EVALUATION OF METALLIC INTERCONNECTS FOR USE IN INTERMEDIATE TEMPERATURE SOFC

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ABSTRACT

Foil samples of Haynes 230 and 430 stainless steel were coated with thin layers of Mn and La metal, oxidized in air and humidified hydrogen atmospheres at 800°C for various periods of time, and evaluated for use as metallic interconnects in planar SOFC. A Mn-coating on the interconnects promoted the formation of the spinel phase (Mn, Cr)3O4 while suppressing the formation of Cr2O3 during oxidation. The area specific resistance (ASR) of the oxide layer on the Mn-coated Haynes 230 samples (~0.24 Ωcm² at 800°C) was significantly less than that formed on the uncoated sample (~1.2 Ωcm² at 800°C). The oxide layer formed on the La-coated Haynes 230 consisted primarily of the perovskite phase La(Cr, Mn)O3. The ASR of the perovskite oxide layer formed on the La-coated Haynes 230 was an order of magnitude lower than the oxide layer, primarily Cr2O3, formed on uncoated Haynes 230. Planar SOFC stacks operated with coated interconnects delivered double the maximum power and exhibited half the total stack resistance as compared to stacks operated with uncoated Haynes 230 interconnects.

INTRODUCTION

In planar solid oxide fuel cell (SOFC) stacks, the individual cells are typically connected in series with interconnect plates located between adjacent cells. The interconnect plates have the dual role of providing electronic continuity between cells as well as serving as barriers that separate the fuel in the anode chamber from the oxidant in the cathode chamber. For SOFCs that operate at temperatures below 800°C, interconnects constructed from metal plates or foils are attractive due to their mechanical strength, ease of fabrication, and potential low cost. The metallic interconnect should exhibit good oxidation resistance as well as high electronic conduction in both anodic (pO2 < 10⁻² atm) and cathodic (pO2 ~ 0.21 atm) environments at operating temperatures < 800°C. Potential alloy candidates for use as interconnect materials include Ni and Cr-based superalloys, such as Haynes 230 or Inconel 718, or stainless steels such as ferritic SS 430.
At temperatures below 800°C, the oxidation kinetics of these Cr-base alloys is sufficiently slow to warrant their use as interconnects (1, 2). However, in both oxidant (air) and fuel (humidified hydrogen) atmospheres, the primary oxide that forms on these alloys is \( \text{Cr}_2\text{O}_3 \), which is a poor electronic conductor (3-6). The formation of this resistive oxide layer on the metallic interconnects increases the total stack resistance. In addition, Cr evaporation from \( \text{Cr}_2\text{O}_3 \) can be substantial enough to poison some SOFC cathodes (7, 8). One approach to improving the electronic properties of the oxide layer that forms on the metallic interconnect is to suppress the formation of the resistive \( \text{Cr}_2\text{O}_3 \) phase and promote the formation of a more conductive phase. This can be accomplished by depositing thin films of various metals onto the interconnect surface before oxidation (9). Upon heating, the deposited metal will oxidize, react with the chromium from the interconnect alloy, and subsequently form Cr-based oxides other than \( \text{Cr}_2\text{O}_3 \). For example, a coating of Mn metal on an alloy containing Cr will result in the formation of the more conductive spinel phase \( (\text{Mn, Cr})_2\text{O}_4 \), while a coating of La metal will promote the formation of the perovskite phase \( \text{LaCrO}_3 \) (10-11).

**EXPERIMENTAL**

Commercially available 430 ferritic stainless steel (SS 430) and the Ni-Cr superalloy Haynes 230 were purchased in foil form with a thickness of 5 mils. One inch square sample coupons were cut for deposition, oxidation, and conductivity studies. Interconnects for four inch square planar SOFC stacks were fabricated from the alloy foils by laser machining. Thin layers of manganese and lanthanum were deposited onto the metallic foils with a Denton SJ/20C Electron Evaporator System (EES). The thickness of the Mn coatings was measured \textit{in situ} with an Inficon XTC/2 crystal monitor and after deposition with a Dektak surface profilometer. Coated and uncoated sample coupons of Haynes 230 and SS 430 were oxidized in both flowing air and humidified hydrogen (\( \text{pH}_2\text{O} \sim 0.07 \text{ atm} \)) at 800°C for various periods of time. The oxide layers were evaluated with optical and scanning electron microscopy (SEM) after oxidation. In addition, the as-deposited metal coatings and oxides formed after oxidation were analyzed with x-ray diffraction (XRD) and electron dispersive spectroscopy (EDS) in an SEM.

