COMPARISON OF POWER DENSITIES AND CHEMICAL-POTENTIAL VARIATION IN SOFC’S WITH MULTI-LAYER AND SINGLE-LAYER OXIDE ELECTROLYTES

Prashant Soral*, Uday Pal* and Wayne L. Worrell**

*Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

**University of Pennsylvania
Philadelphia, PA 19104

ABSTRACT

Electrochemical transport in several multi-layer and single-layer mixed-conducting-oxide structures has been described by presenting a detailed calculation of the power density characteristics and the variation of the oxygen-chemical-potential gradient as a function of the external load and thickness of the oxide layers. Engineering implications of the analysis in terms of designing efficient as well as mechanically and chemically stable fuel cells with a layered electrolyte structure are also provided.

INTRODUCTION

Fuel cells possess significant advantages for power generation, including high efficiency and low emissions. The current solid oxide fuel cell (SOFC) technology is based on yttria-stabilized zirconia (YSZ) electrolytes operating at 1000°C in order to obtain good ionic conductivities (1). The high operating temperature has its drawbacks and lowering the operating temperature will lead to several benefits. However, electrolyte and electrode polarization become limiting factors at an operating temperature of 700 - 800°C. Several solid electrolytes, such as ceria- and bismuth-based oxides have much higher ionic conductivities than stabilized zirconia, and they would be excellent candidates to serve as electrolytes in low-temperature fuel cells. However, poor chemical stability of bismuth-based oxides and higher electronic conductivities of ceria-based oxides in reducing atmospheres preclude their use in solid oxide fuel cells, where one side of the electrolyte is exposed to a reducing gas (2). It is therefore intuitive to conceive of a multi-layer system of different conducting oxides where one can control the stability, optimize the transport properties, decrease the electrode polarization resistance and make the device more efficient. To design such a system it is essential to predict the chemical-potential variation, and the ionic and electronic fluxes through the layered structure, under an external load and chemical-potential gradient, so that one can tailor the thicknesses of the layers to optimize power density characteristics and be sure that the structure is chemically, mechanically and structurally stable. The purpose of the paper is to present a detailed calculation of the power density characteristics and the variation of oxygen-chemical-potential through several multi-layer and single-layer mixed-
conducting-oxide structures, as a function of the external load at 800°C and identify the most favorable electrolyte structure.

THEORY

The following parameters of the electrolyte structure shown in Fig. 1 are assumed to be known:

- thickness of each oxide layer, \( d_k \), where \( k \) varies from 1 to \( n \)
- oxygen partial pressure on both sides of the electrolyte structure \( P_{O_2}^{I} \) and \( P_{O_2}^{II} \), \( P_{O_2}^{I} > P_{O_2}^{II} \)
- ionic conductivity of each layer, \( \sigma_{o_2^->k} \) which in general is independent of \( P_{O_2}(x) \)
- electronic conductivity of each layer, \( \sigma_{e^->k} \) or \( \sigma_{h^->k} \) which generally changes with oxygen pressure as \( \sigma_{e^->k} = \sigma_{e^->k}^{0}P_{O_2}^{-1/n} \) or \( \sigma_{h^->k} = \sigma_{h^->k}^{0}P_{O_2}^{1/n} \), respectively
- the load consisting of external resistance, \( R_{ext} \).

By assuming no polarization occurs at the interfaces and that \( \sigma_{e^->k} \) dominates the electronic conductivity (which is generally the case), Yuan et. al. (3) have shown that the following equation holds:

\[
\frac{n\sigma_{o_2^->k}RT}{4J_{o_2^->k}F^2\ln} \left( \frac{RT\sigma_{o_2^->k}\ln\frac{P_{O_2}^{I}}{P_{O_2}^{II}}}{4F^2R_{ext}A} + \sigma_{o_2^->k}J_{o^->} + \frac{J_{o_2^->k}\sigma_{o_2^->k}\sum d_k}{R_{ext}A} \right) = d_k
\]

Since there is an equation for each oxide layer in the electrolyte, there are a total of \( n \) equations. The steady-state-oxygen-ion flux through the layers, \( J_{o_2^->} \), and the \( n-1 \) interfacial oxygen pressures \( P_{O_2}^{(k)} \) can be obtained by solving the system of equations described above. Once the oxygen flux has been computed, the voltage across the multi-layer electrolyte, \( E_{ext} \), the steady-state-electronic flux, \( J_{e} \), and the external current, \( I_{ext} \) can be calculated. Also, once we determine \( J_{o_2^->} \) and \( J_{e} \), the oxygen partial pressure variation in each oxide layer can be obtained. The reader is referred to (3) for further details.

