PEROVSKITE BASED PROTECTIVE COATINGS
FOR SOLID OXIDE FUEL CELL METALLIC INTERCONNECTS

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ABSTRACT

Recent improvements in solid oxide fuel cell (SOFC) performance through the use of anode supported (thin electrolyte) cells has allowed the typical operating temperature to be lowered to 800°C or less. At this operating temperature, lower cost Ni or Fe based metallic interconnects become a potential replacement for the brittle and expensive chromite based ceramic interconnects that were used at higher cell operating temperatures. However, the use of metallic interconnects is not without problems. Typically, the alloys that are under consideration contain Cr at levels such that $\text{Cr}_2\text{O}_3$ is the native oxide grown at elevated temperatures. On one hand, this is preferable since $\text{Cr}_2\text{O}_3$ has a higher electronic conductivity than alternative protective scales, such as $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$. On the other hand, in the cathode environment $\text{Cr}_2\text{O}_3$ can form a number of vapor species that contribute to cell degradation by contamination of the cathode/electrolyte interface. The coating of chromium containing alloys with $\text{LaCrO}_3$ based perovskites is a potential method of decreasing the contamination effects of Cr vapor species. In this study, magnetron sputtering was used to deposit $\text{LaCrO}_3$ and Ca doped $\text{LaCrO}_3$ thin films. The coated samples were heated in air at various temperatures, and the changes in the film properties as a result of annealing are reported. In addition, annealing in a reducing environment (5% $\text{H}_2$ in $\text{N}_2$) was also studied as a method of controlling the reaction pathway for crystallization of the “as deposited” films. Both the substrates and $\text{LaCrO}_3$ films were characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction, and atomic force microscopy. Area specific resistance (ASR) measurements were also made on the coated samples after the initial annealing step and after 100 hours at 800°C in air.

INTRODUCTION

Solid oxide fuel cell (SOFC) technology holds great potential for future electrical energy production (1). This is not only because SOFCs are more efficient than current commercial methods of electricity production, but also because they emit lower levels of...
pollutants than these alternative methods. In addition, because of their high operating temperature relative to other types of fuel cells, they are ideal for combined cycle SOFC/turbine applications, where efficiency may approach 70-80%. At typical operating temperatures (700-1000°C), internal reforming of hydrocarbon fuels using their excess heat is also a possibility. Despite these very attractive attributes, SOFC have yet to be widely commercialized. The impediments to commercialization are related to a number of cell and stack materials issues. For instance, in planar type SOFC, reliable and effective seals that can be thermally cycled, are stable relative to other SOFC components, and will last the expected 40,000 hrs, have yet to be developed. Another example is the typical Ni/YSZ anode materials which, if not properly designed, degrades due to Ni particle sintering, or may build up carbon deposits if the anode gas mixture is not correctly chosen. In this paper, work designed to solve another material issue, the development of low cost and effective interconnects for planar SOFC, is discussed.

Until recent years the operating temperatures of the typically SOFC was 1000°C. This temperature was required to achieve high ionic conductivity of the YSZ electrolyte. However, with the advent of thin electrolyte SOFC (10-20 μm), operating temperatures of 700-800°C suffice to give equivalent conductivities to the thicker electrolyte SOFC. The lowering of the temperature needed for cell operation meant that a number of lower cost materials became potential replacements for previously used materials. One such opportunity was the replacement of the LaCrO₃ based ceramic interconnects with low cost high temperature alloys (2). Besides lower cost, the high temperature alloys also have the added benefit of higher mechanical strength, and higher thermal conductivity. These are particularly useful for planar designs where interconnects provide mechanical support, and the higher thermal conductivity gives a more uniform temperature distribution in the fuel cell stack. The best candidate high temperature alloys are chromia formers. This is because chromia has at least acceptable electronic conductivity relative to other native oxides of high temperature alloys. However, chromia scales are not as resistant to oxide growth at elevated temperatures as the alumina formers, and thus over the long term the oxide scales continue to grow and increase resistance. In addition, in the severe SOFC cathode environment, volatile Cr species can migrate and contaminate the cathode/electrolyte interface, causing degradation of cell performance. Thus, while the high temperature chromia forming alloys are the best replacement candidates for LaCrO₃ based SOFC interconnects, additional improvement in corrosion resistance and a solution to the chromia volatility issue remain to be addressed.

