSB is the stable composition with respect to phase and structural stability. In this study, other DWSB compositions which have total dopant concentration above 30 mol% were not prepared for long term stability tests because of their lower initial conductivities.

5.3.2.2 Conductivity behavior of 25DSB

Jiang et al. have shown that the aging phenomenon (without phase transformation) is most dominant at ~ 500 °C for cubic stabilized bismuth oxides with RE₂O₃ (RE = Dy, Ho, Er, Tm and Yb) as well as Y₂O₃ [33]. These compositions had an exponential decrease in conductivity for an initial period of time and reached a plateau. Also, the amount of conductivity degradation was different depending on the polarizability of dopant cation [33, 34]. Among the dopants, Dy provided the greatest conductivity stability with time at 500 °C due to its higher polarizability than other dopants [33, 34].
To confirm previous result and identify conductivity degradation mechanism, another 25DSB composition was annealed at 500 °C for 96 hours similar to Jiang et al. [33]. Figure 5-7 shows the comparison of relative conductivity between this work and Jiang et al. [33] for 25DSB with time. This figure shows that 25DSB in this work has the same conductivity trend as that of Jiang et al. That is, 25DSB has initial conductivity degradation for a short period of time before reaching a plateau. This conductivity degradation was analyzed and explained by Jiang et al. as due to the ordering of the oxygen sublattice [12, 26, 33, 52]. However, Figure 5-4 shows that the conductivity of 25DSB gradually decreases after ~ 96 hours with higher degradation rate than before when 25DSB was annealed at this temperature for 300 hours.

Figure 5-8 shows the XRD patterns of two 25DSB compositions which were annealed at 500 °C for different time periods. This figure also includes the JCPDS pattern of cubic phase (Fm $\bar{3}$m) and rhombohedral phase (R $\bar{3}$m) of Bi$_2$O$_3$. The 25DSB which was annealed for ~ 96 hours maintained cubic fluorite structure, while 25DSB had mixed phases of cubic and rhombohedral after 300 hour annealing at 500 °C. It was analyzed that the mixtures were consisted of cubic phase (Fm $\bar{3}$m, Space Group 225) and rhombohedral phase (Bi$_{0.775}$Dy$_{0.225}$O$_{1.5}$, R $\bar{3}$m, Space Group 166). Similarly CrystalDiffract Programs were used for phase analysis. We generated calculated XRD patterns of mixtures of two phases and compared that with observed XRD pattern. It was found that the observed pattern of 25DSB annealed at 500 °C for 300 hours is approximately composed of 60% cubic phase and 40% rhombohedral phase. It is believed that ordering phenomenon results in conductivity degradation initially and the phase change from cubic to rhombohedral is taking effect resulting in a gradual decrease in conductivity for 25DSB composition after ~ 96 hours.
It is interesting to note that the nature of secondary phase is different between doubly doped DWSB and singly doped 25DSB. 25DSB undergoes phase change from cubic to rhombohedral, while DWSB experiences phase instability resulting from the decomposition of (WO₃)-(Bi₂O₃) cubic phase when the total dopant concentration is not sufficient. However, it is shown that W as a second dopant contributes to the improvement of phase stability for long term annealing at 500 °C compared with singly doped 25DSB. Consequently, 25D5WSB or 20D5WSB showed enhanced conductivity stability than 25DSB.

However, further study will be necessary to find another doubly doped bismuth oxide electrolyte composition. Though high dopant concentration provided better conductivity stability for DWSB, it resulted in a lower initial conductivity. In Chapter 6, in addition to DWSB, new doubly doped bismuth oxide based electrolytes will be discussed.
Figure 5-1. X-ray diffraction patterns of 10D5WSB, 15D5WSB, 20D5WSB and 25D5WSB; inset represents magnified version of $2\theta = 27 \sim 29$ °C.
Figure 5-2. Lattice parameter versus (Dy + W) dopant concentration of DWSB compositions measured at room temperature.
Figure 5-3. Arrhenius plot of conductivities for 10D5WSB, 15D5WSB, 20D5WSB and 25D5WSB.
Figure 5-4. (a) Conductivity and (b) relative conductivity for 10D5WSB, 15D5WSB, 20D5WSB, 25D5WSB and 25DSB annealed at 500 oC as a function of time; the initial grain conductivity of 10GDC was added in (a).
Figure 5-5. Typical impedance spectra of (a) 25D5WSB and (b) 10GDC in air at 500 °C.
Figure 5-6. XRD patterns for 10D5WSB, 15D5WSB, 20D5WSB and 25D5WSB annealed at 500 °C for different time periods; parenthesis represents the total annealing hours for each composition.
Figure 5-7. Relative conductivity comparison for 25DSB composition which is taken from between the present work and Jiang et al. [33] at 500 °C as a function of time.
Figure 5-8. XRD patterns of 25DSB composition of as sintered, annealed at 500 °C for 96 hours and 300 hours.
Table 5-1. Conductivity activation energies for 10D5WSB, 15D5WSB, 20D5WSB and 25D5WSB.

<table>
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<th>Composition</th>
<th>$E_a$ (eV) $(\leq 600 \degree C)$</th>
<th>$E_a$ (eV) $(\geq 600 \degree C)$</th>
<th>$\Delta E_a$ (eV)</th>
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<tr>
<td>10D5WSB</td>
<td>1.077±0.007</td>
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<td>15D5WSB</td>
<td>1.128±0.017</td>
<td>0.713±0.047</td>
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<td>20D5WSB</td>
<td>1.127±0.008</td>
<td>0.782±0.053</td>
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<tr>
<td>25D5WSB</td>
<td>1.122±0.007</td>
<td>0.895±0.036</td>
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Table 5-2. Conductivity of various compositions before and after annealing at 500 °C for different hours.

