ELECTROCHEMICAL VAPOR DEPOSITION: THEORY AND EXPERIMENT

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ABSTRACT

Electrochemical Vapor Deposition (EVD) refers to the growth of a metal oxide layer due to the presence of an electrochemical potential gradient. In the simplest case the oxide growth can be modeled with the Wagner oxidation theory for metals. In this work the theory for the growth of ionically conducting $Zr(Y)O_{2-x}$ will be discussed along with the growth of electronically conducting $LaCrO_3$. Experimental parameters important to EVD growth along with results of the EVD grown films of stabilized zirconia will be presented.

INTRODUCTION

Due to the high operating temperatures the material demands upon Solid Oxide Fuel Cell (SOFC) components are quite stringent. Typically, the materials used in a SOFC are stabilized zirconia as the electrolyte, nickel-zirconia cermet as the anode, strontium doped lanthanum manganite as the cathode, and doped lanthanum chromite as the interconnection material. The electrodes are porous (25-40%) and can be simply fabricated with slurry coating techniques [1,2]. The electrolyte and interconnect are difficult to fabricate because they need to be gas tight, yet thin (30 - 50 microns), and mechanically stable. Due to the high volatility of CrO_3 [3,4] the densification of $LaCrO_3$ into thin layers is a more demanding challenge than the fabrication of the electrolyte. Several techniques have been investigated for the fabrication of these thin layers such as radio frequency sputtering, tape casting, plasma spraying, hot isostatic pressing, and low temperature CVD [5-13]. None of these methods, to date, have equaled the performance of electrochemical vapor deposition for depositing thin gas tight

sition is the key technology used by Westinghouse for making thin layers of the electrolyte as well as the interconnection material $LaCrO_3$. In this paper the theory and experiment underlying electrochemical vapor deposition will be discussed.

THEORY

Electrochemical vapor deposition (EVD) is a technique which was introduced by Isenberg for forming metal-oxide films upon porous substrates [14,15]. The first step in film formation proceeds by a normal CVD type reaction.

A porous substrate separates the reactant metal chlorides from a mixture of O_2 (or H_2) and steam. Deposits of the metal oxide form in the pores of the substrate and eventually lead to pore closure. Once pore closure is complete the reactants are no longer in direct contact. Film growth proceeds due to the large oxygen partial pressure gradient which exists across the substrate resulting in the diffusion of oxygen anions from the H_2O/O_2 side to the metal chloride side. The second step, scale growth, proceeds due to the reaction of oxygen anions with metal chlorides:

Step 2, Scale growth:

Film growth can be rate limited by a) gas diffusion, b) surface kinetics, or c) charge transport in the film. When the rate of film growth is governed by solid state diffusion the kinetics are similar to the Wagner oxidation of metals. In Wagner oxidation the rate of scale growth is inversely proportional to the oxide thickness, L [16,17].

$$\frac{dL}{dt} = K \frac{1}{L} \quad (4)$$

The integrated form of equation 4 yields the parabolic rate law

$$L^2 = 2Kt + C_0 \quad (5)$$

where C_0 is a constant of integration.

Figure 1: Transport processes occurring during EVD growth.

The diffusion processes which take place during EVD growth are shown schematically in Figure 1. Since diffusion through the oxide layer is rate limiting the reactions at the interface are considered to be rapid such that thermodynamic equilibria are established at the oxide / oxygen interface and the metal/oxide interface. The partial pressure of oxygen (P_{O_2}) on the H_2O/O_2 interface is determined by the equilibrium between the gases. Similarly the oxygen partial pressure on the metal chloride side (P_{O_2}') is determined by the equilibrium between $MeCl_x$, Cl_2 , and MeO_2 . The large oxygen partial pressure gradient across the film results in a flux of ions. Electroneutrality is preserved by an opposing electronic flux so that at steady state no net current flows.

Thus, the sum over the cationic, anionic, electron and hole currents is zero.

In terms of ionic flux the growth rate can be expressed as [17]:

$$\frac{dL}{dt} = \frac{2}{z} J_i \frac{mw}{\rho} \quad (6)$$

where z is the total electron charge on the cations, ρ is the density, and mw the molecular weight of the growing oxide.

