Co_xFe_{1-x} oxide coatings on metallic interconnects for solid oxide fuel cells

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Abstract

In order to improve the performance of Cr-containing steel as an interconnect material for solid oxide fuel cells, CoFe alloy coatings with Co:Fe ratios of 9:1, 8:2, 7:3, 6:4, and 5:5 are deposited by electrodeposition and then oxidized to Co_xFe_{1-x} oxide coatings with a thickness of ~6 μm as protective layers on the interconnect. The area specific resistance of the coated interconnect increases with the Fe content. Higher Co content oxide coatings are more effective in limiting the growth of the chromia scale while all coatings are effective in inhibiting Cr diffusion and evaporation. With the Co_{0.8}Fe_{0.2} oxide coated interconnect, the electrochemical performance of the Sm_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O₃ cathode is improved. Only 1.54 atomic percentage of Cr is detected on the surface of the Sm_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O₃ cathode while no Cr is detected 0.66 μm or more into the cathode. Co_xFe_{1-x} oxide coatings are promising candidates for solid oxide fuel cell interconnects with the advantage of using existing cathode species for compatibility and performance enhancement.

Keywords:CoFe alloy;Coating; Interconnect; Area specific resistance; Cr diffusion

1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion devices with high efficiency and environmental advantages[1, 2]. Among all components, the interconnect is a key one to connect individual cells, provide electrical conductivity, and separate fuels and oxidizing gases. Metallic interconnects are the primary choice due to its low cost, good machinability, and good electrical conductivity [3-5]. Cr-containing stainless steels, such as AISI 441 and Crofer 22 APU, have high thermal conductivity and similar coefficient of thermal expansion (CTE) to the electrodes and are the most promising interconnect candidates[6, 7]. However, the long-term use of the Cr-containing stainless steels in SOFCs is still challenged by two major issues. First, the electrical conductivity is almost always lowered due to oxidation. Second, Cr diffusion and evaporation through the formation of volatile Cr species, such as CrO_3 and $\text{CrO}_2(\text{OH})_2$, poison the cathode and block oxygen reduction reaction (ORR) sites[8]. The application of a protective coating on the stainless steel surface has been demonstrated to lower the rate of area specific resistance (ASR) increase. It is also effective in reducing oxidation rate and inhibiting Cr diffusion and evaporation and thus cathode poisoning.

Many coating materials have been reported to protect metallic interconnects. A perovskite $\text{La}_{0.1}\text{Sr}_{0.9}\text{Co}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ coating on Crofer22H was demonstrated to decrease the ASR and improve the electrochemical performance of the cathode [9]. A $(\text{La},\text{Sr})\text{CrO}_3$ coating was reported to have good adhesion to the interconnect and acceptable ASR [10]. Spinel materials are also promising protective layers because they have relatively high electrical conductivity and can be

doped with a wide range of transition metal cations to improve their performance. For example, Co_3O_4 was reported as protective coatings for metallic interconnects[11, 12]even though the accumulative chromia scale between the substrate and the coating layer was thick and the electrical conductivity was relatively low (6.7 S cm^{-1} at 800°C [13]).In addition, the Co_3O_4 coating is unstable after long term operation at high temperatures, voids were reported within the grains [14]. Worse yet, the CET of Co_3O_4 is $\sim 40 \times 10^{-6} \text{ K}^{-1}$ at 800°C , which is almost three times larger than that of AISI 441 steel [15, 16].Doping Fe in the Co_3O_4 spinel is beneficial[17]. $(\text{Mn},\text{Co})_3\text{O}_4$ [18], $(\text{Cu},\text{Mn})_3\text{O}_4$ [6], and $(\text{Cu}, \text{Mn},\text{Co})_3\text{O}_4$ [19]have been demonstrated as promising protective coatings because of their high conductivity, stability, and oxidation resistance, even though Mn is not desired for Mn-free cathodes. Fortunately, the CTE of spinel can be adjusted by doping of species that are intrinsic to the cathode. For example, CoFe_2O_4 spinelhas a CTE of $19 \times 10^{-6} \text{ K}^{-1}$ at 800°C , which is much closer to that of AISI 441 [20].