A number of methods may be used to improve the protective scale properties of Cr containing alloys targeted as potential metallic interconnect materials. The addition of reactive elements such as La, Ce, Zr and Y can be used to improve oxide scale adhesion and slow scale growth rate (3,4). The presence of small amounts of these elements in the alloy, or added to the surface, is thought to change the scale growth direction from one in which Cr is the primary diffusing species to one in which oxygen diffusion inward is the main factor controlling scale growth. This leads to better scale adhesion and slower growth rates for the oxide scale. Electrical conductivity of the scales can also be improved by the addition of various dopants. Some of these may be the same elements that lead to the reactive element effect (5), while others serve only to improve the electrical conductivity (6) with little effect on scale adhesion or growth characteristics. Recently, interest has focused on changing the native oxide that forms on a high temperature interconnect alloy to one that is both conductive and is more...
thermodynamically stable than the Cr$_2$O$_3$ scale. This can be accomplished by controlling the amount of Mn, or other minor constituents added to the alloy. Addition of the correct amount of Mn leads to the formation of MnCr$_2$O$_4$ spinel as the outer most surface oxide. This spinel layer is a relatively good electronic conductor and does reduce the Cr evaporation. However, degradation of cell performance continues to be a problem (7), despite the lowered Cr evaporation rate. The problem is that the Cr preferentially deposits in the electrochemically active region near the cathode electrolyte interface during passage of current through the cell (8). This non-equilibrium deposition of Cr at the worst possible place in the cell (triple phase boundary) means that much lower Cr species vapor pressures must be achieved.

A number of research groups are investigating the use of coatings to improve conductivity of scale and reduce chromia volatility for high temperature alloy interconnects (9-11). Typically, perovskites such as calcium or strontium doped lanthanum chromites have been investigated, although spinel phases are also being considered. In general, these coatings lead to improved resistance to scale growth, improved long term conductivity of the cathode/interconnect interface, and reduced chromia volatility. However, despite the improved performance of the metallic interconnects when coated with protective layers, in those cases where real cell tests are performed with the coated interconnects, degradation still occurs. Clearly, additional improvement is necessary.

In this study, structural evolution of magnetron sputtered LaCrO$_3$ and Ca doped LaCrO$_3$ films as a function of annealing temperature and annealing environment is reported. The films are characterized by powder x-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM). In addition, area specific resistance (ASR) measurements of the films as a function of annealing environment are reported. The general applicability of the results found here is then discussed.

**EXPERIMENTAL**

Thin films were deposited by RF and DC magnetron sputtering onto Cr-containing stainless steel (SS) substrates. High-chromium ferritic Fe-23Cr steel coupons (SS 446) with the following chemical composition: Fe (73 wt%), Cr (23 wt%), Mn (1.5 wt%), Ni (0.3 wt%), Si (1.0 wt%), Al (1.0 wt%), C (0.2 wt%) were used as a substrate material. The stainless steel substrates (10x10x5 mm) were polished with a diamond spray to a mirror surface. The substrates were coated in the rf sputtering mode under $8 \times 10^{-3}$ torr Ar$^+$. EDS analysis of the "as-deposited" film composition gave an approximate La/Cr ratio of 56/43 at%. After sputtering, the SS sample with deposited film was annealed at 500, 600, and 800°C for 1 h using a controlled heating rate of 30°C/min. After 1 h at the annealing temperature, the samples were cooled at the same rate as during the heating. The samples were annealed both in air and in forming gas (5 wt% H$_2$/95 wt% N$_2$).

A Siemens x-ray diffractometer was used to determine the crystal structure of LaCrO$_3$ films. SEM analysis was done using a JEOL JSM-840A, and AFM using a JEOL JSPM-4210 scanning probe microscope.

ASR data were collected following the method described by Goodenough(12). Electrodes were applied using Pt paint (SPI 04990-AB) and Pt mesh. Currents ranging from 1 mA to
50 mA were used, and samples were tested in the temperature range of 600-900°C. ASR is defined by \( ASR = \rho L = RA \), where \( \rho \) = resistivity, \( L \) = film thickness, \( R \) is measured resistance, and \( A \) is the area of the electrodes. In the geometry described by Goodenough however, the measured voltage drop is due to two oxide layers. Thus the resistance measured is \( R_T = R_{A1} + R_{A2} \) where \( R_T \) is the total measured resistance, and \( R_{A1} \) and \( R_{A2} \) are the resistances of the areas of oxide covered by electrodes \( A1 \) and \( A2 \) respectively. From the definition of ASR we can write that \( R_{A1} = \rho L_1/A1 \), and \( R_{A2} = \rho L_2/A2 \), then \( R_T = \rho L_1/A1 + \rho L_2/A2 \). If it is then assumed that \( L \) is the same for both sides of the sample, and that \( A1 = A2 \), then \( R_T = 2\rho L/A \), where \( A \) is now the area of one electrode. Then solving for \( \rho L \) we have \( ASR = \rho L = AR_T/2 \).