Electrolyte: For an ionic conductor such as $Zr(Y)O_{2-x}$ the general expression for the ionic flux is given by [17]:

$$J_i = - \left[\frac{kT}{se^2} \int_{P_{O_2}}^{P_{O_2}'} \sigma_{e,i} d \ln P_{O_2} \right] \frac{1}{\Delta L} \quad (7)$$

where k is Boltzmann's constant, T is absolute temperature, e the charge on an electron, and $\sigma_{e,i}$ the sum of the electron and hole conductivities. From equations 4, 6, 7 and the Nernst-Einstein relation the rate constant for film growth can be derived yielding:

$$K = \frac{1}{16} \left[\int_{P_{O_2}}^{P_{O_2}'} [h'] D_h - \int_{P_{O_2}'}^{P_{O_2}'} [e'] D_e \right] d \ln P_{O_2} \quad (8)$$

where $[h']$ and $[e']$ represent the mole fraction of holes and electrons and D_h and D_e their respective diffusion coefficients. The pressure at which the electronic conductivity changes from n type to p type is represented by P_{O_2}' . The rate constant is integrated in parts to take into account the variation in $[h']$ and $[e']$ with the partial pressure of oxygen.

The variation of $[h']$, $[e']$, D_h and D_e with T and P_{O_2} has been studied by Weppner [18,19]. This information can be used to numerically calculate the EVD film growth of $Zr(Y)O_{2-x}$ [24]. For 10 m/o $Zr(Y)O_{2-x}$ the rate of film growth is calculated using this model to be on the order of 6 microns/hour at 1300 K in agreement with experimental observations [22].

Interconnect: The interconnector material, doped $LaCrO_3$ is known to be a p-type conductor [25]. For a p-type

conductor the general expression for the ionic flux is given by [17]:

$$J_1 = - \left[\frac{kT}{8e^2} \int_{P_{O_2}}^{P_{O_2}''} \sigma_1 d \ln P_{O_2} \right] \frac{1}{\Delta L} \quad (9)$$

where σ_1 is the ionic conductivity. In LaCrO_3 the mobility of oxygen is much greater than the mobilities of either cation. Therefore, the ionic conductivity of cations can be neglected in these calculations. From equations 4, 6, 9 and the Nernst-Einstein relation the rate constant for film growth can be derived yielding [17]:

$$K = - \frac{D_{V_O}}{6} \int_{P_{O_2}}^{P_{O_2}''} [V_O] d \ln P_{O_2} \quad (10)$$

where $[V_O]$ represents the mole fraction of oxygen ion vacancies and D_{V_O} its diffusion coefficient. The pressure dependence of V_O is determined by the defects present in doped LaCrO_3 . A discussion of defects present in doped LaCrO_3 is given by Flandermeyer [25]. There has been no work to date reporting D_{V_O} in LaCrO_3 . This information is necessary to complete the modeling of the EVD growth for the interconnect. Estimates of D_{V_O} from oxygen permeation studies [26] and EVD growth rates [20] indicate that the ionic conductivity of Mg doped LaCrO_3 is so low, that very high temperatures (1600 K) are necessary to achieve EVD deposition rates of 3 microns/hour.

Whether experimentally EVD film growth is rate limited by solid state diffusion is not entirely clear. A parabolic growth rate has been reported for both Zr(Y)O_{2-x} and LaCrO_3 [20-22] film growth. Yet under different experimental conditions a linear growth has also been observed [14]. It is possible that the film growth is a mixture of two mechanisms beginning with linear growth and changing to parabolic. In-situ measurements of the rate of film growth, varying P_{O_2} and T , are necessary to accurately determine the exact mechanism involved in EVD of metal oxide films.

EXPERIMENT

Figure 2: Schematic of EVD reactor for growth of Zr(Y)O_{2-x} .

The EVD reactor is shown in Figure 2. An important design criterion is the separation of the reactor into two isolated compartments: the $\text{H}_2\text{O}/\text{O}_2$ (high P_{O_2}) compartment, and the metal chloride (low P_{O_2}) compartment. It is essential for EVD film growth that a large O_2 chemical potential difference exists across the substrate. Once pore closure is complete the two compartments must not be in contact, thus, the sealing and mounting of the substrate is critical. In our work a non-porous Al_2O_3 seal is used to mount an Al_2O_3 substrate (open porosity 40%, pore size 5-10 microns) upon the inner Al_2O_3 tube of the reactor.

In general most of the lanthanide and actinide chlorides are very hygroscopic. The presence of H_2O in the metal chloride compartment lowers the O_2 chemical potential gradient which slows down or can halt the EVD process altogether. Thus the metal chloride source must be dry. This can be achieved by prior drying of the metal chloride powders. Alternatively, dry chlorides can be formed through in-situ chlorination of the metals or their corresponding oxides. All three methods have been explored in this laboratory and we have found that the least corrosive and least expensive manner is simply the use of the metal chloride powders which have been dried in HCl at

400 °C prior to use.

