ABSTRACT

Bismuth oxide and doped ceria are among the highest ionic conducting solid oxide electrolytes and are therefore less resistive for low temperature operation than the conventional zirconia based electrolytes. Unfortunately, bismuth oxide is unstable at low oxygen partial pressures and ceria yields an efficiency loss due to the appearance of electronic conduction under reducing conditions. We demonstrated earlier (1) that a bilayered electrolyte of erbia stabilized bismuth oxide (ESB) on the oxidizing side and a layer of samaria doped ceria (SDC) on the reducing side, could be used to prevent the decomposition of bismuth oxide and block electronic conduction under fuel cell conditions. This arrangement has the potential to perform as a low temperature SOFC electrolyte, the feasibility of which is examined in this paper. In this work we present a model, for defect flux in bilayers, that enables us to resolve the issues of stability and efficient power generation for a bilayer. We show how the thickness ratio may be optimized with respect to open circuit potential, conductivity and the stability of the bismuth oxide layer. To verify the feasibility of the bilayer for low temperatures, the area specific resistance of an SDC/ESB bilayer is plotted as a function of thickness ratio.

INTRODUCTION

Solid oxide fuel cells (SOFC's) have great potential for use in electrical power generation. Unfortunately, SOFC's must operate at high temperatures (> 800 °C) in order to be able to deliver acceptable electric power. High temperatures demand (a) specialized (expensive) materials for the fuel cell interconnects and insulation, (b) time to heat up to the operating temperature and (c) energy input to arrive at the operating temperature. Therefore, if fuel cells could be designed to give a reasonable power output at lower temperatures tremendous benefits may be accrued, not the least of which is reduced cost. The problem is, at lower temperatures the conductivity of the conventional solid oxide electrolyte (yttria stabilized zirconia) decreases to the point where it cannot supply electrical current efficiently to an external load.

Bismuth oxide has the highest ionic conductivity of the solid oxide electrolytes and could, in theory, deliver electrical power effectively at low temperature. Unfortunately, bismuth oxide is unstable at low (<10^-13 atm.) oxygen partial pressures (P_O2) in the presence of an active reducing agent such as H_2 or CH_4. Several attempts have been made...
to stabilize bismuth oxide (2, 3) in low oxygen partial pressures with limited success, but obviously not enough success to make it practical.

Ceria, although not as conductive as bismuth oxide, has also received consideration as a potential low temperature solid oxide electrolyte (4). However, ceria is a mixed conductor and in reducing atmospheres (low P_{O2}) it displays significant n-type conduction. This reduces the ionic transference number and the open circuit potential (OCP) sufficiently to make ceria less efficient for application in a low temperature SOFC.

A number of researchers (1, 5-7) have proposed using a bilayered electrolyte (see Fig. 1) as a means of preventing the decomposition of bismuth oxide or the reduction of ceria in low P_{O2}. The feasibility of a bilayered electrolyte proposed by Wachsman et al (1) and consisting of a layer of erbia stabilized bismuth oxide (ESB - Bi_{0.8}Er_{0.2}O_{1.5}) on the oxidizing side and a layer of samaria doped ceria (SDC - Ce_{0.8}Sm_{0.2}O_{1.5}) on the reducing side will be examined in this paper.

\[ P_{I}^{(2)} > P_{I}^{(1)} \]

**Figure 1.** Conceptual representation of a bilayered solid-oxide electrochemical cell showing effect of relative thickness on interfacial P_{O2} (shown for simplicity with a linear P_{O2} gradient).

Virkar (6) used a simple equivalent circuit to calculate the interfacial P_{O2} between a zirconia/ceria bilayer and a zirconia/bismuth oxide bilayer. The primary conclusion from this analysis was that for the P_{O2} at the interface to be high enough to maintain stability, the electronic conductivity on the air side (ceria or bismuth oxide in this case) must be significantly higher than that of the zirconia layer on the fuel side. One major flaw with this analysis was that it neglected the effect of the P_{O2} dependence of the ionic and electronic conductivities, \( \sigma_i \) and \( \sigma_e \) respectively. Moreover, they countered themselves by later showing (7) that a higher open-circuit potential may be obtained with the
zirconia on the air side of the zirconia/ceria bilayer rather than the fuel side, a fact supported by other studies (1).

