SOLID STATE OXYGEN KINETICS IN Er$_2$O$_3$ STABILIZED Bi$_2$O$_3$

E. D. Wachsman, N. Jiang, D. M. Mason and D. A. Stevenson
Electrocatalysis Laboratory
Departments of Chemical Engineering
and Materials Science & Engineering
Stanford University
Stanford, CA 94305-5025

ABSTRACT

The conductivity and mechanism of oxygen-ion transport in 20 mole % erbia-stabilized bismuth oxide (ESB) was investigated using AC impedance spectroscopy and an equivalent circuit for oxygen-ion transport is described. A change in the slope of conductivity vs. reciprocal temperature, at ~600°C, indicating two different conductivity activation processes, is attributed to an order-disorder transition of the oxygen sublattice. At high temperatures, the oxygen sublattice is disordered resulting in a high concentration of mobile oxygen vacancies and a low apparent activation energy. At low temperatures the oxygen sublattice orders. The higher activation energy in this temperature regime is ascribed to the extra energy required to free a vacancy from the ordered state. A reversible aging phenomenon in the conductivity of ESB was observed. When ESB is annealed in the lower temperature region, the conductivity decays with time. Heating above the transition point completely reverses this process and returns the conductivity to its initial value. Differential thermal analysis and x-ray diffraction were used to investigate this conductivity aging phenomenon which is ascribed to ordering of the oxygen sublattice.

1. INTRODUCTION

The anion deficient fluorite structure is common to most of the solid oxide electrolyte systems. It is the structure of the high temperature phase responsible for the observed high conductivity of these electrolytes. The fluorite structure consists of an FCC cation sublattice with oxygen ions in the tetrahedral positions. Zirconia electrolytes are stabilized in this structure by the addition of aliovalent cations and have anion vacancy concentrations proportional to the dopant’s concentration and relative charge (typically ~5%), which develops reasonable ionic conductivities at high temperatures (~1 ohm$^{-1}$ cm$^{-1}$ @ 1000°C). Stabilized-Bi$_2$O$_3$ electrolytes have an intrinsic vacancy concentration of 25% of the anion sites, and are receiving considerable interest due to their order of magnitude greater ionic conductivity at comparable temperatures. This greater conductivity of stabilized-Bi$_2$O$_3$ electrolytes opens the window for lower operating temperatures, thus significantly increasing the number of applications for solid-oxide electrolytes. Among the stabilized-Bi$_2$O$_3$ electrolytes, Bi$_2$O$_3$ stabilized
with 20 mole % Er₂O₃ (ESB) has the greatest conductivity and is the electrolyte studied in this investigation.

The Arrhenius behavior of the conductivity of several stabilized-Bi₂O₃ electrolytes, including ESB, exhibit an interesting change of slope or "knee" at about 600°C. This change in activation energy is quite different from that observed in typical solid-state conductivity/diffusion processes in that the activation energy is lower at high temperature than at low temperature. This change in activation energy is due to an order-disorder transition of the oxygen sublattice. The question persists as to the nature of the ordered and disordered structures in stabilized-Bi₂O₃ electrolytes and how these structures relate to the ionic conductivity observed in these materials. We address these issues in our present study.

2. EXPERIMENTAL

Polycrystalline erbia-stabilized bismuth oxide (ESB) disks, 2.5 cm in diameter and 0.15 cm thick, of nominal composition \((\text{Bi}_2\text{O}_3)_{0.8} (\text{Er}_2\text{O}_3)_{0.2}\) were obtained from Trans-Tech, Inc. Electron microprobe analysis showed the actual composition to be 81.7 mole % bismuth oxide and 18.3 mole % erbia. Porous Au electrodes were obtained by painting an Engelhard paste onto the surface of the disks and annealing in air at 800°C for 5 hours to drive off the binders. This process was repeated two to three times for each disk in order to obtain a surface resistance of less than 0.2 ohm.

The samples were placed in a quartz sample holder, with spring loaded Au wires for electrical contact and a K-type thermocouple for temperature measurement, inside a quartz tube. The quartz tube was wrapped with a 318 stainless steel wire mesh and grounded in order to minimize any stray inductance and placed inside a Lindberg furnace.