OXIDE STRUCTURES CONSIDERED

Several authors have proposed the use of ceria as an electrolyte that offers high ionic conductivity. In this respect, Kudo and Obayashi (4) reported that gadolinia-doped ceria (GDC) at
750°C had the same ionic conductivity as calcia-stabilized zirconia at 1000°C. GDC has been selected as the electrolyte offering the low ionic resistance in the oxide structures considered here.

Barnett (5) has suggested that very thin, catalytically-active oxide layers on YSZ can be helpful in enhancing electrode reaction kinetics. Mogensen (6) has reported the use of doped ceria on the fuel side of a SOFC, where ceria would be heavily reduced, thus providing a good combination of electronic and ionic conductivity. Based on Han and Worrell’s work (7), a mixed conductor such as terbia-doped YSZ (YZTb) can be used on the cathode side. The transport properties and composition of the oxides constituting the electrolyte structures are listed in Table I.

Selection of the electrolyte on the basis of power density characteristics alone suggests the use of a thin electrolyte. Consideration of the mechanical strength of the electrolyte, on the other hand, favors a thick electrolyte structure. Oxide structures with two different thicknesses have, therefore, been considered - 10μm thick structures, representing thin electrolytes and 100μm thick structures, representing the thick, more durable electrolytes. The situations analyzed include the following:

**Multi-layer Structures:**
1. Cathode/ YZTb, 0.2 μm/ GDC, 100 μm/ YSZ, 2 μm/ Y2O3-doped ceria (YDC), 0.2 μm/ Anode; 2. Cathode/ YZTb, 0.2 μm/ GDC, 10 μm/ YSZ, 2 μm/ YDC, 0.2 μm/ Anode; 3. Cathode/ GDC, 100 μm / YSZ, 2 μm/ Anode; 4. Cathode/ GDC, 10 μm / YSZ, 2 μm/ Anode

**Single-layer Structures:**
1. Cathode/ YSZ, 100 μm/ Anode; 2. Cathode/ GDC, 100 μm/ Anode; 3. Cathode/ YSZ, 10 μm/ Anode; 4. Cathode/ GDC, 10 μm/ Anode

**DISCUSSION**

For the present analysis, it has been assumed that the cathode is exposed to an oxygen partial pressure of 0.1 atm (same order as air), $P_{O_2}^i$, and the anode is at an oxygen partial pressure of $10^{-19}$ atm (fuel atmosphere in a SOFC), $P_{O_2}^n$. It is desirable to have an open-circuit potential as close to the Nernst potential as possible, and a low ionic resistance. Table II compares these characteristics for the 100μm and 10μm thick electrolyte structures. It is apparent that the two-layer and the four-layer composite electrolytes combine the high open-circuit potential of the single-zirconia structure and the low ionic resistance of the single-ceria structure.

**Power Density Characteristics:**

This section discusses the performance of the electrolyte structures in terms of the power density characteristics. Expressions for $E_o$ and $I_{ox}$ (3) can be combined to yield:
Power Density = \frac{1}{R_{ee}} \left( \frac{RT}{4F} \ln \frac{P_{O_2}^I}{P_{O_2}^II} - J \sum_{k=1}^{n} \frac{d_k}{\sigma_{O^{2-}k}} \right)^2 \tag{2}

Figure 2 shows the variation of power density with external load for the 100μm and 10μm thick electrolyte structures. The power densities achievable for practical values of current densities are shown in Figure 3. Comparison with typical performance of single cells used in current SOFC stack designs (1) and with the behavior of a few electrolytes studied for low-temperature SOFC's indicates that the multi-layer electrolyte structures analyzed are superior in terms of power density characteristics. However, for the multi-layer electrolytes, the improvement in power density obtained over the single-layer YSZ structure, is significant only in case of the 100μm thick electrolytes.

Chemical Potential Variation:

In addition to the power density characteristics, the oxygen-chemical-potential variation in the electrolyte needs to be studied in order to predict the thermodynamic stability of the SOFC. In order to explain the oxygen-chemical-potential variation, we represent the oxygen potential at any point \(x_k\) within the \(k^{th}\) oxide in an electrolyte structure (Figure 1) as follows (3):

\[
P_{O_2}(x_k) = \frac{P_{O_2}^{k-1}}{\exp \left( \frac{4F}{RT} \left[ I_{ion} R_{ion}^{k} + (\phi_k^{k-1} - \phi_l^{k}) \right] \right)} \tag{3}
\]

where \(\phi\) represents the electrical potential of the compensating species, and \(R_{ion}^{k}\) is the ionic resistance of a single-layer structure of oxide \(k\), having thickness \(x_k\) (\(x_k\) varies from 0 to \(d_k\), see Figure 1). On integrating the expression for the electrical potential gradient that exists across an oxide layer, we have,

\[
\phi_k^{k-1} - \phi_l^{k} = -\frac{RT}{F} \ln \left( \frac{J_l \sigma_{O_2}^{k} \left( \frac{P_{O_2}^{k-1}}{P_{O_2}^{k}} \right)^{\frac{1}{4}} \left( \frac{p_{O_2}^{k-1}}{p_{O_2}^{k}} \right)^{\frac{1}{4}} + J_s \sigma_{\phi}^{k} \exp \left( \frac{J_s F^2}{\sigma_{\phi}^{k} RT} x_k \right) \right) \exp \left( \frac{J_l F^2}{\sigma_{O_2}^{k} RT} x_k \right) \tag{4}
\]