Generally, however, a zirconia/ceria bilayer electrolyte has no intrinsic advantage over just a thin zirconia electrolyte itself, other than providing a non-porous substrate for zirconia deposition, due to the relatively low conductivity of zirconia. Additionally, the rationale of preventing contact of, e.g., a ceria electrolyte with a reducing gas is conceptually an over simplification of the use of a bilayered electrolyte. Instead, one should consider the functional gradient of the oxygen partial pressure through the electrolyte and use this to modify or block electronic transport.

The relative electronic contribution to the conductivity at any point through a mixed conductor depends on the local oxygen activity. The P$_{O_2}$ gradient across a cell is fixed by the gas phase on either side. In a multi-layered structure the gradient within each layer is further determined by the relative thickness and transport properties of that layer (ignoring kinetic effects at the solid-solid and solid-gas interfaces). Theoretically, one can increase the local oxygen activity at the anode-electrolyte interface (Fig. 1), for a dense bilayered anode/electrolyte structure by increasing the thickness of the mixed-conducting anode relative to that of the electrolyte.

This higher interfacial P$_{O_2}$ affects the material properties of both layers. Significantly, the interfacial P$_{O_2}$ can be elevated to the point where bismuth oxide is thermodynamically stable. Consequently, close to full theoretical open circuit potential is obtainable in this arrangement since the bismuth oxide effectively blocks electronic conduction.

Wachsman et al (1) experimented on SDC/ESB bilayered electrolytes and were able to achieve higher open-circuit potentials and power densities for the bilayers than for SDC alone. However, they didn't optimize the thickness ratio of the layers nor did they show any calculations for the interfacial pressure.

In this work we will develop a model for defect flux in bilayered solid oxide electrolytes such as those suggested by Wachsman et al (1) and we will seek to show how the thickness ratio may be optimized for maximum open-circuit potential while keeping bismuth oxide thermodynamically stable. Finally, we will examine the low temperature limits of this particular bilayer for a targeted area specific resistance (ASR) of 0.1-0.2 $\Omega$cm$^2$ (8).

The ASR is generally defined as

$$\text{ASR} = \frac{L}{\sigma_T} \quad [1]$$

where $L$ is the total thickness and $\sigma_T$ is the total conductivity of the electrolyte. For a bilayer the ASR becomes

$$\text{ASR} = \left( \frac{L}{1+t} \right) \left( \frac{t}{\sigma_A} + \frac{1}{\sigma_B} \right) \quad [2]$$
where $\sigma_A$ and $\sigma_B$ are the conductivities of layer A and B respectively and $t$ is the thickness ratio of the layers A and B such that $t = \frac{L_A}{L_B}$.

Fig. 2 shows a plot of the projected ASR for an SDC-ESB bilayer at different temperatures and total thickness. The SDC and ESB conductivity values (2, 9) used were determined in air so the effect of an oxygen potential gradient and electronic conductivity in SDC are neglected, this is a significant simplification at high temperature (1073 K) (10). However, significance of these factors should diminish with decreasing temperature. Fig. 2 shows that, in principle, an SDC-ESB bilayer should be able to approach the target ASR value of 0.1-0.2 $\Omega$cm$^2$ (8). Therefore, the remaining issue to be resolved is the determination of the optimum thickness ratio for the SDC-ESB bilayer to achieve stability of the ESB while maximizing the conductivity. In the following sections we present a model which enables us to resolve these issues.

Figure 2. ASR as a function of relative ($t = \frac{L_{SDC}}{L_{ESB}}$) and total thickness and temperature.

**BILAYERMODEL**

**Bismuth Oxide Defect Equilibria**

One quarter of the oxygen sites in the fluorite lattice of bismuth oxide is vacant due to the +3 charge on the bismuth cation. Therefore, bismuth oxide may be thought of as a "dopant" in a fluorite lattice as follows

$$\text{Bi}_2\text{O}_3 \xrightarrow{\text{FIO}_2} 2\text{Bi}^{3+}_\text{F}^1 + \text{V}_\text{O}^{**} + 3\text{O}_\text{O}^X$$

where FIO$_2$ is a hypothetical fluorite oxide representing the fluorite structure for a typical FI$^{4+}$ cation (e.g., Zr$^{4+}$). The corresponding charge neutrality equation is
Or in other words there is one oxygen vacancy for every two bismuth atoms. However, the stoichiometry of \( \text{Bi}_2\text{O}_3 \) also tells us that there are three oxygen atoms for every two bismuth atoms, i.e.,

\[
3[\text{Bi}^{/\prime}_\text{F}] = 2[O^{\bullet\bullet}_\text{O}]
\]