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<th>$\sigma(t=250h)$</th>
<th>$\sigma(t=300h)$</th>
<th>$\sigma(t=500h)$</th>
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<td>10D5WSB</td>
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<td>15D5WSB</td>
<td>0.029 (-1.53)</td>
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</tr>
<tr>
<td>20D5WSB</td>
<td>0.016 (-1.79)</td>
<td>0.015 (-1.82)</td>
<td>0.0092 (-2.04)</td>
<td>--------</td>
<td>--------</td>
</tr>
<tr>
<td>25D5WSB</td>
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<td>0.0070 (-2.15)</td>
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<tr>
<td>25DSB</td>
<td>0.018 (-1.75)</td>
<td>0.014 (-1.84)</td>
<td>0.0075 (-2.12)</td>
<td>0.0048 (-2.32)</td>
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</table>
CHAPTER 6
NEW DOUBLY DOPED BISMUTH OXIDE ELECTROLYTES

6.1 Introduction

In our previous study of DWSB compositions [79], we found that double doping made it possible to reduce total dopant concentration for the stabilization of the cubic phase, resulting in the highest ionic conductivity reported to date. However, DWSB compositions with relatively low total dopant concentration experienced large conductivity degradation at 500 °C [85]. Therefore, it is meaningful to develop new electrolyte systems and examine their conductivity stability.

Iwahara et al. demonstrated that depending on the dopant ionic radius of added oxides, Bi$_2$O$_3$-Ln$_2$O$_3$ (Ln = La – Yb) exhibits the rhombohedral phase at relatively large Ln$^{3+}$ radius and exhibits the fcc phase for comparatively small radius of Ln$^{3+}$ [87]. They also reported that Bi$_2$O$_3$-Ln$_2$O$_3$ could be composed of mixed fcc and rhombohedral phases with a cationic radius of intermediate size, depending on composition [87].

As discussed earlier, oxygen vacancies tend to order in cubic-stabilized bismuth oxide below 600 °C. Our studies of cubic-stabilized bismuth oxide showed that the polarizability and concentration of the dopant cation played an important role in the ordering rate [33]. For lanthanide dopant, it was found that the ordering rate was slowest for Dy and fastest for Yb since Dy$^{3+}$ was the most polarizable and Yb$^{3+}$ the least polarizable of the dopant cations within the fcc-stability window [33]. In our previous work, other dopants with larger ionic radii than Dy were not considered because a pure cubic phase could not be obtained using these dopants. However, the success of the DWSB electrolyte indicates that cubic-phase stabilization is achievable using the double dopant strategy. Therefore, we should consider lanthanides dopants such as Ce, Gd and Tb since they have even greater polarizability than Dy.
The objective of this Chapter 6 is to develop a new optimal double dopant electrolyte system which satisfies both goals of high initial conductivity and long-term stability in the IT range. For this purpose, the total dopant concentration used to stabilize bismuth oxides was limited to below 20 mol%. Depending on the dopant ratio and the relative amount of dopants, phase purity was investigated. Subsequently, the conductivity behavior and stability in IT ranges were examined.

6.2 Experimental Procedure

In this study, three new electrolyte systems were developed. These are

\[(\text{Tb}_4\text{O}_7)_x(\text{WO}_3)_y(\text{Bi}_2\text{O}_3)_{1-x-y} \text{ (xT}_y\text{WSB)}, \quad (\text{Dy}_2\text{O}_3)_x(\text{Gd}_2\text{O}_3)_y(\text{Bi}_2\text{O}_3)_{1-x-y} \text{ (xD}_y\text{GSB)} \quad \text{and} \quad (\text{Dy}_2\text{O}_3)_x(\text{CeO}_2)_y(\text{Bi}_2\text{O}_3)_{1-x-y} \text{ (xD}_y\text{CSB)}\]

Details on electrolyte pellet fabrication and conductivity measurements are shown in Chapter 3 and Chapter 4.

6.3 Results and discussion

6.3.1 (Tb\text{O}_7)\text{-(Bi}_2\text{O}_3) \text{ and (Tb}_4\text{O}_7)-(\text{WO}_3)-(\text{Bi}_2\text{O}_3) \text{ System}

The terbium oxide-bismuth oxide system has been investigated for the phase composition and conductivity [88-90]. However, it has also been noted in the literature that Tb-stabilized bismuth oxide shows mixed conductivity due to the multivalent state of the Tb cation [89]. In this study, we paid more attention to the phase stability and overall time-dependent conductivity trend of this material system. First, terbium doped bismuth oxides ((\text{TbO}_{1.75})_x(\text{BiO}_{1.5})_{1-x}) containing 15-25 mol\% Tb\text{O}_7 were synthesized. Figure 6-1 shows the XRD patterns of 15TSB, 20TSB and 25TSB. Among the three compositions, a single cubic phase was obtained for 25TSB. Mixed phases of cubic (\text{\delta-Bi}_2\text{O}_3) and rhombohedral (\text{Bi}_{0.775}\text{Tb}_{0.225}\text{O}_{1.5}) were observed for 15TSB and 20TSB. Therefore, we found that 25 mol\% Tb was necessary to stabilize cubic structure of TSB system. On the basis of the success of double doping in DWSB system, Bi\text{O}_3-based electrolytes using Tb and W as dopants ((\text{TbO}_{1.75})_x(\text{WO}_3)_y(\text{BiO}_{1.5})_{1-x-y}) were prepared in
order to enhance long term stability as well as reduce total dopant concentrations. Figure 6-2 shows the XRD patterns of 8T4WSB and 10T5WSB. In the case of 8T4WSB, a small amount of secondary phase was found, while 10T5WSB had a pure cubic structure. This result demonstrates that using the double doping strategy, we could reduce the total dopant concentration for cubic-phase stabilization as was the case for the DWSB system.

Conductivity testing was carried out for 25TSB and 10T5WSB. The bulk conductivities of 25TSB and 10T5WSB are plotted as log $\sigma$ vs. 1000/$T$ in Figure 6-3. Conductivity values of these compositions are compared with 8D4WSB and 20ESB in this Arrhenius plot. For the case of 25TSB, its initial conductivity was lower than that of other DWSB and ESB systems. However, the disparity between activation energies was much smaller than that of the other system. For 10T5WSB, even though the conductivity was lower than that of 8D4WSB at high temperature, it had comparable conductivity at low temperature.