The electronic conductivity of the oxide coating was measured as a function of temperature in both air and humidified hydrogen atmospheres with a two-probe technique. The conductivity fixture was spring loaded ensuring constant pressure and minimizing changes in contact resistance with changing temperature. Platinum foils and wires were used as leads and baselines were measured to account for the resistance of the leads. Coated and uncoated metallic foil interconnects were evaluated in 4-cell planar SOFC stacks with an active area of \( \sim 25 \text{ cm}^2 \) per cell. The stacks were operated at 800 to 850°C with air as the oxidant and humidified hydrogen as the fuel. The current-voltage and power characteristics of stacks with uncoated and coated interconnects were measured and compared. In addition, the resistance of coated and uncoated interconnects in the stack was measured \textit{in situ} and monitored with time. Lead wires were connected to both the metallic interconnects and to collector screens placed on both sides of the interconnect. The voltage drop across the cells and interconnects was measured as a function of stack current, from which the resistances of the individual cells and interconnects were estimated.
RESULTS AND DISCUSSION

Haynes 230 and SS 430 sample coupons were coated on both sides with 2000 angstroms of Mn and oxidized in humidified hydrogen and dry air for various periods of time at 800°C. X-ray diffraction (XRD) patterns of the as-received Haynes 230, the Mn-coated Haynes 230, and oxidized Mn-coated Haynes 230 after 4 days in hydrogen are shown in Figure 1. The as-deposited coating is metallic Mn as shown in Figure 1(b). Upon heat up and during the initial stages of oxidation at 800°C, the Mn metal readily oxidizes to form MnO. Over a period of time at 800°C, the MnO phase subsequently reacts with the Cr in the Haynes 230 and slowly converts to the spinel phase MnₙCr₃₋ₙO₄. As shown in Figure 1(c), the oxide coating formed on the Mn-coated Haynes 230 after 4 days at 800°C in humidified hydrogen consists primarily of MnO and the spinel phase MnₙCr₃₋ₙO₄. The XRD pattern shows no indication of Cr₂O₃, which is the primary phase that forms on uncoated Haynes 230. Similarly, XRD patterns of the as-received SS 430, Mn-coated SS 430, and oxidized Mn-coated SS 430 after 4 days in humidified hydrogen at 800°C are shown in Figure 2. The oxide layer formed on the Mn-coated SS 430 after 4 days in hydrogen at 800°C consists mainly of MnO and the spinel phase (Mn, Cr, Fe)₂O₄. The oxide layer formed on uncoated SS 430 oxidized in the same conditions was comprised of the corundum phase (Fe, Cr)₂O₃ and the spinel phase (Fe, Cr)₂O₄ (12). The Mn coating suppresses the corundum phase and promotes the formation of the spinel phase as seen in Figure 2(c). Mn coated samples of Haynes 230 and SS 430 oxidized in air at 800°C exhibited similar results with the formation of MnO and Mn-based spinels and not the corundum phases Cr₂O₃ and (Fe, Cr)₂O₃.

![Figure 1. XRD patterns of (a) Haynes 230, (b) Mn coated Haynes 230, and (c) Mn coated Haynes 230 oxidized for 4 days in humidified hydrogen at 800°C.](image-url)
Figure 2. XRD patterns of (a) 430 stainless steel, (b) Mn coated 430 stainless steel, and (c) Mn coated 430 stainless steel oxidized for 4 days in humidified hydrogen at 800°C.

Figure 3. XRD patterns of (a) Haynes 230, (b) La coated Haynes 230, (c) La coated Haynes 230 oxidized for 6 hours in air, and (d) La coated Haynes 230 oxidized for 7 days in air.

Haynes 230 sample coupons were coated with 2000 angstroms of La on both sides and oxidized in humidified hydrogen and dry air for various periods of time at 800°C. X-ray diffraction (XRD) patterns of the as-received Haynes 230, the La-coated Haynes 230, and the oxidized La-coated samples after 6 hours and 7 days in air at 800°C are shown in Figure 3. As shown in Figure 3(b), the coating as deposited by electron beam deposition consisted of both La metal and La₂O₃. During heat up and initial stages of oxidation, the La metal readily oxidized to form La₂O₃ as shown in Figure 3(c). After oxidation for 7 days at 800°C in air, the primary phase that forms is the perovskite La(Cr,Mn)O₃ as...
shown in Figure 3(d). Oxidation of La-coated Haynes 230 in humidified hydrogen for periods up to 3 weeks yielded primarily La2O3 with only trace amounts of the LaCrO3 perovskite phase. Although LaCrO3 is thermodynamically stable in hydrogen at 800°C, the kinetics of conversion of La2O3 to the perovskite phase may be slow in hydrogen and may require longer times for complete conversion.