AC impedance measurements were obtained with an HP 4284A Precision LCR Meter over the frequency range 20 Hz to 1 MHz. Compensation for both series and parallel components of the test lead resistance, capacitance and inductance over the entire frequency range was performed using the instruments internal compensation circuitry. Measurements were taken over the temperature range 200 to 750°C in air.

The aging phenomenon was investigated using the above conductivity technique as well as with x-ray and thermal analysis. For the structural and thermal analysis, a disk was broken into several pieces and annealed in air at 500°C in a box furnace. The pieces were aged up to 500 hours and then rapidly quenched to room temperature. Powder diffraction patterns were obtained with Cu Kα radiation over the 2θ range 10 to 70°. Differential thermal analysis data was obtained with a Dupont 2100 Thermal Analysis System using a 1600 DTA cell in air.
3. **AC IMPEDANCE**

Complex impedance plots for ESB and a variety of other lanthanide stabilized bismuth oxides have been published with varying results. Verkerk and Burggraaf (1) investigated the oxygen transfer on ESB with Pt electrodes over the frequency range $10^{-2}$ to $10^{3}$ Hz as a function of $P_{O_2}$ at 700°C. For $P_{O_2} = 0.1$ to 1.0 atm, their results indicate a single semicircle shifted along the real axis from the origin. The corresponding equivalent circuit is described by a single resistive element attributable to bulk conductivity, in series with a parallel Warburg impedance - double layer capacitance circuit attributable to the interface. Both Duran (2), for ESB and yttria stabilized bismuth oxide (YSB), and Dordor (3), for YSB, presented results indicating a single parallel circuit element at low temperature (~200°C) followed by two and then three equivalent circuit elements as the temperature is increased. These results are essentially identical to ours, as will be described below. Meng (4) investigated bismuth oxide, both singly and doubly stabilized with Y$_2$O$_3$, Nb$_2$O$_5$, Sm$_2$O$_3$ and Pr$_6$O$_{11}$, and similarly showed a single semicircle at 253°C which evolved into two semicircles at 400°C. However, as the temperature was increased beyond 500°C the high frequency semicircle exhibited inductive behavior.

At 200°C, a plot of the imaginary vs real components of impedance, Figure 1, consists of a single semicircle, in agreement with the results of Duran, Dordor and Meng (2-4). The equivalent circuit for this high frequency semicircle consists of a single parallel RC circuit and is attributable to the bulk conductivity. As the temperature is increased two more circuit components become evident, Figures 2-4. At the low frequency end of the spectrum another semicircle appears. Extrapolation of the high frequency (bulk conductivity) semicircle results in a high frequency intercept that no longer goes through the origin. Thus there is an additional high frequency (beyond the limits of our equipment) component of the bulk conductivity.

The high frequency end of the low frequency semicircle is linear and intercepts the real axis at 45°. This frequency dispersion is best described by a Warburg impedance, $Z_w$, in parallel with a capacitance. This low frequency semicircle has been ascribed to the electrolyte-gas phase interface (1) and to a grain boundary effect for ESB (2) and YSB (2,3). Due to the $P_{O_2}$ dependence described by Verkerk and Burggraaf (1) we agree with the assignment of this equivalent circuit element to the electrolyte-gas phase interface. The observed capacitance of this circuit component is therefore due to the double layer, $C_{dl}$.

Although we can not extend our measurement range to higher frequency, we can tentatively assign the highest frequency component of the bulk conductivity to a series resistance. This is consistent with the typical bulk conductivity circuit for both zirconia (1,5,6) and bismuth (1) based oxygen ion conductors. The overall equivalent circuit is therefore as depicted in Figure 5. The bulk conductivity consists of a resistance, $R_f$, in series with a parallel circuit, $R_d$-$C_g$ (the meaning of the resistance subscripts will become evident in the Discussion section). This in turn is in series with a parallel circuit, $Z_w$-$C_{dl}$, associated with the interface.
The geometry of our samples is that of a parallel plate capacitor. For the results in Figures 1-4, a disk was cut into an 0.8 x 0.8 cm square resulting in an area to thickness ratio, A/d, of 6. We have varied the A/d ratio from 6 to 34 and observed that the capacitance is proportional to this ratio. Thus, the capacitive element we observed in the bulk conductivity semicircle can be attributed to the geometric capacitance, $C_g$.