Long term stability testing was performed on 25TSB and 10T5WSB at 500 °C for 100 hours in order to determine the effect of Tb as a dopant cation on conductivity and stability. Figure 6-4 compares the time-dependent conductivity behavior for 25TSB and 10T5WSB with 20ESB under isothermal operation of 500 °C.

It is observed that 25TSB was fairly stable for about 80 hours, but experienced a gradual decrease in conductivity. On the other hand, 10T5WSB has higher initial conductivity than 25TSB with less total dopant concentration and the initial conductivity was maintained for about 35 hours before degrading.

Phase stability was examined after long term stability tests at 500 °C. Figure 6-5 and Figure 6-6 show the XRD patterns of 25TSB and 10T5WSB annealed at 500 °C, respectively. 25TSB experienced cubic to rhombohedral phase transformation. This phase change may be the
cause of the observed gradual decrease in conductivity after 80 hours of annealing. For 10T5WSB, the cubic phase was fairly well maintained, but the crystallinity was considerably reduced.

It is complicated to understand the precise conductivity degradation mechanism at 500 °C. Previous results on a few DWSB compositions demonstrate that phase change and ordering can contribute to conductivity degradation together. Therefore, the ordering phenomenon may also affect the conductivity degradation of 25TSB and 10T5WSB.

6.3.2 (Dy2O3)–(Gd2O3)-(Bi2O3) System

Doping with larger-radii lanthanides such as Gd result in the formation of the rhombohedral phase [33]. Nevertheless, since double doping reduces the dopant concentration needed to stabilize cubic Bi2O3 (as demonstrated in the DWSB electrolyte system) [79], we anticipate that Bi2O3 doped with the correct ratio of Dy3+ and Gd3+ should attain the desired fcc structure. Moreover, it is expected that Dy- and Gd-doped Bi2O3 electrolytes (DGSB) will have improved long term stability because Gd has even greater polarizability than Dy.

Verkerk et al. examined Dy2O3 doped Bi2O3 system (DSB) and achieved the fcc structure with 28.5-50 mol% Dy2O3 [38], while Takahashi et al. investigated Gd2O3 doped Bi2O3 system (GSB) and attained the fcc structure with 35-50 mol% Gd2O3 [36]. In our previous study of the DWSB electrolyte system, we achieved cubic phase-stabilization with a lower total dopant concentration compared to the single dopant system, resulting in higher conductivity [79]. Therefore, we expect to achieve the cubic phase through double doping of Dy3+ and Gd3+ at lower total dopant concentrations.

Various (DyO1.5)x(GdO1.5)y(BiO1.5)1-x-y (xDyGSB) compositions were prepared to find optimal dopant ratio and dopant concentration. Figure 6-7(a) shows the XRD patterns of 8D4GSB, 6D6GSB and 4D8GSB which were first calcined at 800 °C for 16 hours. As Gd
concentration increases, the amount of rhombohedral phases increases. In particular, 8D4GSB has almost single cubic phase, but the rhombohedral phase is dominant for 4D8GSB. An additional calcination was carried out under the same condition to ensure the phase of each composition. We found that after the second calcination, 8D4GSB has a pure cubic phase and the other compositions tend to contain more cubic phase as compared with the single calcination powders. This may be due to the slightly larger ionic radius of Gd$^{3+}$ than Dy$^{3+}$. As was the case for DWSB, it appears that the content of Dy$_2$O$_3$ should be larger than that of Gd$_2$O$_3$ in order to achieve cubic-phase stabilization.

Three compositions with 15 mol% total dopant concentrations were also prepared. Figure 6-8 shows the XRD patterns of 10D5GSB, 7.5D7.5GSB and 5D10GSB. The rhombohedral phase is more dominant than the cubic phase for all three compositions when a single calcinations step is carried out. After the second calcination, 10D5GSB is nearly cubic phase pure, but the rhombohedral phase was still dominant for 7.5D7.5GSB and 5D10GSB.

Based on phase observations from other DGSB compositions, 12D6GSB was lastly prepared. As shown in Figure 6-9, mixed cubic and rhombohedral phases were observed even after a second calcination. For the Dy- and Gd-doped Bi$_2$O$_3$ electrolyte system (DGSB), there is a tendency to form the rhombohedral phase as Gd concentration or total dopant concentration increases. In this work, various DGSB compositions were prepared to find the correct ratio and net concentration of Dy$^{3+}$ and Gd$^{3+}$ needed to obtain the fcc phase. However, it seems that DGSB system has narrow fcc-stability window based on the observed XRD results. Here, 8D4GSB, 10D5GSB and 12D6GSB were selected to examine conductivity and long term stability.
Figure 6-10 shows the Arrhenius behavior of the three DGSB compositions. 20ESB was added for comparison. Particularly, 12D6GSB showed a discontinuity at around 550 °C when conductivity was measured from high temperature to low temperature. It is thought that this discontinuity corresponds to the phase transition from the fcc phase to the rhombohedral phase. For this composition, it was not possible to achieve a pure fcc phase even after the second calcination. This indicates that the fcc phase is not stable and easily transforms to the rhombohedral phase on cooling. We again measured conductivity from low to high temperature and obtained an almost straight line without recovering to the original conductivity at high temperature.

The long term tests were performed for these 8D4GSB, 10D5GSB and 12D6GSB compositions at 500 °C for about 100 hours. Figure 6-11 shows the conductivity behavior of these compositions as well as 20ESB at 500 °C as a function of time. 8D4GSB and 10D5GSB underwent large conductivity degradation initially without delay and reached a plateau. This conductivity trend is very similar to that of 20ESB. On the other hand, 12D6GSB showed low initial conductivity, but almost maintained this initial conductivity for 100 hours. It is believed that the phase change from cubic to rhombohedral is almost complete during conductivity measurements. Afterwards, no conductivity degradation was observed during long term stability tests at 500 °C.