The electronic conductivity of the oxide coatings was measured as a function of temperature in both air and humidified hydrogen atmospheres. The area specific resistance (ASR), measured in air as a function of temperature, of the oxide layers on uncoated and Mn-coated Haynes 230 and SS 430 sample coupons after oxidation in hydrogen for 4 days at 800°C is shown in Figure 4. The oxide coatings exhibit semiconducting behavior with electronic conductivity increasing with increasing temperature. The electronic conductivity of the oxide layer on the Mn-coated Haynes 230 is higher than that on the uncoated samples in the temperature range 300 to 800°C, as shown in Figure 4(a). At 800°C, the area specific resistance of the oxide layer on the uncoated Haynes 230 is ~ 1.17 Ωcm² while that for the Mn-coated Haynes 230 is significantly lower with a value of ~ 0.24 Ωcm². The decrease in ASR with Mn coating is attributed to the formation of the more conducting MnCr3-xO4 spinel phase and the suppression of the highly resistive Cr2O3 phase. However, the ASR of the oxide layer formed on Mn-coated SS 430 is higher than that formed on uncoated SS 430 in the temperature range 400 to 800 °C, as shown in Figure 4(b). At 800°C, the ASR of the two oxide layers are similar with a value of 0.59 and 0.71 Ωcm² for the uncoated and Mn-coated samples, respectively. The low ASR of the uncoated SS 430 sample is due to the presence of (Fe, Cr)2O3 in the oxide layer which primarily consists of (Fe, Cr)2O3 and

![Figure 4. Area specific resistance of the oxide on the metallic interconnect as a function of temperature after four days of oxidation in humidified hydrogen at 800°C for (a) uncoated and Mn coated Haynes 230 and (b) uncoated and Mn coated 430 stainless steel. Measurements conducted in air.](image)
(Fe, Cr)₃O₄ (10, 12). The area specific resistance of the oxide layer on Mn-coated Haynes 230 and SS 430 measured in both air and humidified hydrogen atmospheres is shown in Figure 5. In both cases, the oxide layers, which consist primarily of MnO and a Mn-based spinel phase, exhibit lower area specific resistance in hydrogen than in air at temperatures below 800°C. The electrical conductivity of uncoated and La-coated Haynes 230 after oxidation at 800°C in air for 7 days was measured in air. The area specific resistance of the oxide layers as a function of inverse temperature is shown in Figure 6. In the temperature range 300 to 800°C, the ASR of the oxide layer on the La-coated Haynes 230 sample is approximately an order of magnitude lower than that formed on uncoated Haynes 230. At 800°C, the ASR of the La-coated sample is ~0.06 Ωcm² as compared to ~0.55 Ωcm² for the uncoated sample. The lower ASR of the La-coated samples is due to the presence of the highly conductive La(Cr, Mn)O₃ perovskite phase and the suppression of the more resistive Cr₂O₃ phase.

The resistance of uncoated and Mn-coated Haynes 230 and SS 430 interconnects was also measured in situ while operating in planar SOFC stacks. The voltage loss as a function of stack current (ohmic resistance) of interconnects measured in a stack operating at 850°C for two days is shown in Figure 7. The slope of voltage vs. current for the uncoated Haynes 230 is ~ 0.03, which corresponds to an approximate ASR of 0.75 Ωcm² based on an active area of 25 cm²/cell. By contrast, the area specific resistances of the uncoated SS 430, Mn-coated SS 430, and Mn-coated Haynes 230 interconnects were substantially lower and nearly the same with a value of ~0.05 Ωcm². The lower ASR of the Mn-coated interconnects and uncoated SS 430 is attributed to the formation of the Mn and Fe-based spinel phases in the oxide layer. The resistance of the interconnects was
Figure 6. Area specific resistance of the oxide on the metallic interconnect as a function of temperature for uncoated and La coated Haynes 230 oxidized for seven days in air at 800°C. Measurements conducted in air.

Figure 7. Voltage loss as a function of current (ohmic resistance) of uncoated and Mn coated Haynes 230 and SS 430 interconnects measured in a stack operating at 850°C for two days.

monitored as a function of time while in the stack under operating conditions. Figures 8 and 9 show the results of in situ measurements of uncoated and Mn-coated Haynes 230 and SS 430 interconnects at various times. As shown in Figure 8(a), the ASR of the uncoated Haynes 230, although high at ~ 0.75 Ωcm\(^2\), exhibited little change after 4 days of operation at 850°C. The stable ASR with time at temperature is consistent with the low oxidation kinetics reported for Haynes 230. On the other hand, the ASR of the uncoated SS 430 decreased with time over the period of 4 days. The decrease in ASR with time may be related to the rapid oxidation kinetics of SS 430 and the formation of the (Fe, Cr)\(_2\)O\(_4\) spinel phase in the oxide layer. Similar behavior was exhibited with the Mn-coated interconnects as shown in Figure 9. The ASR of the Mn-coated Haynes 230

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sample remained relatively constant while that of the Mn-coated SS 430 sample decreased over a period of 4 days. The difference in ASR behavior with time exhibited by Haynes 230 as compared to SS 430, Mn-coated and uncoated, may be related to the difference in their respective oxidation kinetics.

