ELECTROCHEMICAL VAPOR DEPOSITION OF YTTRIA-STABILIZED ZIRCONIA FILMS

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ABSTRACT

Tubular solid oxide fuel cells employ yttria-stabilized zirconia electrolyte film as an oxygen ion conductor at high temperatures. These yttria-stabilized zirconia electrolyte films are deposited by an electrochemical vapor deposition (EVD) process. The electrochemical transport of oxygen ions during the EVD process is analyzed by measuring the film growth as a function of EVD reaction time; the film growth is found to be parabolic with time. Wagner's transport theory for parabolic growth and the defect model for yttria-stabilized zirconia have been used to calculate the average electronic transport number and the partial electronic conductivity of the electrolyte film. The analysis of the data revealed that the electrolyte film growth is controlled by diffusion of electrons. It is also shown that the electrochemical transport that occurs during EVD of the electrolyte is similar to the phenomena of oxygen semi-permeability wherein electrons migrate from the low oxygen partial pressure side to the high oxygen partial pressure side and oxygen ions migrate in the reverse direction maintaining charge neutrality.

1. INTRODUCTION

Solid oxide fuel cells employ yttria-stabilized zirconia electrolyte to operate as an oxygen ion conductor at high temperatures (1,2). A schematic cross-section of the tubular solid oxide fuel cell is shown in Figure 1. In this design, the cell components viz. air and fuel electrodes, electrolyte and cell interconnection, are deposited as thin layers over a porous calcia-stabilized zirconia tube; this porous tube functions both as a structural member supporting other cell components and as a functional member allowing oxygen and/or air to permeate through its pores to the air electrode. Table 1 summarizes the materials and fabrication processes for the various cell components (2,3).

For optimum cell performance, the yttria-stabilized zirconia electrolyte must be free of porosity so as not to allow gases to permeate from one side of the electrolyte to the other; it should be uniformly thin.
to minimize ohmic loss; and it should have high oxygen ion conductivity with transport number for oxygen ions close to unity and a transport number for electrons as close to zero as possible (4). Therefore, an understanding of the growth mechanism of the yttria-stabilized zirconia electrolyte film is necessary to identify the rate controlling step and to determine the conditions for depositing electrolyte films with desired properties. In this paper, the growth of thin films of yttria-stabilized zirconia electrolyte by an electrochemical vapor deposition process is described and analyzed.

2. EXPERIMENTS AND RESULTS

The electrochemical vapor deposition process for depositing thin films of different cell components including the electrolyte has been discussed previously (5-8). Briefly, to deposit yttria-stabilized zirconia electrolyte films, chlorides of zirconium and yttrium are volatilized in a predetermined ratio and passed over outer surface of the porous air electrode. Oxygen mixed with steam at a predetermined ratio is passed inside the porous calcia-stabilized zirconia tube over which the porous air electrode is deposited. In the first stage of the reaction, designated as the chemical vapor deposition (CVD) stage, molecular diffusion of oxygen, steam and metal chlorides occurs through the porous air electrode and these react to fill the air electrode pores with the yttria-stabilized zirconia electrolyte according to the following reactions:

\[
2 \text{MeCl}_y + y \text{H}_2\text{O} = 2 \text{MeO}_{y/2} + 2y \text{HCl} \]  \tag{1}

\[
4 \text{MeCl}_y + y \text{O}_2 = 4 \text{MeO}_{y/2} + 2y \text{Cl}_2 \]  \tag{2}

where Me is the cation specie (zirconium and/or yttrium); and y is the valency associated with the cation.

The temperature, the pressure and the different gas flow rates are so chosen that the above reactions are thermodynamically and kinetically favored.

During the second stage of the reaction after the pores in the air electrode are closed, electrochemical transport of oxygen ions maintaining electroneutrality occurs, through the already deposited electrolyte in the pores, from the high oxygen partial pressure side (oxygen/steam) to the low oxygen partial pressure side (chlorides). The oxygen ions upon reaching the low oxygen partial pressure side react with the metal chlorides and the electrolyte film grows in thickness. This second stage of the reaction is termed the electrochemical vapor deposition (EVD) stage.