Phase stability was identified by means of X-ray diffraction after long term annealing at 500 °C. Figure 6-12 shows XRD patterns of 8D4GSB and 10D5GSB before and after annealing. Even though both compositions experienced similar conductivity degradation trends with time, XRD results were totally different. 8D4GSB maintained the cubic phase, while 10D5GSB underwent a complete transformation from cubic to rhombohedral after 100 hour annealing at
500 °C. This result indicates that ordering of oxygen sublattice is involved in the conductivity degradation of 8D4GSB [14]. However, 10D5GSB experienced an almost complete phase change from cubic to rhombohedral during only 24 hour annealing at 500 °C as shown in Figure 6-12(b). This XRD result demonstrates rhombohedral phase is more stable than cubic for 10D5GSB even though a pure cubic phase was achievable with two calcinations steps. It is also noteworthy that after the rhombohedral phase is formed, no conductivity degradation was observed for 10D5GSB. Cubic-stabilized bismuth oxides are known to undergo occupancy ordering and positional ordering which result in conductivity degradation at 500 °C [26]. Therefore, this observation suggests that rhombohedral phase may not experience ordering phenomenon. However, it is still unclear how dopant ionic radius and dopant concentration affect ordering of the oxygen sublattice or phase change.

6.3.3 (Dy2O3)-(CeO2)-(Bi2O3) System

Fung et al. have reported that phase change from cubic to rhombohedral can be suppressed by the addition of a small amount of ZrO2 or ThO2 to stabilize Y2O3-Bi2O3 (YSB) electrolyte system [47, 49]. With additions of less than 5 mol% of these additives, the cubic phase was retained at 650 °C for over 1000 hours. In addition, Huang et al. reported that small additions of CeO2 suppress aging of stabilized Y2O3-Bi2O3 oxides [91]. In this study, 2 mol% of CeO2 was added to Dy2O3-Bi2O3 oxides to enhance phase stability. (Dy2O3)0.10(CeO2)0.02(Bi2O3)0.88 (10D2CSB) was prepared through solid state synthesis. Long term conductivity results were examined at 500 °C and 600 °C for this composition.

First, (CeO2)x-(Bi2O3)1-x (xCSB) electrolyte system were prepared. Four compositions having 15 mol%, 20mol%, 30 mol% and 40 mol% CeO2 as a dopant were fabricated and are referred to as 15CSB, 20CSB, 30CSB and 40CSB. Figure 6-13 shows the XRD patterns of calcined 15CSB, 20CSB, 30CSB and 40CSB. All compositions had mixed phases of β-Bi2O3
and CeO$_2$. No change was observed even with two calcinations steps. Therefore, it is believed that the mixed phases are very stable and the sole use of a Ce dopant is unable to stabilize the cubic structure.

Based on the success with DWSB compositions, 10D2CSB with 2 mol% CeO$_2$ was prepared and examined. It was found that 10D2CSB had a pure cubic phase. To examine the time-dependent conductivity behavior at 500 °C and 600 °C, samples with this composition were annealed at these temperatures for various periods of time, respectively. Figure 6-14 shows that 10D2CSB experienced an initial conductivity drop and reaches to a plateau. This trend is similar to that of 20ESB. While the conductivity of 10D2CSB was fairly stable at 600 °C for about 200 hours with the highest initial conductivity, but it did subsequently experience a gradual decay as shown in Figure 6-15.

After long term stability tests, phases of 10D2CSB samples annealed at 500 °C and 600 °C were examined by XRD as shown in Figure 6-16. Surprisingly the cubic phase was maintained for 10D2CSB which had been annealed at 500 °C. Therefore, again it can be deduced that the ordered structure of the oxygen sublattice resulted in an initial conductivity drop and the addition of CeO$_2$ was not effective at mitigating the ordering phenomenon at 500 °C.

In addition, XRD result of 10D2CSB annealed at 600 °C demonstrates that this composition underwent a phase change during annealing for 500 hours. From Figure 6-15 and Figure 6-16, it was believed that the use of CeO$_2$ as a dopant was an effective way to suppress phase transformation at 600 °C, but the conductivity degradation was accompanied by a phase change from cubic to rhombohedral (Bi$_{0.775}$Dy$_{0.225}$O$_{1.5}$) at the end. A slightly higher concentration of CeO$_2$ (> 2 mol%) is expected to suppress the phase transformation at 600 °C, ultimately.
Figure 6-1. X-ray diffraction patterns of (Tb₄O₇)x(Bi₂O₃)₁₋ₓ, where x = 0.15, 0.20 and 0.25.
Figure 6-2. X-ray diffraction patterns of 8T4WSB and 10T5WSB.
Figure 6-3. Arrhenius plot of conductivities for 10T5WSB, 25TSB, 8D4WSB and 20ESB.
Figure 6-4. Isothermal comparison of time-dependent conductivity for 10T5WSB and 25TSB annealed at 500 °C; 20ESB data is added for comparison.
Figure 6-5. XRD patterns of 25TSB as-sintered and annealed at 500 °C for 120 hours.
Figure 6-6. XRD patterns of 10T5WSB as sintered and annealed at 500 °C for 100 hours.
Figure 6-7. XRD patterns of 8D4GSB, 6D6GSB and 4D8GSB (a) first calcined (b) second calcined at 800 °C for 16 hours.
Figure 6-8. XRD patterns of 10D5GSB, 7.5D7.5GSB and 5D10GSB after (a) first calcination and (b) second calcination at 800 °C for 16 hours.
Figure 6-9. XRD patterns of 12D6GSB after the first and second calcinations steps at 800 °C for 16 hours.
Figure 6-10. Arrhenius plot of conductivity for 8D4GSB, 10D5GSB, 12D6GSB and 20ESB; the conductivities were measured in both direction of temperature measurements, HL (High to Low) and LH (Low to High) for 12D6GSB.
Figure 6-11. Conductivity vs. time for 8D4GSB, 10D5GSB and 12D6GSB annealed at 500 °C; 20ESB is shown for comparison.
Figure 6-12. XRD patterns of (a) 8D4GSB and (b) 10D5GSB as-sintered and annealed at 500 °C for 100 hours.
Figure 6-13. XRD patterns of calcined $(\text{CeO}_2)_x(\text{Bi}_2\text{O}_3)_{1-x}$ ($x=0.15, 0.20, 0.30$ and $0.40$).
Figure 6-14. Conductivity vs. time for 10D2CSB at 500 °C; 20ESB was added for comparison.
Figure 6-15. Conductivity vs. time for 10D2CSB, 8D4WSB and 10D5WSB at 600 °C; inset represents the conductivity behavior of these compositions for 100 hours.
Figure 6-16. XRD patterns of 10D2CSB as sintered, annealed at 500 °C for 100 hours and annealed at 600 °C for 500 hours.
CHAPTER 7
HIGH PERFORMANCE LSM-ESB AND LSM-DWSB COMPOSITE CATHODES