![Figure 8. Voltage loss as a function of current (ohmic resistance) of uncoated Haynes 230 and SS 430 interconnects measured in a stack operating at 850°C for two to four days.](image)

![Figure 9. Voltage loss as a function of current (ohmic resistance) of Mn coated Haynes 230 and SS 430 interconnects measured in a stack operating at 850°C for two to four days.](image)

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Figure 10. A comparison of the voltage-current and power-current characteristics of 4-cell planar SOFC stacks operating at 800°C with uncoated Haynes 230, Mn-coated Haynes 230, Mn-coated SS 430, and La and Mn coated Haynes 230 interconnects.

Coated and uncoated Haynes 230 and SS 430 interconnects were evaluated in 4-cell planar SOFC stacks. The voltage-current and power-current characteristics of 4-cell stacks operating at 800°C for four days with uncoated Haynes 230, Mn-coated Haynes 230, Mn-coated SS 430, and La and Mn coated Haynes 230 interconnects are shown in Figure 10. The Mn-coated interconnects were coated with 2000 angstroms of Mn on both sides, thus the Mn-coating was exposed to both the oxidant (air) and the fuel (humidified hydrogen) sides of the stack. In the case of the La and Mn-coated interconnects, 2000 angstroms of La was deposited on one side while 2000 angstroms of Mn was deposited on the other. The La-coated side was exposed to the cathode side (air) where the La(Mn, Cr)O₃ perovskite forms and the Mn-coated side was exposed to the anode (hydrogen) side where the (Mn, Cr)₂O₄ spinel forms. The 4-cell stack with the uncoated Haynes 230 interconnects delivered a maximum power of ~22.5 W with a net stack resistance of ~ 0.16 Ω. The stacks operated with Mn-coated Haynes 230, Mn-coated SS 430, and La and Mn-coated Haynes 230 performed considerably better with higher power levels and lower average stack resistances. The total resistance of stacks with coated interconnects was ~0.07 Ω, which is less than half the resistance of the stack with uncoated Haynes 230 interconnects. The decrease in stack resistance increased the maximum power delivered by the stack by a factor of two, from ~22.5 W for the stack with uncoated Haynes 230 interconnects to ~47 to 57 W for the stacks with coated interconnects.

CONCLUSIONS

Commercially available foils of the Ni-Cr superalloy Haynes 230 and the ferritic stainless steel 430 were coated with thin layers of Mn and La by electron beam deposition and evaluated for use in intermediate temperature SOFC. The coated and uncoated metallic...
interconnects were oxidized in both air and humidified hydrogen atmospheres at 800°C for various periods of time and the resulting oxide layers were characterized for phase content and electronic conductivity. During oxidation in air or humidified hydrogen, the Mn coating promoted the formation of the electronically conductive Mn-based spinel phases (Mn, Cr)2O4 and (Mn, Cr, Fe)2O4 while suppressing the formation of the resistive Cr2O3 corundum phase. Whereas, after oxidation in air the oxide layer formed on the La-coated interconnects primarily consisted of the perovskite phase La(Mn, Cr)O3. The area specific resistance of the oxide layer formed on the Mn-coated Haynes 230 was significantly lower (~0.24 Ωcm² at 800°C) than that for the oxide on uncoated Haynes 230 (~1.2 Ωcm² at 800°C). However, in the case of SS 430, the ASR of the oxide on the uncoated interconnect was lower than that of the Mn-coated interconnect. The ASR of the oxide layer formed on the La-coated Haynes 230 samples, oxidized in air at 800°C for 7 days, was an order of magnitude lower than the oxide layer formed on uncoated Haynes 230. Uncoated and coated interconnects were evaluated in 4-cell planar SOFC stacks. While operating at 800°C, the total resistance of the stack was reduced by a factor of two, from ~0.16 Ω with uncoated Haynes 230 interconnects to ~0.07 Ω with Mn and La-coated interconnects. This resulted in a doubling of the maximum power from ~23 W for the stack with uncoated Haynes 230 interconnects to >47 W for the stacks with coated interconnects.

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