The forementioned two stages of reaction, viz. the CVD stage and the EVD stage, responsible for the growth of the yttria-stabilized zirconia...
electrolyte film, are schematically shown in Figure 2. In this deposition process, the flows of the metal chloride vapors are maintained above a critical level to eliminate any gas phase control of the EVD reaction. Furthermore, the ratio of yttrium chloride to zirconium chloride is so chosen that the electrolyte deposited contains about 10 mole% yttria; this composition ensures the highest oxygen ion conductivity in yttria-stabilized zirconia \((9,10)\).

For an analysis of the growth of the yttria-stabilized zirconia film, films were deposited at \(1473^\circ\text{K}\) for different EVD reaction times. The equilibrium calculations indicated that at this temperature the oxygen partial pressures inside and outside the air electrode tube were about \(1.0 \times 10^{-4} \text{ atm}\) and \(4.3 \times 10^{-18} \text{ atm}\), respectively. A representative electrolyte film is shown in the metallographic cross-section in Figure 3. The film thicknesses were measured metallographically, and the square of the film thickness is plotted in Figure 4 as a function of the EVD reaction time. This plot was found to be a straight line indicating that the electrolyte film growth is parabolic with time. The rate of growth of the electrolyte film, \(dx/dt\), can therefore be expressed as:

\[
\frac{dx}{dt} = \frac{K'}{x} \quad \text{or} \quad x^2 = 2 K' t
\]

where \(x\) is the electrolyte film thickness in cm;
\(t\) is the reaction time in seconds;
and \(K'\) is the parabolic rate constant in cm\(^3\)/sec.

From the slope of the straight line in Figure 4, \(K'\) is calculated as being equal to \(0.37 \times 10^{-8} \text{ cm}^3/\text{sec}\).

3. GROWTH MECHANISM OF THE YTTRIA-STABILIZED ZIRCONIA ELECTROLYTE FILM

In this section, Wagner's transport theory for parabolic growth is used to identify the rate controlling step during the EVD growth of the electrolyte and the rate controlling transport parameters are estimated. Next, the defect structure of the yttria-stabilized zirconia is described and applied to the film growth data to determine the partial electronic conductivity of the electrolyte as a function of oxygen partial pressure. Based on this analysis, the actual electrochemical transport reactions that occur during EVD growth of the electrolyte are elucidated. Finally, the possible use of such growth rate measurements as a function of temperature to arrive at a model for the electrolyte EVD growth rate is outlined.

(a) Rate Controlling Step in the EVD Growth of the Yttria-Stabilized Zirconia Electrolyte:

It was found in the previous section that the EVD growth of the
electrolyte is parabolic with time; the parabolic rate constant, \( K' \), being
equal to \( 0.37 \times 10^{-8} \text{cm}^3/\text{sec} \). This parabolic rate constant can also be
expressed in terms of the rate of equivalents of oxygen consumed in the
reaction as follows:

\[
K' = K \gamma V_{eq}
\]

where \( K \gamma \) is the parabolic specific rate constant in equiv./cm-sec;
and \( V_{eq} \) is the equivalent volume of oxygen in ZrO\(_2\)-10\% Y\(_2\)O\(_3\)
in cm\(^3\)/equiv.