The differing literature results with respect to the high frequency semicircle warrant explanation. The lack of a high frequency bulk-semicircle in Verkerk and Burggraaf (1) results can be explained by two differences in the experimental conditions. First, they report having only scanned the frequency range up to 1 kHz, which is below the range where this semicircle was observed by Duran (2), Dordor (3) and in this study. Second, they report using a much smaller A/d ratios, ~0.98 which would significantly reduce any $C_g$ effect. With regards to the inductive loop described by Meng (4), our only possible explanation is that we also observed an inductive element prior to fully compensating all of the parasitic elements in the test leads.

Several investigators have shown that the conductivity-temperature dependence of a variety of lanthanide stabilized bismuth oxides exhibit two activation energies (7-10). Since the observed conductivity activation energy depends on the measurement frequency, one must obtain the conductivity from the real-axis intercept of a complex impedance plot; otherwise, the Arrhenius behavior will be skewed so as to artificially obtain two slopes (5). A plot of the bulk conductivity, calculated from the real-axis intercept, $R_f + R_d$, as a function of reciprocal temperature is shown in Figure 6. Two slopes are in fact observed, with corresponding activation energies of 15 kcal/mole above 600°C and 28 kcal/mole below 600°C.

The observation of two activation energies requires that two processes are involved in the bulk conductivity mechanism. As such, one would expect to observe two elements in the equivalent circuit attributable to the bulk conductivity with a single activation energy corresponding to each element. This expectation is consistent with our proposed equivalent circuit.

The high frequency intercept of the bulk conductivity semicircle, $R_f$, varies with temperature. Since the low frequency intercept, $R_f + R_d$, is the sum of the high frequency intercept, $R_f$, and the resistive element of the semicircle, $R_d$, one can calculate each of the individual resistive elements by simple subtraction. Above -500°C, the rate of decrease of $R_f$ with increasing temperature becomes proportionally greater than that of $R_d$. The resulting temperature dependence of the conductivity of each of these resistive elements is plotted in Figure 6. As can be seen from the plot, the conductivity calculated from $R_f$ has the same slope as the low temperature region and the conductivity calculated from $R_d$ has the same slope as the high temperature region of the total conductivity.
4. CONDUCTIVITY AGING

Samples aged at temperatures below the knee in the Arrhenius plot (<600°C) exhibit a monotonic decay in conductivity with time. This aging phenomenon is completely reversible; when samples are heated to temperatures above the order-disorder transition temperature, the conductivity reverts back to its original value. Similar results were observed by Carter for calcia stabilized zirconia, CSZ (11).

A plot of the decay in conductivity of ESB with time is shown in Figure 7. The conductivities measured at several temperatures below 600°C were normalized relative to the initial conductivity at their respective temperature. These curves are best described qualitatively by typical precipitation behavior. This behavior is described first with respect to temperature and then with respect to time. At high temperatures (550-575°C), there is a delay which increases with temperature before the onset of decay. This delay is typical for the dependence of nucleation on supersaturation or the small thermodynamic driving force for small amounts of supercooling below the transition temperature. At lower temperatures (350-500°C), the rate of decay increases with increasing temperature and is controlled by growth kinetics.

The time dependence in the low temperature growth controlled region is shown in Figures 8 and 9. At short times, Figure 8, the logarithm of conductivity is linear with time. At long times, Figure 9, the resistivity is linear with t½. These results are described in the Discussion section.

5. DIFFERENTIAL THERMAL ANALYSIS

Differential Thermal Analysis (DTA) was used to investigate this aging phenomenon and the order-disorder transition of unaged ESB. ESB was heated and cooled thru the transition temperature and the differential temperature between ESB and a reference thermocouple was measured. The results for no aging, 100 hours and 500 hours at 500°C are shown in Figure 10. The aged samples exhibit an endotherm upon heating, with both the magnitude of the endotherm and the temperature of onset increasing with aging time. The unaged sample exhibits no endotherm upon heating. However, a thermal transition is signified by a change in slope centered at the 600°C conductivity transition point (the onset of the transition is 584°C and the completion is at 615°C, with the extent of the transition region dependent on sample size) and is more evident in the 3X magnification of scale, Figure 11. Below the transition region, the slope is 4.7 x 10⁻⁵ °C/mg/°C and above the transition region the slope is 7.6 x 10⁻⁵ °C/mg/°C. These slopes are proportional to heat capacity. Hence, the increase in slope above the transition temperature may be related to a greater degree of freedom in the disordered state.
Upon cooling, the reverse change in slope is observed for all of the samples, with some hysteresis of the transition toward lower temperature. Reheating of the aged samples results in identical temperature profiles to that of the unaged sample, thus confirming the reversibility of the aging phenomenon.