7.1 Introduction

It has been recognized that La$_{1-x}$Sr$_x$MnO$_{3-\delta}$ (LSM) is the most promising cathode material for high-temperature solid oxide fuel cells (SOFCs) due to its good thermal and chemical stability [92, 93]. Currently, considerable efforts have been devoted to reducing cell operating temperature because lower temperature operation allows for a wider choice of interconnect and other balance-of-plant materials and also results in reduced problems with sealing and thermal degradation [10, 94]. However, LSM is not suitable for intermediate temperature (IT) SOFCs because of its negligible ionic conductivity as well as its high activation energy for oxygen dissociation. To improve cathode performance, an ionic conducting phase such as gadolinia-doped ceria (GDC) and yttria-stabilized zirconia (YSZ) was added into LSM to form a composite cathode, and resulted in a significant decrease in the interfacial resistance compared with pure LSM [95-98]. It is well understood that cathode properties can be enhanced using ionic conductors with high conductivity by increasing triple phase boundary (TPB) lengths [98]. Murray et al. showed that the area specific resistance (ASR) of LSM-GDC composite cathodes was two to three times lower than that of LSM-YSZ composite cathodes on YSZ electrolytes [96].

Recently, bismuth based oxides have been examined as a promising material for electrolyte and cathode in IT-SOFCs because of their high oxygen ionic conductivity [20, 99]. It has also been shown that bismuth oxides improve catalytic effects on the oxygen dissociation reaction which is often considered to be the rate-limiting step in the oxygen reduction reaction of SOFC cathodes [100-103]. Therefore, many studies were carried out using stabilized bismuth oxides as
the ionic conducting phase to further reduce interfacial polarization resistance of composite cathodes [92, 93, 99, 104-106].

In this study, two LSM-containing composite cathodes: LSM-ESB and LSM-DWSB were designed to investigate cathode performance and chemical compatibility. The composition details of each composite cathode are (La$_{0.80}$Sr$_{0.20}$)MnO$_{3-\delta}$-$(\text{Er}_2\text{O}_3)_{0.20}(\text{Bi}_2\text{O}_3)_{0.80}$ (LSM-ESB) and (La$_{0.80}$Sr$_{0.20}$)MnO$_{3-\delta}$-$(\text{Dy}_2\text{O}_3)_{0.08}(\text{WO}_3)_{0.04}(\text{Bi}_2\text{O}_3)_{0.88}$ (LSM-DWSB). LSM-ESB cathodes were used on ESB and Gd$_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) electrolytes, respectively, to identify the effect of electrolytes on cathode polarization.

7.2 Experimental Procedure

7.2.1 Electrode Preparation

Conventional LSM powder with a surface area of 5.6 m$^2$/g was purchased from Fuel Cell Materials. To obtain LSM-ESB (or DWSB) electrode slurries, LSM and ESB (or DWSB) powders of the same weight ratio were mixed with alpha terpineol (Alfa Aesar), Di-n-butyl phthalate (DBP) and ethanol. 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 hour, another coating of electrode slurry was applied to the electrolyte substrates. The doubly-coated cells were then sintered at 800 °C for 2 hours 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.

7.2.2 Electrolyte Preparation

In this work, three different electrolyte substrates - 20ESB, 8D4WSB and 10GDC - were fabricated in order to compare the effect of the electrolyte on cathode performance. To get dense Gd$_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (10GDC) pellets, 10GDC (Anan Kasei Co. Ltd., Japan) was used. Details on the fabrication of bismuth oxide-based and 10GDC electrolyte pellets were described in Chapter 3.
7.2.3 Characterizations

Electrochemical performance of the electrodes was carried out through electrochemical impedance spectroscopy (EIS) using a Solartron 1260. The impedance of a symmetric cell was measured with 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 °C to 750 °C in 50 °C increments.

XRD patterns (XRD, Philips APD 3720) were obtained using CuKα radiation at room temperature between 20° and 80° (2θ). Electrode microstructures were analyzed by scanning electron microscopy (SEM). Secondary and backscattered microstructural images were observed through a JEOL JSM 6400 SEM.

7.3 Results and Discussions

7.3.1 LSM-20ESB Composite Cathode

Figure 7-1 shows XRD patterns of LSM and ESB powder mixtures before and after heat-treatment at 900 °C for 50 hours. LSM and ESB solid solutions are consisted of perovskite and cubic structures. No additional phases were observed after heat treatment, suggesting these materials are chemically compatible.

It is assumed that better connectivity of the ionic conduction phase and electronic conduction phase effectively extends the triple phase boundary (TPB), resulting in enhanced electrochemical activity of the composite cathode [92]. In fact, studies have shown that the optimal composition of composite cathodes with ESB as an ionic conduction phase was achieved with about 50wt.% ESB content [92, 99]. Therefore, in this study, LSM-ESB mixtures were prepared by mixing LSM and ESB powders in equal amounts (50wt.%).
Figure 7-2 shows impedance spectra measured in air at 700 °C for the three different cells. Electrolyte ASR has been subtracted from the real component of each data point for easy comparison of cathode ASR. In this way, the low-frequency intercept in real-axis corresponds to the cathode polarization resistance.