Substituting the values of \( K' \) and \( V_{eq} \) in Equation [4], one gets:

\[
K' = 0.7 \times 10^{-9} \text{ equiv/cm-sec}
\]  

Using Wagner’s transport theory for parabolic growth (11), the
specific rate constant, \( K\gamma \), can be written as:

\[
K\gamma = \frac{R T}{2 |Z| F^2} \left\{ \frac{P_{O_2}^n}{P_{O_2}^0} \right\} \frac{(\sigma_1 + \sigma_2) \sigma_3}{(\sigma_1 + \sigma_2 + \sigma_3)} \ d \ln P_{O_2}
\]

where \( R \) is the gas constant (1.987 cal/deg-mole);
\( T \) is the EVD reaction temperature (1473\(^\circ\)K);
\( Z \) is the valence of oxygen (2);
\( F \) is the Faraday constant (23060 cal/volt-mole);
\( \sigma_1, \sigma_2 \) and \( \sigma_3 \) are the partial cationic, anionic and electronic
conductivities of the electrolyte, respectively, in \( \Omega^{-1}\text{-cm}^{-1} \);
and \( P_{O_2}^n \) and \( P_{O_2}^0 \) are oxygen partial pressures at the electrolyte-
chloride and the electrolyte-oxygen/steam interfaces (4.3 \( \times \) 10\(^{-18}\) and 1.0 \( \times \) 10\(^{-4}\) atm, respectively).

It is known from previous work (10,12) that in yttria-stabilized
zirconia, at oxygen partial pressures from 1 atm to about 10\(^{-20}\) atm, the
partial electronic conductivity \( (\sigma_3) \) and the partial cationic conductivities
\( (\sigma_1) \) are negligible as compared to the partial anionic (oxygen ion)
conductivity \( (\sigma_2) \). Therefore:

\[
\sigma_2 \approx \sigma_1 + \sigma_2 \approx \sigma_1 + \sigma_2 + \sigma_3
\]
Substituting Equation [7] in Equation [6]:

$$K_\gamma = \frac{R \cdot T}{2 \cdot \ln P_0^0} \int_{P_0'}^{P_0^0} \sigma_3 \, d \ln P_0^0$$

[8]

In order to calculate the electronic transport number of the electrolyte film, $t_s$, from Equation [8], we need to substitute $\sigma_3$ with the following expression:

$$\sigma_3 = t_s \left( \sigma_1 + \sigma_2 + \sigma_3 \right) = t_s \sigma_\ell$$

[9]

where $\sigma_\ell$ is the total conductivity of the yttria-stabilized zirconia electrolyte, which is virtually independent of oxygen partial pressure from 1 atm to about $10^{-22}$ atm between 873°K and 1573°K [10,12].

Substituting Equation [9] in Equation [8]:

$$K_\gamma = \frac{R \cdot T \cdot \sigma_\ell}{2 \cdot \ln P_0^0} \int_{P_0'}^{P_0^0} t_s \, d \ln P_0^0$$

[10]

or

$$\tilde{t}_s = \frac{2 \cdot K_\gamma \cdot \ln P_0^0}{R \cdot T \cdot \sigma_\ell \left( \ln P_0^0 - \ln P_0^p \right)}$$

[11]

where $\tilde{t}_s$ is the average electronic transport number of the electrolyte film.

Using the average value of $\sigma_\ell$ at 1473°K for ZrO$_2$-10% Y$_2$O$_3$ as equal to 0.3 0-cm$^{-1}$ (9,10,12,18), $\tilde{t}_s$ is calculated to be $0.6 \times 10^{-4}$.

From Equation [8], it is clear that the partial electronic conductivity ($\sigma_3$) controls the parabolic specific rate constant, $K_\gamma$; in other
words, the EVD growth of the electrolyte film is controlled by the
electronic transport through the electrolyte with the rate controlling
average electronic transport number being \(0.6 \times 10^{-4}\).

(b) Determination of Partial Electronic Conductivity of
Yttria-Stabilized Zirconia:

In this section, the defect structure of the yttria-stabilized zirconia
is combined with the EVD growth data to determine the partial electronic
conductivity of the yttria-stabilized zirconia electrolyte film. In low oxygen
pressures, the defect equilibrium reaction of yttria-stabilized zirconia with
oxygen can be expressed as (14-16):

\[
0(0)^0 = \frac{1}{2} \text{O}_2 + V(0)^{\cdot \cdot} + 2 e'
\]  

\[
K_{12} = \frac{P_{0_2}^{1/2} [V(0)^{\cdot \cdot}] [e']^2}{[0(0)^0]}
\]

where \(K_{12}\) is the equilibrium constant for Reaction [12];
\(O(0)^0, V(O)^{\cdot \cdot}\) and \(e'\) are neutral oxygen, oxygen vacancy with
two positive charge and free electron, respectively;
and \([\ldots]\)'s are the respective concentrations.