RESULTS AND DISCUSSION

SEM and XRD data on amorphous LaCrO\(_x\) films deposited by RF magnetron sputtering on stainless 446 and then heated to 500, 600, and 700°C are shown in Figure 1 and Figure 2 respectively. In the “as deposited” state and after heating to 530°C in air the samples are amorphous to x-ray diffraction. EDX analysis of the sample heated to 530°C showed an increase in the oxygen content of the film, which accounts for the slight amount of morphology difference between the “as deposited” film and that heated to 530°C that can be seen in the SEM image. After heating the samples further to 600°C, XRD detected the formation of the monazite type LaCrO\(_4\) phase and small amount of La\(_2\)CrO\(_6\) phase. Again after this transformation there is additional morphology change in the sample. Finally, XRD data then indicate that heating to 700°C leads to the formation of the targeted LaCr\(_2\) perovskite phase. In SEM image D, there is a considerable increase in porosity of the film associated with the transformation from monazite to perovskite phase. The

Figure 1. SEM images of LaCrO\(_x\) magnetron sputtered films. A- “as deposited”; B- heated in air to 530°C; C- heated in air to 600°C; and D- heated in air to 700°C.
molecular volume and theoretical density of LaCrO$_4$ are 82.30 Å$^3$ molecule$^{-1}$ and 5.15 g/cm$^3$ respectively, and for LaCrO$_2$ these values are 58.58 Å$^3$ molecule$^{-1}$ and 6.77 g/cm$^3$ respectively (13). Clearly, it is loss of oxygen and the change in density that leads to increase in porosity. This is an unfortunate result however, since denser films are needed to both block oxidation of the substrate and prevent Cr evaporation more effectively.

In an attempt to prevent the monazite phase from forming, and thus prevent the formation of porosity, additional amorphous magnetron sputtered films were annealed in forming gas (5% H$_2$ in N$_2$ balance) instead of air. Recall that the initial composition of the “as deposited” films was deficient in oxygen as measured by EDX analysis. Therefore, the additional oxygen needed to supply the monazite lattice, is coming from the atmosphere present during annealing. It is recognized that phase transformations in amorphous materials are strongly dependent on the composition of the amorphous material (14). This is due to relative ability of different phases to undergo the local organization of atoms needed to nucleate that particular phase. For structures whose composition is far from that of the amorphous material, more extreme localized deviations in composition need to occur before nucleation can occur. However for compounds whose stoichiometry is relatively close to the composition of the amorphous material, only small localized deviations need to occur. The result is that the nucleation activation energy for the compound closest to the composition of the amorphous material will be at a minimum and then the formation of that compound will be favored. Therefore, by limiting the oxygen content of the films to only the oxygen present in the amorphous film, when the sample is annealed, the formation of the monazite phase will be frustrated by the lack of oxygen, and the formation of the perovskite favored, since its stoichiometry will be closest to the film composition.

Figure 2. X-ray diffraction data of LaCrO$_x$ sputtered films, after being heated in air to the temperature listed in each scan.
Figure 3 shows AFM images of amorphous LaCrO₃ magnetron sputtered films that were annealed in air (left) and in forming gas (right). Note that the grains size of the sample annealed in forming gas is considerably smaller than that for the air annealed sample. Also, notice that the porosity of the air annealed sample, that was clearly noticeable in the SEM images, is not as noticeable in the AFM images, although, some pores can be seen. Clearly, annealing in forming gas has significantly altered the morphology of the films.

In order to clearly identify if indeed the monazite phase is avoided, in-situ high temperature XRD data on films annealed in air and forming gas were collected. Figure 4 shows the in-situ high temperature XRD data for a Ca doped LaCrO₃ film (La₀.₇Ca₀.₃CrO₃) heated in air. As expected the LaCrO₃ monazite phase is formed first. Also note that, in this case, additional intermediate phases are formed (here La₂CrO₆ and CaCrO₄). Figure 5 shows the same XRD experiment carried out on an identical film sample, except now the atmosphere contains hydrogen. In this case, only the desired perovskite phase is formed. Also of interest is the fact that the CaCrO₄ phase that was still present in the air annealed sample, even at high temperature, does not form.