Therefore

\[
[O^{\bullet\bullet}_\text{O}] = 3[V^{\bullet\bullet}_\text{O}]
\]

Or, in other words, oxygen atoms occupy three quarters of the available anion sites; a fact also evident in equation [3].

Since bismuth oxides exhibit some p-type conductivity at high \( P_{O_2} \) (2, 3) the equilibrium with the gas phase may be written (using Kröger-Vink notation) as:

\[
V^{\bullet\bullet}_\text{O} + \frac{1}{2} O_2 \leftrightarrow O^{\bullet\bullet}_\text{O} + 2h^* ; \quad K_{\text{OX}} = \frac{p^2}{[V^{\bullet\bullet}_\text{O}]^2 [O_2]^\frac{1}{2}}
\]

where \( p \) is the concentration of holes.

Anti-Frenkel disorder in the oxide, whereby an oxygen atom migrates from its site on the lattice to an interstitial site leaving behind a vacancy, may be represented in a similar fashion by

\[
O^{\bullet\bullet}_\text{O} \leftrightarrow V^{\bullet\bullet}_\text{O} + O^{\prime}_1 ; \quad K_{\text{AF}} = [V^{\bullet\bullet}_\text{O}][O^{\prime}_1]
\]

Thermally generated, intrinsic, electron-hole pair formation in the oxide is given by

\[
\text{null} \rightarrow e^* + h^* ; \quad K_{\text{int}} = np
\]

where \( n \) is the concentration of electrons.

When considering all the defect equations the charge neutrality relation for the system becomes:

\[
n + [\text{Bi}^{/\prime}_\text{F}] + 2[O^{\prime}_1] = 2[V^{\bullet\bullet}_\text{O}] + p
\]
Significant amounts of electrons and oxygen interstitials are not observed in bismuth oxide in typical pressure ranges \((P_{O_2} > 10^{-13} \text{ atm.})\), therefore the charge neutrality equation reduces to:

\[
[Bi^{/}/F_1] = 2[V^{**}_O] + p
\]  

Eqns. [7] and [11] may be combined to yield

\[
[Bi^{/}/F_1] = 2V + K^2_{OX} V^2 P^4
\]  

where for simplicity \(V\) replaces the usual notation for vacancy concentration as does \(P\) for oxygen partial pressure, \(P_{O_2}\). Eqn. [10] is a quadratic equation with one meaningful solution for the concentration of oxygen vacancies as a function of local \(P_{O_2}\)

\[
V(P) = \frac{1}{16} \left[ \left( \frac{8[Bi^{/}/F_1] + K_{OX} P^2}{2} \right)^{1/2} - K^2_{OX} P^4 \right] \]  

Eqn. [13] may be substituted in eqn. [7] to give an equation for the concentration of holes as a function of \(P_{O_2}\)

\[
p(P) = \frac{1}{4} K^2_{OX} P^4 \left[ \left( \frac{8[Bi^{/}/F_1] + K_{OX} P^2}{2} \right)^{1/2} - K^2_{OX} P^4 \right] \]  

**Thickness Ratio as a Function of Interfacial Pressure**

Following the approach of Duncan and Wachsman (10), the flux equations for vacancies and holes in a bismuth oxide electrolyte of length \(L\) in a \(P_{O_2}\) gradient are:

\[
\begin{align*}
j_v &= -\frac{\sigma_v}{Z_v q^2 L} \left( kT \ln \frac{V(x=L)}{V(x=0)} - Z_v q \Phi_{th} \right) \\
&= -\frac{\sigma_v}{Z_v q^2 L} \left\{ kT \ln \left( \frac{8[Bi^{/}/F_1] + K_{OX} P^2 L}{2} \right)^{1/2} - K^2_{OX} P^4 L \right\} \]  