It is known that in yttria-stabilized zirconia, the concentration of
the majority defect, oxygen vacancies, is much larger than the
concentration of the minority defect, free electrons (4,17). Hence, the
concentration of oxygen vacancies, \([V(O)^{\cdot \cdot}]\), is not affected by Reaction
(12) and is independent of the oxygen partial pressure, \(P_{0_2}\). Equation
[13] can therefore be written as:

\[
[e'] = K_e P_{0_2}^{-1/4}
\]

where \(K_e\) is a thermally activated constant.

If the free electron mobility is concentration-independent, then the
partial free electronic conductivity, \(\sigma_e\), is proportional to the concentration
of electrons, \([e']\), and

\[
\sigma_e = \sigma_e^0 P_{0_2}^{-1/4}
\]
where \( \sigma_e^o \) is the partial electronic conductivity at \( P_{O_2} = 1 \text{ atm} \) and it is also a thermally activated constant.

Under high to medium oxygen pressures, the defect equilibrium reaction of yttria-stabilized zirconia with oxygen can be written as (14-16):

\[
\frac{1}{2} O_2 + V(0)' = O(0)^0 + 2 h'
\]  

\[ [16] \]

\[
K_{16} = \frac{[O(0)^0][h']^2}{[V(0)'] P_{O_2}^{1/2}}
\]

where \( K_{16} \) is the equilibrium constant for Reaction [16];

\[ [17] \]

and \( h' \) and \( [h'] \) are free electron hole and its concentration, respectively.

Similar derivation as done above for low oxygen pressure conditions can be performed on Equations [16] and [17], and the free electron-hole conductivity, \( \sigma_h \), under high to medium oxygen pressures can be expressed as:

\[
\sigma_h = \sigma_h^o P_{O_2}^{1/4}
\]

\[ [18] \]

where \( \sigma_h^o \) is the free-electron hole conductivity at \( P_{O_2} = 1 \text{ atm} \) and is also a thermally activated constant.

In the oxygen partial pressure range of the EVD experiments (between \( 10^{-4} \) and \( 10^{-18} \text{ atm} \)), the partial free electronic conductivity, \( \sigma_e \), is much greater than the partial free electron-hole conductivity, \( \sigma_h \) (14,15). Therefore, one can write:

\[
\sigma_3 = \sigma_e + \sigma_h \approx \sigma_e
\]

\[ [19] \]

Substituting Equation [19] in Equation [8]:

\[
K_f = \frac{RT}{2 |z| F^2} \left[ \frac{P_{O_2}^{*}}{P_{O_2}^0} \right] \sigma_e d \ln P_{O_2}
\]

\[ [20] \]
Substituting for $\sigma_e$ from Equation [15] in Equation [20]:

$$K_7 = \frac{R T}{2 |Z| F^2} \left( \sigma_e^o P_{O_2}^{-1/4} \right) d \ln P_{O_2}$$

or

$$K_7 = \frac{4 R T \sigma_e^o}{2 |Z| F^2} \left( P_{O_2}^{-1/4} - P_{O_2}^{-1/4} \right)$$

Using the value of $K_e$ from Equation [5] and solving Equation [22], we find that the partial electronic conductivity at 1473°K and 1 atm oxygen pressure, $\sigma_e^o$, is equal to $0.6 \times 10^{-8}$ atm(0-cm)$^{-1}$; this value of $\sigma_e^o$ compares favorably with $\sigma_e^o$ calculated by earlier workers [14]. Substituting this value of $\sigma_e^o$ in Equation [15], the partial free electronic conductivity at 1473°K can be expressed as:

$$\sigma_e = 0.6 \times 10^{-8} P_{O_2}^{-1/4}$$

Similar EVD growth rate measurements at other temperatures can be used for the determination of the partial electronic conductivity of yttria-stabilized zirconia as a function of temperature.