As one measure of the ability of LaCrO₃ films to carry out their function as interconnect, area specific resistance measurements were made. Table 1 summarizes the results of these measurements for La₀.₇Ca₀.₃CrO₃ and LaCrO₃ films heated both in air and forming gas. As a reference, it is expected that the ASR value of an effective SOFC interconnect should be less than 0.1 ohms-cm² after 40,000 hours of stack operation. In the data shown in Table 1 note that all samples initially start out with an acceptable ASR value; however, the ASR values continue to increase as the films oxidize.

|                | La₀.₇Ca₀.₃CrO₃ | La₀.₇Ca₀.₃CrO₃ | LaCrO₃   | LaCrO₃   |
|----------------|----------------|----------------|----------|----------|
|                | air 800°C      | forming gas    | air 800°C| forming gas|
| After formation| .011 Ω-cm²     | .014 Ω-cm²     | .044 Ω-cm²| .013 Ω-cm²|
| 1000 Hrs at    | .036 Ω-cm²     | .44 Ω-cm²      | 0.11 Ω-cm²| 0.21 Ω-cm²|
| 800°C          |                |                |          |          |
Figure 4. In-situ high temperature x-ray diffraction data collected on a Ca doped \( \text{LaCrO}_x \) magnetron sputtered film annealed in air.

Figure 5. In-situ high temperature x-ray diffraction data collected on a Ca doped \( \text{LaCrO}_x \) magnetron sputtered film annealed in forming gas.
after further annealing, only the Ca doped sample initially treated in air is below the targeted 0.1 ohm-cm². It is interesting that for the LaCrO₃ films shown in Table 1 the ASR value for the sample annealed in forming gas was much lower just after the initial treatment. However, after an additional 100 hours at 800°C in air the ASR of the sample pretreated in air had the lowest ASR value among the samples tested.

To try and understand the ASR results, cross sections of these test specimens were made and SEM images collected, these are shown in Figure 6. The sample represented by the left image was initially treated in air and the sample shown in the right image was initially treated in forming gas. EDX analysis was also done on these cross sections; the designations of the various layers are based on this EDX data. Several things are fairly obvious in these images. First, for the sample annealed in forming gas, the LaCrO₃ appears to be thinner, suggesting a denser film. Also, the forming gas treated sample shows considerably less Cr₂O₃, evidence that denser films do indeed prevent oxidation of the underlying metal more effectively. Also note, that both samples show significant SiO₂ formation. However, they differ in the morphology of the SiO₂ layer. The sample annealed initially in forming gas has a much more continuous layer of silica relative to the air annealed sample. This may be the reason for the faster decay in ASR performance for the samples annealed in forming gas, that is, the dense film decreases the rate of oxidation, and that slower oxide growth then favors the formation of a continuous SiO₂ layer. Of course, this does not explain why the Ca doped sample annealed in air is the best performer with respect to long term ASR. The presence of the CaCrO₄ phase might be one explanation for this, but more research is required to confirm this result. Further analysis of the Ca doped samples is currently underway. Also, it is fairly obvious from these results that metal substrates with lower Si content will be necessary to avoid formation of insulating SiO₂ layers.

Figure 6. Cross sectional SEM images of LaCrO₃ films on SS446 substrates. The sample on the left was annealed at 800°C in air, and the sample on the right was annealed at 800°C in forming gas. Both samples were subsequently heated in air at 800°C for 100 hours.

CONCLUSIONS

Dense LaCrO₃ and La₉₋₇Ca₇CrO₃ films can be obtained from amorphous magnetron sputtered precursor coatings by limiting the oxygen available in the initial heat treatment used to crystallize the films. When this is done, the formation of a less dense intermediate phase (LaCrO₄ monazite phase) is avoided. Thus the voids created by the transition from

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the monazite to the perovskite do not form. The subsequent dense film prevents oxidation of the metal substrate more effectively. However, the presence of Si in the metal substrate, and thus the formation of SiO₂, degrades the electrical properties (ASR) to unacceptable levels. The effect on ASR by the formation SiO₂ is made worse by the denser films, since the morphology of the underlying silica layer is more continuous. The best performing film with respect to ASR values, was a Ca doped LaCrO₃ film that was initially annealed in air. The reason this sample has the best ASR value is unclear, but may have to do with the presence of CaCrO₄ as a minor constituent of the film.

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