Table 7-1 shows the activation energy and area specific resistance (ASR) of these cells. At 700 °C, the ASR of Cell 1 was 0.26 Ω cm², while that of Cell 3 was 0.08 Ω cm². So, the polarization of LSM-ESB is about four times lower than that of pure LSM with the same ESB electrolyte. This result demonstrates that the addition of ESB phase increases the TPB and consequently leads to improved cathode performance.

It is also important to understand the effect of the electrolyte substrate on the interfacial resistance. Figure 7-3 shows the ASR for three different cells as a function of temperature. Murray et al. reported that ASR of pure LSM is 7.82 Ω cm² and 2.67 Ω cm² on YSZ and GDC electrolyte at 700 °C, respectively [96]. In this study, the ASR of pure LSM on ESB electrolyte was about 30 times lower than that of pure LSM on YSZ electrolyte. This result clearly shows that pure LSM has better cathode performance on ESB electrolyte than on either YSZ or GDC electrolytes. This may be attributed to the fact that bismuth oxide-based electrolytes enhance the oxygen dissociation and surface oxygen exchange rate [99, 102, 103, 107].

In this study, the ASR of LSM-ESB composite cathode was obtained on two different electrolytes (ESB and GDC). The same cathode exhibited about 70% smaller polarization resistance on ESB than on GDC.

The stability of cell 3 (LSM-ESB cathode) was also examined. Figure 7-4 shows that LSM-ESB composite cathode maintained the same performance for 100 hours in the range of
0.08 ± 0.001 Ω cm², while that of Ag-ESB increased by more than 70% after 100 hours at 650 °C [106].

7.3.2 LSM-8D4WSB Composite Cathode

In previous Chapters, we found that 8D4WSB has higher conductivity than single doped 20ESB. Therefore, it is expected that even better cathode performance can be achieved by replacing 20ESB with 8D4WSB in composite cathode. To check compatibility between LSM and 8D4WSB, heat treatment was carried out. Figure 7-5 shows XRD patterns of LSM and 8D4WSB powder mixtures before and after heat-treatment at 900 °C for 50 hours. As was the case for LSM-ESB composite cathodes, no additional peaks were observed except for a small peak at ~ 28.3° (2θ).

In the same way, LSM-8D4WSB (LSM-DWSB) mixtures were prepared by mixing equal amounts of LSM and 8D4WSB powders (50wt.%). Figure 7-6 shows the ASR of LSM-DWSB on ESB (Cell 4) and LSM-DWSB on DWSB (Cell 5) along with previous results for Cell 1 and Cell 3 for comparison. Cell 5 had almost same cathode ASR as Cell 3 even though electrolyte ASR of Cell 5 was lower than that of Cell 3 due to the higher conductivity of 8D4WSB compared with 20ESB. In addition, the LSM-DWSB composite cathode had higher ASR than LSM-ESB composite cathode on the same ESB electrolyte substrate. Details on ASR of these cells at each temperature are shown in Table 7-1. This may be attributed to a lattice mismatch between 8D4WSB and 20ESB in cathode-electrolyte interface. 8D4WSB has higher ionic conductivity than 20ESB, but further study will be necessary to use this composition for the composite cathode material to achieve better performance than LSM-ESB.

Figure 7-7 shows cross-sectional backscattered images of two different cells. Both samples show good adhesions between composite cathode and electrolyte. LSM and ESB also appear to be uniformly dispersed. Microstructural optimization based on particle size and relative
composition of two constituents in composite cathodes is expected to further enhance the
cathode performance.
Figure 7-1. XRD patterns of (a) Pure LSM (b) 20ESB (c) a mixture of LSM and ESB (d) a mixture of LSM and ESB, after firing at 900 °C for 50 hours
Figure 7-2. Impedance spectra of Pure LSM on ESB (Cell 1), LSM-ESB on GDC (Cell 2) and LSM-ESB on ESB (Cell 3) measured at 700 °C in air.
Figure 7-3. Arrhenius plot of ASR vs. temperature for Pure LSM on ESB (Cell 1), LSM-ESB on GDC (Cell 2), LSM-ESB on ESB (Cell 3) and Jiang et al. [93].
Figure 7-4. ASR vs. time for LSM-ESB on ESB (Cell 3) at 700 °C.
Figure 7-5. XRD patterns of (a) Pure LSM (b) 8D4WSB (c) a mixture of LSM and 8D4WSB (d) a mixture of LSM and 8D4WSB, after firing at 900 °C for 50 hours.
Figure 7-6. Arrhenius plot of ASR vs. temperature for LSM-DWSB on ESB (Cell 4) and LSM-DWSB on DWSB (Cell 5) including previous Cell 1 and Cell 3.
Figure 7-7. Cross-sectional micrographs of (a) LSM-ESB cathode on ESB (Cell 3) (b) LSM-ESB cathode on GDC (Cell 2).
Table 7-1. Activation energy and ASR of three different samples

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Composition</th>
<th>Ea (KJ/mol)</th>
<th>ASR (Ω cm²) at 700 °C</th>
<th>ASR (Ω cm²) at 600 °C</th>
<th>ASR (Ω cm²) at 500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>Pure LSM on ESB</td>
<td>130</td>
<td>0.26</td>
<td>1.63</td>
<td>16.4</td>
</tr>
<tr>
<td>Cell 2</td>
<td>LSM-ESB on GDC</td>
<td>120</td>
<td>0.20</td>
<td>1.13</td>
<td>9.1</td>
</tr>
<tr>
<td>Cell 3</td>
<td>LSM-ESB on ESB</td>
<td>120</td>
<td>0.08</td>
<td>0.46</td>
<td>4.0</td>
</tr>
<tr>
<td>Cell 4</td>
<td>LSM-DWSB on ESB</td>
<td>115</td>
<td>0.10</td>
<td>0.51</td>
<td>4.2</td>
</tr>
<tr>
<td>Cell 5</td>
<td>LSM-DWSB on DWSB</td>
<td>120</td>
<td>0.08</td>
<td>0.45</td>
<td>3.9</td>
</tr>
</tbody>
</table>
Dysprosium- and tungsten-stabilized bismuth oxide (DWSB) was developed and its structure and conductivity were examined. Through double doping, the total dopant concentration required to stabilize the cubic structure was reduced down to 12 mol% for this DWSB electrolyte system. We found that the 8D4WSB composition had the highest conductivity, achieving $\sigma = 0.57$ and $0.098 \text{ S/cm}$ at 700 and 500 $^\circ\text{C}$, respectively. The conductivity and lattice parameter of DWSB compositions increased linearly as the total dopant concentration decreased with fixed 2:1 dopant ratio within the fcc phase-stability window. In addition, the disparity in conductivity activation energies above and below the order-disorder transition decreased as the total dopant concentration increased.