From (3), it can be seen that the oxygen-chemical-potential profiles across an electrolyte structure can be completely described by the variation of the ionic potential drop, \(I_{ion} R_{ion}^{k}\) and the electrical potential drop of the compensating species across the electrolyte.

We first analyze the behavior of the single-layer structures. Fig. 4 describes the effect of electrolyte structure, electrolyte thickness and external load on the ionic and electrical potential.
drops. The electrical potential drops are always more significant than the ionic potential drops and can be used to explain the relative positions of the oxygen-potential profiles. The thickness remaining constant, a decrease in the electrical potential drops on decreasing the load (Fig. 4a,4b) shifts the oxygen-potential profiles to higher partial pressures. For a given normalized thickness and external load, a decrease in the thickness of the single-layer electrolyte increases the electrical potential drop (Fig. 4c,4d) and therefore, lowers the oxygen-potential profile. Fig. 5 shows the effect of external load and electrolyte thickness on the oxygen-potential profiles for the single-layer YSZ and GDC electrolytes.

In case of the multi-layer structures, the interface $P_{O_2}$ depends upon the ionic and electrical potential drops that exist within the GDC layer (Fig. 6). For a constant electrolyte thickness, the increase in ionic potential drops on decreasing the load dominates over the decrease in electrical potential drops and this leads to a decrease in the $P_{O_2}$ at the GDC/YSZ interface. Fig. 7a shows this behavior for the 100µm thick two and four-layer structures. For the multi-layer structures, the ionic potential drops are important for low external loads and the electrical potential drops are more significant for high external loads (Fig. 6a-6b). Comparison of Figs. 4d and 6b indicates that, under a constant external load, the effect of electrolyte thickness on the behavior of the ionic potential drops across GDC in the four-layer structure is similar to that for the single-layer electrolytes. However, unlike the single-layer structures, a decrease in the thickness of the composite electrolyte leads to a decrease in the electrical potential drop at the GDC/YSZ interface. For a given $R_{ex}$, the combination of higher ionic and electrical potential drops in case of the 100µm electrolytes leads to a lower $P_{O_2}$ at the GDC/YSZ interface when compared to the 10µm electrolytes (Figure 7b).

As regards to the thermodynamic stability of the SOFC, the two-layer and the four-layer electrolytes considered are found to be suitable for use under the conditions analyzed. It is clear that in case of the multi-layer structures, in order to ensure a high oxygen partial pressure at an interface such as the GDC/YSZ interface in the present case, both the ionic and electrical potential drops at the interface should be kept low. This can be accomplished by the use of an oxide having a high ionic and electronic conductivity on the cathodic side and an oxide having a low electronic conductivity on the anodic side. The importance of the ionic potential drop or the electrical potential drop in determining the interface $P_{O_2}$ depends upon the external load.

Consideration of the power density characteristics alone indicates that either the 10µm thick single-layer YSZ electrolyte or the 100µm thick multi-layer structures are suitable for use in low-temperature SOFC's. Among the multi-layer structures, the four-layer electrolyte offers the added advantage of enhanced exchange reaction kinetics, due to the presence of the mixed-conducting-electrolyte layers in contact with the electrodes. The thin YZTb and YDC (0.2µm) layers in contact with the electrodes do not significantly affect power density values or the oxygen-chemical-potential profiles, as can be seen by comparing the characteristics for the two and four-layer structures in Figures 3 and 7. The choice will then depend upon factors such as the mechanical strength of the electrolyte, which favor the 100µm thick composite structure, as it has a greater thickness and therefore a greater durability.
Besides the thermal expansion coefficient mismatch between YSZ and GDC there may be problems associated with the utilization of YDC, adjacent to YSZ, on the anode side. The lattice expansion of ceria on reduction to non-stoichiometric CeO$_{2x}$ can make the YDC layer spall off (10). The problem may be solved by interchanging the YSZ and GDC layers in the multi-layer electrolyte. The chemical and mechanical compatibility between YZTb and YSZ would be an added advantage (7). The power density characteristics for the structure - YZTb, 0.2µm/YSZ, 2µm/GDC, 100µm/YDC, 0.2µm - were therefore analyzed. For the external loads considered, the power density characteristics are essentially independent of the sequence in which the YSZ and GDC layers are present in the multi-layer electrolytes. However, as can be seen from Figure 8, the YZTb/YSZ/GDC/YDC structure may not be suitable due to the low oxygen partial pressures that will be encountered in the GDC layer.