A number of coating techniques have been utilized to deposit coating layers, including sputtering [21], plasma spray [22], physical vapor deposition [23], slurry coating [24], screen painting [25], and electroplating with thermal oxidation [26]. Among various reported coating techniques, electroplating is a simple and cost-effective approach, and can deposit dense structures. The electroplated metallic layer can be oxidized to produce a dense oxide layer.Desirably, Co and Fe can be co-deposited because of their relatively close standard electrode potentials ($-0.28 \text{ V}_{\text{SCE}}$ for Co^{2+}/Co and $-0.44 \text{ V}_{\text{SCE}}$ for Fe^{2+}/Fe). In addition, coating compositions can be controlled by adjusting the corresponding ion concentrations in the electroplating bath solution and deposition temperature. However, the study of Fe-doped Co_3O_4 has been mainly focused on the CoFe_2O_4 phase. Systematic study of the Co to Fe ratio effect on the protective coatings has not been reported yet.

To address the interconnect stability needs, especially in light of the acceptance of the new generation Co- and Fe-containing cathodes, in this paper CoFe alloy coatings with the Fe content from 10 at% to 50 at% were electroplated followed by oxidation at 800°C for 5 hrs. The electrical property of the coated and bare interconnects was assessed via ASR measurement at 800°C. The oxidation behavior was evaluated based on the chromia scale thickness between the coating layer and the steel substrate. Cr diffusion in the coating layer was investigated using energy-dispersive X-ray spectroscopy (EDS). The effect of the coating layer on the electrochemical performance of the interconnect/ $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (SSCF) cathode/YSZ electrolyte half-cell was investigated using electrochemical impedance spectroscopy (EIS) at 800°C for 100 hrs.

2. Experimental

2.1. Chemicals

$\text{CoSO}_4 \cdot \text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ethylenediaminetetraacetic acid, citric acid, NH_4NO_3 , sucrose, and $\text{NH}_3 \cdot \text{H}_2\text{O}$ were purchased from Alfa Aesar (Ward Hill, MA). α -terpineol as the solvent was purchased from Sigma-Aldrich (St. Louis, MO). Microcrystalline cellulose as a pore forming agent was purchased from Spectrum Chemical Manufacturing Corporation (Gardena, CA). Ethyl cellulose as a binder was purchased from Acros Organics (Morris Plains, NJ). YSZ was purchased from Nexceris (Lewis Center, OH). AISI 441 was produced by ATI Allegheny Ludlum Corporation (Brachenridge, PA).

2.2. Electrodeposition of CoFe alloy

The Co^{2+} and Fe^{2+} solutions consisted of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$, and H_3BO_3 . The details for the five solutions with the Co:Fe molar ratios of 9:1, 8:2, 7:3, 6:4, and 5:5 are shown in Table 1. The pH was adjusted to 3.6 using a HCl solution. A fine polished AISI 441 steel with a size of 15 mm×10 mm×1 mm was used as the cathode during the electrodeposition. It was connected to the negative port of a power source with a $4 \text{ mA} \cdot \text{cm}^{-2}$ constant current density. The process continued for 35 min at 40°C. The coated steel was then oxidized at 800°C for 5 hrs to form CoFe oxide coatings.

Table 1. Compositions of the five solutions used for CoFe electrodeposition.

Fe/(Fe+Co) (at%)	$\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ (mM)	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (mM)	$\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$ (mM)	H_3BO_3 (mM)
10	35	10	5	10
20	30	10	10	10
30	25	10	15	10
40	20	10	20	10
50	15	10	25	10

2.3. ASR measurements

ASR measurements were performed using a four-point probe method. All samples, including the bare interconnect, were run at the same conditions. An interconnect specimen (with or without the coating) was placed between two Pt meshes. A Pd-Ag paste was used to ensure good electrical contact between the interconnect and the meshes. The assembly was then put in a horizontal furnace at 800°C for 100 hrs. A constant current density of $500 \text{ mA} \cdot \text{cm}^{-2}$ was applied

to mimic the actual cell operation and resistances were obtained based on a voltage scan from 0 to 3 V. The measurement was taken every half hour. ASR values were then calculated using the resistance multiplied by the area covered by the paste and divided by two due to the symmetrical test design:

$$ASR = \frac{1}{2} R \times S \quad (1)$$

2.4. Assembly of AISI 441/SSCF/YSZ tri-layers and thermal treatment under current load

The synthesis of SSCF powders was reported in our previous work [27]. SSCF cathodes were deposited on the YSZ electrolyte by screen printing. They were square-like with 0.5 cm² area. Bare and coated AISI 441 alloy pieces were placed on the cathode side as an interconnect respectively and the configuration was shown in our previous paper [28]. The interconnect/SSCF/YSZ half-cells were heated to 800°C in a dry air environment. Afterwards, the half-cells were cathodically polarized using a potentiostat (VersaSTAT 3, Princeton Applied Research, Oak Ridge, TN). The EIS testing program used was a multi-loop process with the frequency from 100 kHz to 0.025 Hz. The amplitude was 10 mV. After that, a current density of 200 mA·cm⁻² was applied to mimic the working condition of an actual fuel cell. EIS data were recorded every 2 hrs during the thermal treatment.