Time-dependent conductivity behavior of these DWSB compositions was investigated between 300 $^\circ\text{C}$ and 700 $^\circ\text{C}$ as a function of anneal temperature. The effect of dopant concentration on long term conductivity was also examined. All DWSB compositions were stable and maintained their initial conductivity at 700 $^\circ\text{C}$, but displayed conductivity degradation between 400 $^\circ\text{C}$ and 650 $^\circ\text{C}$. Phase transformation and ordering of the oxygen sublattice were identified as the source of conductivity degradation. 8D4WSB, the highest conductivity composition, displayed phase instability between 500 and 600 $^\circ\text{C}$ and experienced the fastest conductivity degradation rate at 500 $^\circ\text{C}$. The degradation rate for 8D4WSB was markedly lower below 500 $^\circ\text{C}$ because the kinetics of ordering and/or phase degradation decreased with temperature.

In order to enhance long term stability, new DWSB compositions were fabricated. Of these DWSB compositions, 25D5WSB maintained the highest conductivity of 0.0068 S/cm with phase and structural stability while annealing at 500 $^\circ\text{C}$ for 500 hours. With respect to total
conductivity, 25D5WSB had much higher total conductivity than 10GDC even after long term annealing due to its negligible grain boundary resistance. On the other hand, singly doped 25DSB experienced phase change from cubic to rhombohedral during long periods of annealing at 500 °C, however, the present cubic phase of 25D5WSB had only negligible conductivity degradation with the true cubic phase stabilization at this temperature.

Further, new doubly doped bismuth oxides-based electrolytes were developed to enhance long term stability while maintaining the high initial conductivity at 500 ~ 600 °C. 25D5WSB had excellent long term stability for 500 hours, but had relatively low conductivity due to its higher total dopant concentrations. (Tb₄O₇)-(WO₃)-(Bi₂O₃), (Dy₂O₃)-(Gd₂O₃)-(Bi₂O₃) and (Dy₂O₃)-(CeO₂)-(Bi₂O₃) electrolyte systems were prepared. Among those systems, (Dy₂O₃)₀.₁₀-(CeO₂)₀.₀₂-(Bi₂O₃)₀.₈₈ was a promising composition which satisfies both goals of conductivity and stability at 600 °C. This composition was very stable for first ~ 200 hours, but experienced a gradual decrease in conductivity due to a phase transformation. It is expected that long-term stability can be enhanced with slightly higher concentrations of CeO₂ without compromising its initial conductivity.

Lastly, LSM-ESB and LSM-DWSB composite cathodes were developed. These composite cathodes had significantly better performance than pure LSM on ESB electrolytes. It was also found that LSM-ESB had better performance on ESB than on GDC due to the high catalytic effect of bismuth oxide-based electrolytes on oxygen dissociation.
APPENDIX A
CONDUCTIVITY COMPARISON

The conductivity of 8D4WSB was observed to be higher in this study than in our previous work [13]. To find out why, the conductivities of several 8D4WSB compositions of different geometries were measured with different current collectors. Each nulling file was made depending on the current collector used. Table A-1 shows sample dimension and the current collector used for 8D4WSB and 12D6WSB. Figure A-1(a) shows that all 8D4WSB compositions had similar conductivity within experimental error over the entire temperature range, but had a slightly higher conductivity than our previous work for 8D4WSB [13]. We suspect that artifacts caused by inductive response of the test leads and the equipment was not fully compensated in our previous results [13]. However, the fact that our currently measured ESB conductivity is the same as the literature gives us confidence in our current results. In addition, the fact that the linear fit of Figure 3-7(a) corresponds to pure δ-Bi₂O₃ at 700 °C also validates our current results. As shown in Figure A-1(b), the conductivity value is also almost the same for 12D6WSB composition regardless of sample dimension even though there is little deviation at high temperature due to increased fractional error in the measurement for small resistance values.
Figure A-1. Reproducibility data for (a) 8D4WSB (this work and previous work [13]) and 20ESB (b) 12D6WSB.
Table A-1. Sample dimension and the current collector used for 8D4WSB and 12D6WSB to confirm reproducibility.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sample dimension (mm)</th>
<th>Current collector</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(Thickness × Diameter)</td>
<td></td>
</tr>
<tr>
<td>8D4WSB-1</td>
<td>2.87 × 7.34</td>
<td>Ag wire + Ag mesh</td>
</tr>
<tr>
<td>8D4WSB-2</td>
<td>2.98 × 7.19</td>
<td>Au wire</td>
</tr>
<tr>
<td>8D4WSB-3</td>
<td>2.96 × 7.19</td>
<td>Pt wire + Ag mesh</td>
</tr>
<tr>
<td>8D4WSB-4</td>
<td>7.19 × 7.25</td>
<td>Pt wire + Ag mesh</td>
</tr>
<tr>
<td>12D6WSB-1</td>
<td>3.04 × 7.12</td>
<td>Ag wire + Ag mesh</td>
</tr>
<tr>
<td>12D6WSB-2</td>
<td>6.61 × 7.14</td>
<td>Pt wire + Ag mesh</td>
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</tbody>
</table>
APPENDIX B
LATTICE PARAMETER CALCULATION