6. STRUCTURE

It is generally acknowledged that the structure of $\delta$-Bi$_2$O$_3$ consists of a FCC cation sublattice with oxygen ions in six of the eight tetrahedral sites. However, it is still not clear how the oxygen ions are arranged to accommodate the two vacant oxygen lattice sites and the resulting high degree of disorder. Three models have been proposed to account for this disorder.

Gattow and Schroder (12) suggested that the oxygen sites are all randomly occupied, hence a 3/4 occupancy factor for each site. This would result in a FCC diffraction pattern with relative intensities proportional to the structure factors tabulated in Table 1.

Sillen observed diffraction peaks corresponding to the ordering of vacancies in $<$111$>$ directions (13). This model is energetically favorable, as calculated by (14). However, several authors have discounted this model as being a result of Si contamination (15,16). Diffraction results from these same authors (15,16), using high temperature neutron diffraction do not show the additional $<$111$>$ orientation peaks, Table 1.

The third model by Willis (17) describes the disorder in terms of a displacement $\delta$ along four $<$111$>$ directions from the normal tetrahedral site, $1/4$ $1/4$ $1/4$. This results in 32 possible sites with an oxygen occupancy factor of 3/16. One problem with this model is that in calculating the structure factors, simple multiplication by this occupancy factor allows up to four oxygens arranged with $\delta$ displacements around a single tetrahedral site. One should instead consider either the Gattow and Schroder or Sillen models as occupancy disorder with the $\delta$ displacement of the Willis model as a local positional disorder superimposed on the occupancy disorder.

Since the aging phenomenon is associated with ordering of the anion lattice, one would expect that additional peaks corresponding to alignment of the vacancies in $<$111$>$, $<$110$>$ or $<$100$>$ directions would become apparent. These peaks would have the structure factors and corresponding relative intensities shown in Table 1. The relative intensities are calculated from the structure factors and the atomic scattering factors where $f$ is the statistical average of the atomic scattering factors of Bi and Er and $f_0$ is the atomic scattering factor of oxygen. As is shown in Table 1, the calculated intensities for the non-FCC peaks are extremely small both due to the structure factor and the fact that the x-ray diffraction (XRD) atomic scattering factor of oxygen is $\sim1/10$ that of Bi and Er.
Table 1. Structure Factors and Relative XRD Intensities for the Lower Angle Reflections of ESB

| Occupancy | Gattow & Sillen Schroder | <111> | <110> | <100> |
|-----------|--------------------------|-----|-----|-----|
| 3/4       | 1                        | 1   | 1   | 1   |
| $|F_{110}|^2$ | -                        | $4f_o^2$ | $4f_o^2$ | -   |
| 0         | 0.2                      | 0.2 | 0   | 0   |
| $|F_{111}|^2$ | $16f_o^2$+36$f_o^2$ | $16f_o^2$ | $16f_o^2+4f_o^2$ | $16f_o^2$ |
| 100       | 100                      | 100 | 100 | 100 |
| $|F_{200}|^2$ | $(4f-6f_o)^2$ | $(4f-6f_o)^2$ | $(4f-6f_o)^2$ | $(4f-6f_o)^2$ |
| 71        | 72                       | 72  | 72  | 72  |
| $|F_{210}|^2$ | -                        | -   | -   | -   |
| 0         | 0                        | 0   | <0.2| 0   |
| $|F_{211}|^2$ | -                        | $4f_o^2$ | -   | $4f_o^2$ |
| 0         | <0.2                     | 0   | <0.2| 0   |
| $|F_{220}|^2$ | $(4f+6f_o)^2$ | $(4f+6f_o)^2$ | $(4f+6f_o)^2$ | $(4f+6f_o)^2$ |
| 97        | 98                       | 98  | 98  | 98  |
| $|F_{221}|^2$ | -                        | -   | $4f_o^2$ | $4f_o^2$ |
| 0         | 0                        | <0.2| <0.2| <0.2|
| $|F_{310}|^2$ | $4f_o^2$ | $4f_o^2$ | $4f_o^2$ | -   |
| <0.2      | <0.2                     | <0.2| <0.2| 0   |