2.5. Characterization

X-ray diffraction (XRD, X'Pert PRO diffractometer, PANalytical B.V., EA Almelo, The Netherlands) analysis was employed to characterize the crystal structures. A field-emission scanning electron microscope (FESEM, LEO (Zeiss) 1550, Oberhochem, Germany) was used to

examine the microstructures. The composition analysis was conducted by an environmental scanning electron microscope (ESEM, FEI Quanta 600 FEG, Hillsboro, USA) attached with an EDS module (BrukerAXS, MicroanalysisGmbh, Berlin, Germany). X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, Kanagawa, Japan) with Ar⁺ sputtering was used to examine elemental concentrations in a sputtering area of 2×2 mm². The sputtering depth was determined with a surface profilometer (Dektak XT, Bruker, Tucson, USA).

3. Results and discussion

3.1. Effect of bath temperature on Fe content in the coating layers

The compositions of the electroplated CoFe layers from three different bath solutions at 25°C, 40°C, and 55°C were determined by EDS and plotted as a function of the Fe atomic concentration in the bath solutions as shown in Fig. 1. When the CoFe layer is deposited at room temperature, the Fe contents in the coating layer are 7.5 at%, 15.5 at%, and 37.4 at%, corresponding to the Fe contents of 10 at%, 20 at%, and 50 at% respectively in the baths. The Fe contents in the coating layers deviate significantly from their original contents. When the bath temperature is increased to 40°C, the Fe contents in coating layer are 10.0 at%, 19.4 at%, and 45.5 at% respectively, much closer to their original contents in the baths, especially for the coating layer with lower Fe contents. The effect of temperature on the Co to Fe ratio in the coatings can be explained on the basis of two dominant factors, polarization and diffusion[29]. In a typical alloy co-deposition system, the more noble metal (Co in the case) is preferentially deposited; polarization and diffusion both increase the content of the more noble metal. This explains why the Fe content (less noble) deviates from the bath composition at 25°C electrodeposition temperature. Higher temperature increases the concentration of all metal ions in the diffusion layer by increasing the

rates of diffusion and convection. At 40°C, both polarization and diffusion should enhance the deposition of the more noble metal (Co). However, with further bath temperature increase, opposite effects from polarization and diffusion have been reported [30, 31] in anomalous co-deposition systems; polarization increases the content of the more noble metal while diffusion decreases it. The tradeoff between polarization and diffusion determines the composition of the coatings [29]. This explains why when the bath temperature is raised to 55°C, the Fe contents in the coating layer are 11.3 at%, 19.3 at%, and 45.7 at% respectively, without much Fe content change compared to that at 40°C, indicating that the temperature effect on the composition of the coatings is not significant when the bath temperature is higher than 40°C. Therefore, the CoFe coating layers are all electrodeposited at 40°C in the following study.

Fig. 1. Fe content in the electrodeposited CoFe coatings as a function of the Fe content in the bath solutions.

3.2. Electrodeposited layer analysis before and after oxidation

The XRD patterns of the deposited CoFe coatings after oxidation at 800°C for 5 hrs are shown in Fig. 2(a). The peaks of the steel substrates can still be detected. The crystal structures

of the CoFe oxide coatings change gradually with the increase of the Fe content in the coating layers. For the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coating, strong Co_3O_4 peaks are detected with minor CoFe_2O_4 peaks. For the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coating, the intensity of the Co_3O_4 peaks decreases and that of the CoFe_2O_4 peaks increases. This trend continues for the $\text{Co}_{0.7}\text{Fe}_{0.3}$ oxide coating. For the $\text{Co}_{0.6}\text{Fe}_{0.4}$ oxide and $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coatings, the Co_3O_4 peaks completely disappear and only CoFe_2O_4 phase exists in the coatings. Meanwhile, weak Fe_2O_3 peaks are detected in the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide, $\text{Co}_{0.7}\text{Fe}_{0.3}$ oxide, $\text{Co}_{0.6}\text{Fe}_{0.4}$ oxide, and $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coatings.