X-ray diffraction patterns were obtained by XRD Philips APD 3720 in Major Analytical Instrumentation Center. Extrapolation method using Nelson-Riley function was carried out to estimate the lattice parameter of cubic-stabilized bismuth oxides [108]. For a given XRD pattern, lattice parameter \( a \) was determined for each individual peak using the following relationship for cubic structure.

\[
a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2}
\]  

(B-1)

The measured lattice parameters were then plotted as a function of Nelson-Riley function.

\[
\frac{\Delta d}{d} = \frac{\Delta a}{a} = K \left( \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)
\]  

(B-2)

This equation holds quite accurately down to very low values of \( \theta \) and not just at high angles. The bracketed terms are called the Nelson-Riley function. The fitted line is in the form of the following equation,

\[
a = a_0 + a_0 KN \quad \left( N = \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right)
\]  

(B-3)

where \( a_0 \) is the true estimation of the lattice parameter and \( a \) is the apparent lattice parameter calculated from each peak position. Figure C-1 shows the apparent measured lattice parameters as a function of Nelson-Riley function for \((\text{Dy}_2\text{O}_3)_{0.10}(\text{WO}_3)_{0.05}(\text{Bi}_2\text{O}_3)_{0.85}\) (10D5WSB) taken at room temperature. From the extrapolation, the true lattice parameter of this composition is 5.553 Å.

This extrapolation method was also applied to high temperature XRD patterns. Figure B-2 shows the XRD patterns of \((\text{Tb}_4\text{O}_7)_{0.25}(\text{Bi}_2\text{O}_3)_{0.75}\) (25TSB) which was taken at 25 °C, 300 °C, 500 °C and 600 °C. Using Nelson-Riley function, Figure B-3 shows the apparent lattice parameter...
versus Nelson-Riley function plots for 25TSB at different temperatures. The increase in intercept is observed with the increase in temperature. This indicates the thermal lattice expansion of cubic-stabilized bismuth oxides.
Figure B-1. Calculated lattice parameter versus Nelson-Riley function for 10D5WSB taken at room temperature.
Figure B-2. XRD patterns of 25TSB measured at 25 °C, 300 °C, 500 °C and 600 °C.
Figure B-3. Calculated lattice parameter versus Nelson-Riley function for 25TSB at different temperatures.
In order to obtain phase identification and the relative amount of each phase in mixtures, CrystalMaker & CrystalDiffract Programs were used. CrystalMaker enables us to build real crystal structure with structure parameters. CrystalDiffract program can generate the diffraction patterns using the structure parameters which include the types and positions of atoms in a unit cell of a crystal. CrystalDiffract also allows us to work with observed and calculated data. By comparing an observed diffraction pattern with a number of calculated patterns, we can identify an unknown substance and further know the relative amount of each phase in case of mixtures.

For example, it was found that 25DSB had the mixtures of two phases after it was annealed at 500 °C for 300 hours. It was analyzed that the mixtures were consisted of cubic phase (Fm$\bar{3}$m, Space Group 225) and rhombohedral phase (Bi$_{0.775}$Dy$_{0.225}$O$_{1.5}$, R$\bar{3}$m, Space Group 166). To obtain the calculated diffraction pattern of two phases, structural parameters of cubic phase and rhombohedral phase were obtained from Yashima et al. [27] and Drache et al. [109], respectively. In case of cubic phase, lattice parameter at room temperature was chosen from Verkerk et al. [38]. The details of these structural parameters are given at Table C-1 and Table C-2.

Using CrystalDiffract program, we can generate calculated XRD patterns of mixtures of two phases and compare this pattern with observed XRD pattern. Figure C-1 shows the calculated XRD pattern of mixtures (Blue) and the observed XRD pattern (Red). By manipulating the relative amount of each phase of calculated mixtures, it was found that the observed pattern of 25DSB is approximately composed of 60% cubic phase and 40% rhombohedral phase.

As was the case for 25DSB, this analysis was performed for aged DWSB compositions. Figure C-2 shows the observed XRD pattern of 10D5WSB which was annealed at 500 °C for 100
hours (Red). This pattern is compared with the calculated mixtures of cubic, tetragonal (Bi$_{14}$WO$_{24}$) [80] and orthorhombic (Bi$_2$WO$_6$) [81]. By manipulating the relative amount of each phase of calculated mixtures, it was analyzed that the observed pattern of 10D5WSB is approximately composed of 61% cubic phase, 31% orthorhombic phase and 8% tetragonal phase.
Figure C-1. XRD patterns of observed 25DSB annealed at 500 °C for 300 hours and calculated mixtures of cubic and rhombohedral phases.
Figure C-2. XRD patterns of observed 10D5WSB annealed at 500 °C for 100 hours and calculated mixtures of cubic, orthorhombic and tetragonal phases.
Table C-1. Structure parameters of cubic Bi$_2$O$_3$ [27, 38].

<table>
<thead>
<tr>
<th>Lattice Parameter</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>α</th>
<th>β</th>
<th>γ</th>
</tr>
</thead>
<tbody>
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<td>5.49</td>
<td>5.49</td>
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Atoms in the Asymmetric Unit

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<th>y</th>
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<tbody>
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</tbody>
</table>
Table C-2. Structure parameters of Bi$_{0.775}$Dy$_{0.225}$O$_{1.5}$ (Rhombohedral) [109].

<table>
<thead>
<tr>
<th>Lattice Parameter</th>
<th>a</th>
<th>b</th>
<th>c</th>
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Atoms in the Asymmetric Unit

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LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Doh Won Jung was born in Seoul, South Korea. He earned a bachelor’s degree from the Department of Materials Science and Engineering, Korea University, Seoul, South Korea, in February 2001. He entered the graduate program in the Department of Materials Science and Engineering at Korea University and experienced the molten carbonate fuel cell under the guidance of Professor Dokyol Lee. He finished his master’s degree in February 2003. In August 2004, he enrolled in the Department of Materials Science and Engineering, University of Florida, to pursue Ph.D under the guidance of Professor Eric D. Wachsman.