We investigated the effect of aging on the structure of ESB using XRD. Three important results were observed. First, no peaks corresponding to the formation of additional phases were observed after 500 hours of aging. Second, a qualitative trend was observed in all of the samples with the intensity of the FCC peaks increasing with aging time; after 500 hours the peak intensities increased by a factor of two over the initial sample. This could be related to Willis type ordering where the $\delta$ becomes smaller with time; however, one can not fully discount the possible influence of thickness variation in preparation of XRD samples. The third, and possibly most important, observation is that after 500 hrs a small peak at 25.5 degrees 20 appears, Figure 12, which is not apparent prior to aging. This peak corresponds both in position and relative intensity to that calculated for a reflection from a (110) plane due to either <111> or <110> occupancy-ordering of vacancies. Based on theoretical calculations (14) we believe that <111> type ordering is more likely. Therefore, this aging phenomenon can tentatively be described as ordering of oxygen vacancies along <111> directions.

Further experiments using electron diffraction are underway to confirm (or refute) the observation of <111> ordering. In addition, neutron diffraction results would more clearly identify the presence (or absence) of this peak, as well as some of the other <111> or <110> ordering peaks, as the neutron scattering factor of oxygen is much closer to that of Bi and Er. Previous neutron diffraction experiments (15,16), having not observed the aging phenomenon, may not have taken the time dependence of ordering under consideration.
7. DISCUSSION

The total conductivity for a given material, $\sigma$, is defined by:

$$\sigma = \sum \limits_{i} z_{i}q[i]b_{i}$$

(1)

where $z_{i}q$, $[i]$ and $b_{i}$ are, respectively, the charge, concentration and mobility of each species "i". For solid oxide electrolytes the conducting species are oxygen vacancies and one can neglect the contribution of electronic species over most of the conductivity domain. This simplifies Equation 1 to:

$$\sigma = \sum \limits_{i} z_{i}q[V_{i}]b_{i}$$

(2)

where now the subscript "i" refers only to the different types of oxygen vacancies. The predominate ionic defect in zirconia, $M^{4+}$, type solid oxide electrolytes are the charged oxygen vacancies, such as $V_{O}^{\circ\circ}$, due to aliovalent cation substitution and Anti-Frenkel disorder. In addition, however, there are numerous perturbations on the local environment of these vacancies that can have a profound influence on their mobility or partial conductivity. Examples of these perturbations are: ionized vacancies due to the occupation of one or more electrons (i.e. $V_{O}^\circ$, $V_{O}^\circ\circ$, $V_{O}'$, etc.); the association of a vacancy with an aliovalent cation (i.e. $[V_{O}^{\circ\circ} Y']^\circ$ in ZrO$_2$); and, as will be discussed, the structural environment.

In the case of ESB, which has no aliovalent cations, we can ignore the effect of coulombic vacancy-cation association. If we ignore the effect of electron occupation, one can look at the limiting case of structural perturbations on vacancy mobility. This is especially important as the intrinsic vacant 25% of the anion lattice sites are neutral. Therefore, as single entities they do not constitute an ionic defect. Rather, as described by Jacobs (14), charged defects can be formed by a pseudo-Frenkel disorder by transposing oxygen ions and vacancies between neighboring sublattices, hence a structural disorder.

Now consider the case of an ordered vs. a disordered oxygen sublattice. The high oxygen ion mobility in solid oxide electrolytes is attributed to the high degree of disorder of the oxygen sublattice. For a periodic or ordered oxygen sublattice one would expect a significantly lower mobility, possibly approaching that of a typical non-conducting oxide. We believe this structural perturbation plays a significant role in the conductivity of ESB.