(c) Electrochemical Transport During EVD Growth of the Yttria-Stabilized Zirconia Electrolyte:

It has been shown above that the migration of electrons controls the EVD growth of the electrolyte. From Equation [14], it is obvious that the migration of electrons in the electrolyte film occurs from the chloride side (low oxygen partial pressure side) to the oxygen/steam side (high oxygen partial pressure side). Furthermore, the majority defects which are also the compensating defects for the electrons in yttria-stabilized zirconia are oxygen vacancies, (Equation [12]). Therefore, the migration of electrons in the electrolyte must be accompanied by the migration of oxygen vacancies in the same direction maintaining electroneutrality. The migration of oxygen vacancies can also be viewed as the migration of oxygen ions, $O^-$, in the opposite direction, i.e., from the oxygen/steam side (high oxygen partial pressure side) to the chloride side (low oxygen partial pressure side). This electrochemical transport can be expressed in the form of general reaction equations as shown below:
The EVD growth rate measurements, described in this paper, were obtained only at one temperature (1473°K). However, such growth rate measurements can be made as a function of temperature to model the growth of yttria-stabilized zirconia films by electrochemical transport. For instance, the values of $\sigma_e^0$ can be obtained as a function of temperature from film growth rate measurements at different temperatures. Since $\sigma_e^0$ is a thermally activated constant, it can be expressed as:

$$\sigma_e^0 = A \exp \left( -\frac{E_e}{RT} \right)$$

where $A$ is a constant related to the total concentration of electrons; and $E_e$ is the activation energy for free electronic conduction.

Plotting $\ln \sigma_e^0$ as a function of $(1/T)$, $E_e$ can be estimated from the slope of the line and $A$ can be estimated from the intercept at $1/T = 0$.

Now, substituting Equation [26] in Equation [22]:

$$K = \frac{4 R T A \exp(-E_e/R T) (P_t^{1/4} - P_{t0}^{1/4})}{2 \ |Z| F^2}$$

This equation can be used to predict the parabolic growth of the yttria-stabilized zirconia film at any given temperature and oxygen partial pressures employed during EVD process.

4. SIMILARITY BETWEEN EVD GROWTH ANALYSIS AND OXYGEN SEMI-PERMEABILITY FLUX ANALYSIS

Oxygen semi-permeability in an electrolyte is defined by the flux of oxygen ions that occurs through the electrolyte when the electrolyte is kept in an oxygen potential gradient. Kleitz (14) showed that when the electrolyte is kept in an oxygen potential gradient, a flux of free electrons or electron holes streams continuously through the electrolyte; it is electrically compensated by a counter migration of oxygen ions. The net effect is a flux of oxygen through the electrolyte. In the oxygen partial pressure range where the free electron conductivity is dominant, the oxygen semi-permeability flux, $J_{O_2}$ is given by the expression (14,18):

$$2 \text{MeCl}_y + y O^2 = 2 \text{MeO}_{y/2} + y Cl_2 + 2y e'$$

$$y H_2O + 2y e' = y O^2 + y H_2$$

$$y H_2O + 2y e' = y O^2 + y H_2$$
\[ J_{0,2} = \frac{RT}{4F^2L} (\sigma_e' - \sigma_e'') \]  \[ 28 \]

where \( \sigma_e' \) and \( \sigma_e'' \) are the partial free electronic conductivities in the low oxygen partial pressure side and the high oxygen partial pressure side of the electrolyte, respectively; and \( L \) is the thickness of the electrolyte.