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\[ j_h = -\frac{\alpha_h}{Z_h q^2 L} \left( k T \ln \frac{p(x = L)}{p(x = 0)} - Z_h q \Phi_{th} \right) \]

\[ = -\frac{\alpha_h}{Z_h q^2 L} \left( \frac{P_L^{1/4} \left[ \left( 8[Bi_{F1}'] \right)^{1/2} - \frac{1}{4} K_{OX} P_L^{1/2} \right]}{P_0^{1/4} \left[ \left( 8[Bi_{F1}'] \right)^{1/2} - \frac{1}{4} K_{OX} P_0^{1/2} \right]} - Z_h q \Phi_{th} \right) \]

where \( \{x: 0 \leq x \leq L\} \), \( \alpha \) is the conductivity, \( Z \) is the charge equivalence, \( q \) is the charge on an electron, \( k \) is Boltzman's constant, \( T \) is temperature, \( L \) is the length of the electrolyte, \( P_L \) and \( P_0 \) are the partial pressures at either side of the electrolyte, \( \Phi_{th} \) is the Nernst voltage and the subscripts \( V \) and \( h \) refer to vacancies and holes.

Similar equations were derived by Duncan and Wachsman (10) for the flux of vacancies and electrons in a fixed-valence-acceptor doped oxide MIEC, such as SDC.

\[ j_v = -\frac{\alpha_v}{Z_v q^2 L} \left( \frac{2 k T}{3} \ln \left( \frac{K_{R}^{1/4} P_L^{1/4} + \frac{1/2 A'}{2} \right)^2 - Z_v q \Phi_{th} \right) \]

\[ = -\frac{\alpha_v}{Z_v q^2 L} \left( \frac{P_L^{1/4} \left[ \frac{1}{2} K_{R}^{1/4} P_L^{1/4} + \left( \frac{1/2 A'}{2} \right)^2 \right]^{1/3}}{P_0^{1/4} \left[ \frac{1}{2} K_{R}^{1/4} P_0^{1/4} + \left( \frac{1/2 A'}{2} \right)^2 \right]^{1/3}} - Z_v q \Phi_{th} \right) \]

where \( \alpha \) is the conductivity, \( Z \) is the charge equivalence, \( q \) is the charge on an electron, \( k \) is Boltzman's constant, \( T \) is temperature, \( L \) is the length of the electrolyte, \( P_L \) and \( P_0 \) are the partial pressures at either side of the electrolyte, \( K_R \) is the equilibrium constant for the reduction of oxygen sites in the oxide, \( A' \) is the fixed-valence-acceptor dopant concentration, \( \Phi_{th} \) is the Nernst voltage and the subscripts \( V \) and \( e \) refer to vacancies and electrons. A description of the defect equilibria for doped ceria may be obtained from Duncan and Wachsman (11).

In a bilayered electrolyte at steady state, charge must be conserved in either layer, therefore the total defect flux is the same in either layer. Hence, for a bilayer consisting of material \( A \) (samaria doped ceria) in one layer and material \( B \) (erbia stabilized bismuth oxide) in the other one may write:
\[ \begin{align*}
\sigma_{V_A} & = \frac{j_A}{q_{L_A}} \\
\sigma_{e} & = \frac{j_B}{q_{L_B}} \\
\sigma_{V_B} & = \frac{j_A}{q_{L_B}} \\
\sigma_{h} & = \frac{j_B}{q_{L_B}}
\end{align*} \]

where the sub-subscript indicates the material type. Accordingly, for \(Z_V = 2\), \(Z_e = -1\) and \(Z_h = 1\) eqn [19] may be written as

\[ \frac{\sigma_{V_A}}{q_{L_A}} \frac{\Phi_{th_A}}{kT} \ln \left( \frac{\frac{1}{2} K_0^2 P_0^{-1} + \left( \frac{A_N}{2} \right)^{\frac{3}{2} - 1} }{\frac{1}{2} K_0^0 P_0^{-1} + \left( \frac{A_N}{2} \right)^{\frac{3}{2} - 1}} \right) \]

\[ \frac{\sigma_{e}}{q_{L_A}} \frac{\Phi_{th_A}}{kT} \ln \left( \frac{\frac{1}{2} K_0^2 P_0^{-1} + \left( \frac{A_N}{2} \right)^{\frac{3}{2} - 1} }{\frac{1}{2} K_0^0 P_0^{-1} + \left( \frac{A_N}{2} \right)^{\frac{3}{2} - 1}} \right) \]