CONCLUSION

Transport phenomena involving oxygen ions and electronic carriers in two different multi-layer oxide structures and two different single-layer oxide structures, under the influence of external load and oxygen-chemical-potential gradient are described. The analysis is used to examine the variation of oxygen-chemical-potential through the layers and the power densities of the structures. It is shown that the power density characteristics and the oxygen partial pressure variation across an electrolyte structure are influenced by several factors, including the external load, the electrolyte thickness, the number of oxides constituting the electrolyte and the intrinsic transport properties of each oxide layer. Based on considerations of electrical efficiency, thermodynamic stability, mechanical durability and exchange reaction kinetics, it appears that a multi-layer structure utilizing mixed-conducting oxide layers of appropriate thickness in contact with the electrodes could serve as an electrolyte in low-temperature (800°C) solid oxide fuel cells.

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Fig. 1 Schematic of a multi-layer structure consisting of ‘n’ different mixed conducting oxides.

Fig. 2 Power density characteristics of the electrolyte structures at 800°C.

Fig. 3 Power density characteristics for the 100μm and 10μm thick electrolyte structures for practical current densities.
Fig. 4 Effect of external load and electrolyte thickness on the ionic and electrical potential drops across the single-layer YSZ and GDC electrolytes.

Fig. 5 Effect of external load and electrolyte thickness on the oxygen-chemical-potential distribution across the single-layer YSZ and GDC electrolytes at 800°C.
Fig. 6 Effect of external load and electrolyte thickness on the ionic and electrical potential drops across GDC in the four-layer electrolyte structures.

Fig. 7(a) Effect of $R_{ex}$ on oxygen-chemical-potential variation across the 100μm thick two and four-layer structures.

Fig. 7(b) Effect of electrolyte thickness under a constant external load of 1Ω on oxygen-chemical-potential variation across the four-layer electrolyte structure.

Fig. 8 Oxygen-chemical-potential variation across the multi-layer structure - YZTb, 0.2μm/YSZ, 2μm/GDC, 100μm/YDC, 0.2μm - at 800°C.

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Table I Composition and conductivities of the oxides constituting the electrolyte structures analyzed (conductivity values are listed at 800°C).

| Oxide Structure | Composition | Ionic Conductivity (S/cm) | Electronic Conductivity (S/cm) |
|-----------------|-------------|---------------------------|-------------------------------|
| YZTb(7) | Yttria (8 m/o) stabilized zirconia + 30 m/o terbia | $\sigma_{\text{O}^+} = 0.0025$ | $\sigma_{\text{e}} = 2.36 \times 10^{-3} \times P_{O_2}^{1/4}$ |
| GDC(6) | $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ ($x = 0.1$) | $\sigma_{\text{O}^+} = 0.074$ | $\sigma_{\text{e}} = 10^{-4} \times P_{O_2}^{-1/4}$ |
| YSZ(8) | Yttria (8 m/o) stabilized zirconia | $\sigma_{\text{O}^+} = 0.025$ | $\sigma_{\text{e}} = 10^{-12} \times P_{O_2}^{-1/4}$ |
| YDC(9) | ($\text{CeO}_2)_{0.95} (\text{Y}_2\text{O}_3)_{0.05}$ | $\sigma_{\text{O}^+} = 0.05$ | $\sigma_{\text{e}} = 1.4 \times 10^{-4} \times P_{O_2}^{-1/4}$ |

Table II Comparison of the open circuit potential and the ionic resistance for the $\approx 100\mu$m and $\approx 10\mu$m thick electrolyte structures at 800°C.

| Thickness | Oxide Structure | Single Zirconia | Single GDC | Two Layer | Four Layer |
|-----------|----------------|-----------------|------------|-----------|------------|
| $\approx 100\mu$m | Open Circuit Voltage (V) | $\approx 0.96$ | 0.91 | $\approx 0.96$ | $\approx 0.96$ |
|             | $R_i = \sum \frac{d_i \Omega}{\sigma_i} / \text{cm}^2$ | 0.397 | 0.135 | 0.143 | 0.151 |
| $\approx 10\mu$m | Open Circuit Voltage (V) | $\approx 0.96$ | 0.91 | $\approx 0.96$ | $\approx 0.96$ |
|             | $R_i = \sum \frac{d_i \Omega}{\sigma_i} / \text{cm}^2$ | 0.04 | 0.013 | 0.021 | 0.03 |