The change in activation energy, at ~600°C, has been ascribed to an order-disorder transition of the oxygen sublattice (7). Above 600°C the oxygen sublattice is disordered, resulting in a low apparent activation energy for conductivity. Below the transition temperature, the oxygen sublattice attains some degree of ordering and the activation energy is significantly greater. This same type of order-disorder phenomenon of the oxygen sublattice has been described for CSZ, with a
transition temperature of ~1000°C (11). The effect of the order-disorder transition on conductivity can be explained by either of two models. The first, put forth by Carter (11), consists of a single concentration of vacancies whose mobility depends on the local structural environment. Thus, as the oxygen sublattice disorders the mobility increases. This model, however, does not explain the two different activation energies observed in stabilized δ-Bi2O3. Therefore, we will develop a second model to explain this "knee" in the Arrhenius plot of stabilized δ-Bi2O3's.

For diffusion in a cubic solid, the diffusivity, D, is related to the jump frequency, \( \Gamma \), and the jump distance, a, by:

\[
D = \frac{1}{6} \Gamma a^2
\]

For interstitial diffusion, the jump frequency is related to the vibration frequency, \( \nu \), the coordination number, \( z \), and the free energy of migration \( \Delta G_m \):

\[
\Gamma = \nu z e^{-\frac{\Delta G_m}{kT}}
\]

However, in a vacancy mechanism an extra term is necessary to account for the formation of vacancies:

\[
\Gamma = \nu z X_v e^{-\frac{\Delta G_m}{kT}}
\]

where \( X_v \) is the equilibrium fraction of vacant sites and is equal to the exponential of the free energy of formation of a vacant site, \( \Delta G_f \):

\[
X_v = e^{-\frac{\Delta G_f}{kT}}
\]

Thus, the diffusivity for vacancy diffusion contains two exponential terms:

\[
D = \left( \frac{1}{6} \nu z a^2 \right) e^{-\frac{\Delta G_f}{kT}} e^{-\frac{\Delta G_m}{kT}}
\]

and hence two activation energies, \( \Delta H_f \) and \( \Delta H_m \):

\[
D = \left( \frac{1}{6} \nu z a^2 \right) e^{-\frac{(\Delta S_f + \Delta S_m)}{\kappa}} e^{-\frac{(\Delta H_f + \Delta H_m)}{kT}}
\]

In stabilized δ-Bi2O3, 25% of all oxygen sites are vacant leading one to expect that \( X_v \) plays a minor role in the temperature dependence of diffusion, and hence conductivity. However, consider that the anomalously large oxygen ion conductivity in δ-Bi2O3 is due to the high degree of disorder in the oxygen sublattice; and that the oxygen sublattice undergoes an order-disorder transition at the knee in the Arrhenius plot of conductivity. Then, one can assume that the local
structural environment has an effect on the mobility of the oxygen vacancies and further that there are two types of structural environments, as signified by the order-disorder transition, with a different type of vacancy associated with each. The vacancies in the disordered regions of the oxygen sublattice have a high mobility, hence mobile vacancies ($V_m$). Whereas, vacancies in ordered domains of the oxygen sublattice, $V_o$, have a significantly lower mobility. Then the concentrations of $V_m$ and $V_o$ are related by:

$$X_v = \frac{[V_m]}{[V_m] + [V_o]}$$

where now $X_v$ is the fraction of mobile vacancies. This reasoning then leads to the observed change in activation energy, as the mobile and ordered vacancies are related by a thermodynamic equilibrium similar to that of Equation 6, where now $\Delta G^f$ is the free energy of formation of mobile vacancies. In addition, this also explains the aging phenomenon. As a sample of ESB is aged, regions of ordered vacancies grow at the expense of mobile vacancies. This type of solid state transition would follow typical precipitation kinetics with the rate of transformation following first order kinetics at short time and becoming diffusion controlled at long time. The observed aging phenomenon shows this type of behavior.

The rate equation for first order kinetics, of species "i", is:

$$\frac{\partial [i]}{\partial t} = k [i]$$

Integrating Equation 10 and substituting $V_m$ for species "i" yields:

$$\ln \left( \frac{[V_m]}{[V_m]_0} \right) = k t$$

where $[V_m]_0$ is the initial concentration of mobile vacancies. Assuming the mobility of ordered vacancies is negligible and that mobility is not concentration dependent, the ratio of conductivity to initial conductivity ($\sigma/\sigma_0$) is:

$$\frac{\sigma}{\sigma_0} = \frac{(zq [V_m] b)}{(zq [V_m]_0 b)} = \left( \frac{[V_m]}{[V_m]_0} \right)$$

Substitution of Equation 12 into Equation 11 yields:

$$\ln \left( \frac{\sigma}{\sigma_0} \right) = k t$$

Thus, if the aging phenomenon follows first order kinetics a plot of the natural logarithm of the conductivity is linear with time, as is displayed in Figure 8.
Carter attributed an observed linear increase in resistivity with the square root of time, for samples aged below 1100°C, to a diffusional process related to anion ordering (11). This is identical to our results for ESB at long times, Figure 9, thus indicating diffusion control.