Since material A and material B share an interface as shown in Fig. 1, then the following substitutions may be made in eqn. [20]: \(P_{LA} = P_{0B} = P_L\), \(P_{0A} = P_0\) and \(P_{LB} = P_L\). Hence eqn. [20] yields:

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\[
\sigma_V = Z_V q \zeta_V \left( \frac{1}{\log P_1 - \log P_0} \int_{\log P_0}^{\log P_1} \frac{1}{V_A(P)} d(\log P) \right)^{-1}
\]

and for \( \{P: P_1 \leq P \leq P_L\} \) (from ref. 12)

\[
\sigma_V = Z_V q \zeta_V \left( \frac{1}{\log P_L - \log P_1} \int_{\log P_1}^{\log P_L} \frac{1}{V_B(P)} d(\log P) \right)^{-1}
\]

Also (from ref. 11)

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and the Nernst voltage is given by

$$
\Phi_{th_{A,B}} = \frac{1}{2q} \ln \left( \frac{P_1^{L_{A,B}}}{P_0^{L_{A,B}}} \right)
$$

Eqn. [21] gives the ratio of the thicknesses of the layers in the bilayer as a function of the pressure at the interface between the two materials and the oxygen-oxide interface. Significantly, if one of the materials is unstable in certain atmospheres then eqn. [21] allows us to set $P_1$ at a pressure that the material is stable. Having done that, one can determine the required relative thickness of the two materials to maintain the stability given the pressure gradient across the bilayer.

Eqn. [21] was plotted in Fig. 3 for an SDC/ESB bilayer and the plot shows that one can maintain the oxygen partial pressure at the bismuth oxide interface by using a suitable thickness ratio of SDC to ESB. As seen in the figure, as the temperature decreases, the thickness ratio, $L_{SDC}/L_{ESB}$, decreases at a given $P_1$. This is a result of the temperature dependence of the mixed ionic electronic conductivity of SDC. As the temperature goes down the electrolytic domain of SDC widens to lower $P_0^2$. Since electronic conductivity in SDC is smaller at lower temperatures, the potential drop through a given

**Figure 3.** Thickness ratio as a function of interfacial pressure at 1073 K and 773 K. Arrows indicate the Bi/Bi$_2$O$_3$ stability limits at the temperatures shown
thickness of SDC is greater resulting in a higher $P_1$. Therefore a greater relative thickness of ESB can be used. In addition, as the temperature goes down, the stability of bismuth oxide to low $P_02$ increases. That is, at 1073 K the Bi/Bi$_2$O$_3$ stability limit is at $P_{O_2} = \sim 10^{-13}$ atm. but at 773 K the stability limit is at $P_{O_2} = \sim 10^{-14}$ atm. These limits are indicated in Fig. 3, and indicate the minimum thickness ratio, $L_{SDC}/L_{ESB}$, that ESB would be thermodynamically stable while blocking electronic conduction and providing theoretical OCP. At 773 K this corresponds to a thickness ratio of $\sim 0.02$ and the electrolyte becomes essentially ESB. For a 100 $\mu$m thick electrolyte this corresponds to an ASR of 0.5 $\Omega$cm$^2$ at 500 $^\circ$C and for a total thickness of 10 $\mu$m, the ASR reduces to a mere 0.05 $\Omega$cm$^2$ at 500 $^\circ$C.

The transference number was determined from the ionic conductivity equations (eqns. [22] an [23]) and the electronic conductivity equations (10). For thickness ratios corresponding to a stable interfacial $P_{O_2}$ at 1073 K as well as 773 K, $t_i > 0.999$. This is a direct consequence of the ESB layer blocking electronic conduction from the SDC layer.

**CONCLUSION**

Bilayered electrolytes are feasible. In principle, they allow the fuel cell engineer to incorporate the best features of two materials and limit the effects of their negative attributes. In the case presented the desirable high ionic conductivities of SDC and ESB were combined favorably. And the undesirable electronic conduction in SDC and low oxygen pressure decomposition for ESB were shown to be controllable via operating temperature and thickness.

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