Combining Equation [15] and Equation [22], the parabolic specific EVD growth rate constant of the electrolyte, \( K_\gamma \), can be written as:

\[ K_\gamma = \frac{4RT}{2|Z|F^2} (\sigma_e' - \sigma_e'') \]  \[ 29 \]

Substituting the value of \( Z \) (2 for oxygen):

\[ K_\gamma = \frac{RT}{4F^2} (\sigma_e' - \sigma_e'') \]  \[ 30 \]

\( K_\gamma \) can also be expressed in terms of flux of oxygen through the electrolyte film as:

\[ \frac{K_\gamma}{\Delta x} = \frac{\dot{n}}{A} = 4J_{0,2} \]  \[ 31 \]

where \( \dot{n}/A \) is the flux of oxygen equivalents expressed in equiv/cm²-sec; \( \Delta x \) is the thickness of the electrolyte film; and \( J_{0,2} \) is the flux of oxygen through the growing electrolyte film.

Combining Equations [31] and [29], one can write:

\[ J_{0,2} = \frac{K_\gamma}{4\Delta x} = \frac{RT}{4F^2\Delta x} (\sigma_e' - \sigma_e'') \]  \[ 32 \]

It is seen that the expressions for flux obtained in Equation [32] from the EVD growth analysis and in Equation [28] from oxygen semi-permeability analysis are similar. This suggests that the EVD growth of the yttria-stabilized zirconia electrolyte films can also be interpreted in terms of the phenomena of oxygen semi-permeability.
5. CONCLUSIONS

The growth of yttria-stabilized zirconia electrolyte films, by the electrochemical vapor deposition (EVD) process, is found to be parabolic with time and the rate controlling step in the EVD process is identified to be the electronic transport (diffusion of electrons) through the electrolyte film. The average electronic transport number of the electrolyte during EVD at 1473°K is calculated to be $0.6 \times 10^{-4}$. Using the defect structure of yttria-stabilized zirconia and the transport theory for parabolic growth, the partial electronic conductivity of the EVD grown electrolyte has been estimated as a function of oxygen partial pressure. It is shown that such growth rate measurements as a function of temperature can be used to predict a model for the electrolyte EVD growth as a function of temperature and oxygen partial pressures. Finally, it is demonstrated that the electrochemical transport that occurs during EVD is similar to the phenomena of oxygen semi-permeability wherein electrons migrate from the low oxygen partial pressure side to the high oxygen partial pressure side and oxygen ions migrate in the reverse direction maintaining electroneutrality.

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TABLE 1
Cell Components, Materials and Fabrication Processes

| Component      | Material              | Fabrication Process                      |
|----------------|-----------------------|------------------------------------------|
| Support Tube   | ZrO$_2$(CaO)          | Extrusion-sintering                       |
| Air Electrode  | La(Sr)MnO$_3$         | Slurry coat-sintering                     |
| Electrolyte    | ZrO$_2$(Y$_2$O$_3$)   | Electrochemical vapor deposition         |
| Interconnection| La(Mg)CrO$_3$         | Electrochemical vapor deposition         |
| Fuel Electrode | Ni-ZrO$_2$(Y$_2$O$_3$)| Slurry coat-electrochemical vapor deposition |

Figure 1 - Schematic cross-section of the tubular solid oxide fuel cell.
Reaction Stage I (CVD)
Molecular Diffusion

Chlorides of Zr and Y

Air Electrode
Substrate

Oxygen and Steam

Air Electrode
Substrate

Reaction Stage II (EVD)
Electrochemical Transport

Chlorides of Zr and Y

Air Electrode
Substrate

Oxygen and Steam

Figure 2 - Two stages of reaction occurring during the deposition of the yttria-stabilized zirconia.
Figure 3 - Metallographic cross section of the EVD grown yttria-stabilized zirconia film over porous air electrode substrate.

Figure 4 - Square of electrolyte film thickness versus deposition time at 1473°K.

\[ K' = 0.37 \times 10^{-8} \text{ cm}^2/\text{sec} \]