The temperature dependence of the conductivity and the associated order-disorder transition can therefore be described in terms of the formation and migration of mobile vacancies. Above 600°C, the oxygen sublattice is disordered, $X_v$ approaches unity and the observed activation energy is that of migration of mobile vacancies. Below 600°C, the oxygen sublattice tends to order, $X_v$ approaches zero and the apparent activation energy is the enthalpy of formation of mobile vacancies. In terms of the equivalent circuit, $R_f$ is the resistance associated with the formation of mobile vacancies and $R_d$ is a diffusion resistance associated with the migration of mobile vacancies.

Further evidence for this can be seen by comparing the activation energies in Table 2. The activation energies of the conductivity calculated from $R_f$ and the aging kinetics are both comparable with that of the bulk conductivity at low temperature. Similarly, the activation energy of the conductivity calculated from $R_d$ is comparable with that of the bulk conductivity at high temperature. Since the aging phenomenon is due to the consumption of mobile vacancies rather than their formation the observed activation energy, $\Delta H^f$, is not expected to be identical to, but only comparable to, that of the conductivity in the low temperature region. Due to the long time involved in these solid state transitions, aging of samples at temperatures less than 500°C has not as of yet progressed to the point where diffusion is limiting; therefore, an activation energy for the diffusion controlled region of the aging phenomenon has not yet been calculated.

| Bulk Conductivity | Individual Components | Rate Constant | $\Delta H^f$ |
|-------------------|-----------------------|---------------|---------------|
| $<600^\circ$C     | $R_f$                 | 28            | 28            |
| $>600^\circ$C     | $R_d$                 | 15            | 12            |

8. CONCLUSION

An order-disorder transition of the oxygen sublattice in ESB is proposed to explain the knee in the Arrhenius plot of conductivity. At high temperatures ($>600^\circ$C) the oxygen sublattice is in a disordered state, conceptually a disordered array of mobile oxygen ions and oxygen vacancies, with a corresponding low activation barrier to migration. As ESB is cooled below the transition temperature, the vacancies tend to form domains of some lower-energy ordered-state with a concomitant reduction in the population of mobile vacancies. Preliminary diffraction results indicate that this ordered state can be described by
the arrangement of oxygen vacancies in <111> directions. The apparent activation energy in the low temperature region is then related to the formation of mobile vacancies.

The kinetics of the reversible aging phenomenon is related to the rate the oxygen vacancies attain this lower-energy ordered-state. Domains of the ordered state grow by consuming mobile vacancies, thus reducing the concentration of conducting species. These results, when compared with those for CSZ (11), indicate a commonality in the transport kinetics and aging phenomenon between zirconia and bismuth oxide electrolytes.

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Figure 1. Complex impedance plot of ESB at 200°C.

Figure 2. Complex impedance plot of ESB at 300°C.

Figure 3. Complex impedance plot of ESB at 400°C.

Figure 4. Complex impedance plot of ESB at 575°C.

Figure 5. Equivalent circuit for ESB.
Figure 6. Bulk and individual component conductivities from \((R_f+R_d)\), \(R_f\) and \(R_d\) intercepts, respectively, as a function of reciprocal temperature for ESB.

Figure 7. Aging phenomenon in ESB; normalized conductivity as a function of time and temperature.

Figure 8. Aging phenomenon in ESB indicating first order kinetics at short time.

Figure 9. Aging phenomenon in ESB at 500°C indicating diffusion control at long time.
Figure 10. DTA of ESB; temperature difference upon heating for no aging, 100 and 500 hours at 500°C.

Figure 11. DTA of un-aged ESB indicating change in slope.

Figure 12. X-ray diffraction of ESB indicating (110) reflection after 500 hours at 500°C.