Since film growth is rate limited by solid state diffusion the composition of the film is directly related to the vapor pressure of the respective chlorides. Thus the composition of the film can be controlled by the temperature of the sublimation beds in the reactor. For instance, to obtain a film of 10 m/o $Zr(Y)O_{2-x}$ the YCl_3 sublimation bed was held at 1230 K and the $ZrCl_4$ was held at 475 K. Argon was used as a carrier gas for the metal chloride vapors. On the opposite side of the substrate a mixture of O_2 in steam was passed. Films were grown under reduced pressure (10 - 20 torr) and temperatures between 1200-1375 K. The composition of the film was confirmed through the peak shift in the XRD patterns [17].

RESULTS

Figure 3: Cross section of EVD grown $Zr(Y)O_{2-x}$.

Electrolyte : A cross section of an EVD grown film of $Zr(Y)O_{2-x}$ is shown in Figure 3. A small portion of the Al_2O_3 substrate is observable at the bottom of the micrograph. In the second layer one observes the build up and closure of the pores with the metal oxides. This layer grew in four hours to a thickness of 40 microns, yielding an approximate growth rate of 8 microns/hour. The composition corresponded to 10 m/o $Zr(Y)O_{2-x}$.

Two types of surface morphology have been observed in EVD growth of $Zr(Y)O_{2-x}$: a faceted type surface, and a cauliflower type surface [23,24]. Extensive studies by Carolan and Michaels varying in reactant concentration and deposition temperature indicated that the morphology was determined by the deposition temperature: with the faceted surface dominating at temperatures below 1300 K, and cauliflower surface dominating at temperatures above 1300 K. The difference in morphology can be explained by a change in relative rates of film growth and surface reconstruction or possibly due to the thermodynamic instability of a surface species at high temperatures [23]. We have modeled the solid state diffusion in $Zr(Y)O_{2-x}$ as a function of temperature and dopant concentration [24]. Calculations show that at temperatures below 1300 K both the diffusion of electrons and holes contribute to the overall kinetics for film growth. At temperatures above 1300 K only diffusion of electrons plays a significant role. It is possible that this change in mechanism contributes to the different morphologies observed for the EVD growth of $Zr(Y)O_{2-x}$.

In light of lowering the operating temperature of SOFC's it is of interest to study the growth of better conducting electrolytes. Although scandium is by far the best candidate initial work indicates that $ScCl_3$ is too corrosive for practical use in a CVD reactor. Therefore, our current efforts are focused on making EVD films with yttrium doped zirconia and co-doped yttrium, yttrium films.

Interconnect: The interconnect material used in SOFC's must have a high electronic conductivity, be stable in both oxidizing and reducing ambients, have a thermal expansion coefficient (TEC) comparable to $Zr(Y)O_{2-x}$, and have

no destructive phase transitions within the operating temperature range. Undoped $LaCrO_3$ has a phase transition at 240 °C changing from orthorhombic (TEC = $6.7 \times 10^{-6}/^{\circ}C$) to rhombohedral (TEC = $9.2 \times 10^{-6}/^{\circ}C$). Dopants (Al, Sr, Mg) are generally added to change the conductivity, TEC, or phase transition. Both Sr, and Al suppress the orthorhombic / rhombohedral phase transition and adjust the TEC to that of $Zr(Y)O_{2-x}$ (TEC = $10.3 \times 10^{-6}/^{\circ}C$).

Addition of Mg does little to the TEC or the phase transition [29]. Nonetheless, the current interconnect used in the Westinghouse concept is Mg doped $LaCrO_3$.

Early reports on the EVD growth of doped LaCrO_3 indicated a problem with the incorporation of dopants into the film [27].

The driving force for scale growth is the formation of the oxide. The difficulty encountered in incorporating other dopants into the LaCrO_3 can be that the corresponding chloride is more stable than the oxide. Thus, an excess of the chloride must be added in order to shift the equilibrium to form the oxide [27]. In principle the experiment for growth of LaCrO_3 is the same.

However, controlling the composition and doping is more difficult. The high operating temperatures also pose a problem for in-situ growth of these materials on SOFC components. There has been very little work to date on the CVD growth of ternary perovskites such as LaCrO_3 . In our laboratory we are focusing on EVD growth as well as alternative CVD methods to lower the deposition temperature of LaCrO_3 thin films.

CONCLUSION

In the modeling of the EVD growth of $\text{Zr(Y)}\text{O}_{2-x}$ it is important to consider the changes in $[e']$, and $[h']$ with Po_2 . At high temperatures only electrons need to be considered in EVD growth. At low temperatures the presence of holes at the metal/chloride interface may play an important role in the observed faceted morphology of EVD grown $\text{Zr(Y)}\text{O}_{2-x}$. For the interconnect LaCrO_3 ionic diffusion is rate limiting EVD film growth and very high temperatures (1600 K) are necessary for moderate growth rates of 3 microns/hour. Information on oxygen diffusion in doped LaCrO_3 is necessary for a more thorough understanding of the EVD growth.

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