The phase concentrations of Co_3O_4 , CoFe_2O_4 , and Fe_2O_3 are calculated based on the XRD peak areas in Fig. 2(a) and plotted as a function of the initial Fe content, as shown in Fig. 2(c). At 10 at% Fe, Co_3O_4 takes up 73.9 wt% in the $\text{Co}_{0.1}\text{Fe}_{0.9}$ oxide coating and CoFe_2O_4 takes up the remaining 26.1 wt%. Then the Co_3O_4 content decreases and the CoFe_2O_4 and Fe_2O_3 contents increase. At 50 at% Fe, no Co_3O_4 is detected in the $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coating while CoFe_2O_4 takes up to 92.2 wt% and Fe_2O_3 increases to 7.8 wt%. The main peak (311) for the CoFe_2O_4 phase is enlarged and shown in Fig. 2(b). The peak intensity increases with the Fe content. Left shift of the peak is observed, especially for the coatings with a higher Fe content (30 at%, 40 at%, and 50 at%). This means that the Fe content in the coatings affects the CoFe_2O_4 crystal structure. The lattice constant of cubic CoFe_2O_4 is calculated to be $8.3259 \pm 0.0026 \text{ \AA}$, $8.3302 \pm 0.0019 \text{ \AA}$, $8.3359 \pm 0.0022 \text{ \AA}$, $8.3581 \pm 0.0017 \text{ \AA}$, $8.3815 \pm 0.0037 \text{ \AA}$ respectively based on Fig. 2(b). This means that higher doping of Fe makes the peaks shift more from cubic Co_3O_4 ($8.1514 \pm 0.0021 \text{ \AA}$) to cubic Fe_3O_4 ($8.4242 \pm 0.0028 \text{ \AA}$). It should be pointed out that the CoFe_2O_4 content increase has a significant impact on the coating performance. The electrical conductivity of CoFe_2O_4 is reported to be 0.85 S cm^{-1} [32], which is much lower than that of pure Co_3O_4 (6.7 S cm^{-1}). More CoFe_2O_4 phase in the coating would decrease its electrical conductivity. Also, we believe the

electrical conductivity of CoFe_2O_4 decreases with the increase of its lattice constant because larger radius leads to lower conductivity in the same crystal structure and the radius of Fe^{3+} is larger than that of Co^{3+} . Co_3O_4 and CoFe_2O_4 are p-type semiconductors and their electrical conductivities are achieved by the electron hopping. Smaller ions, e.g., Co^{3+} has a smaller resistance to electron transport than larger ions, e.g., Fe^{3+} in the same crystal structure. The specific effect can be seen in Table 2. In addition, the continuous increase of the Fe_2O_3 content should significantly decrease the electrical conductivity of the coating because its electrical conductivity is as low as $\sim 10^{-2} \text{ S cm}^{-1}$ at 800°C [33].

Fig. 2. XRD patterns of (a) the CoFe oxide coatings on AISI 441 with different Fe contents (labelled on the secondary y-axis); (b) the enlarged (311) main peak from the CoFe_2O_4 phase for

different Fe contents (labelled on the secondary y-axis); (c) Co_3O_4 , CoFe_2O_4 , and Fe_2O_3 concentrations in the $\text{Co}_x\text{Fe}_{1-x}$ oxide coatings.

At the lowest Fe content, the microstructure of the electrodeposited $\text{Co}_{0.9}\text{Fe}_{0.1}$ coating layer before oxidation is shown in Fig. 3(a). The coating layer is porous with mesh structures. After oxidation at 800°C for 5 hrs, the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coating shows dense polycrystalline structures, shown in Fig. 3(c). The oxidization of $\text{Co}_{0.9}\text{Fe}_{0.1}$ alloy causes volume expansion due to the lower densities for the oxides (Co_3O_4 , CoFe_2O_4 , Fe_2O_3) than the metals (Co, Fe). The volume expansion transforms the porous coating into a fully dense structure with an average grain size of about 200 nm. At the highest Fe content (the $\text{Co}_{0.5}\text{Fe}_{0.5}$ coating), several morphologies appear before oxidation, including cauliflowers, tetrahedra, and crosses, as shown in Fig. 3(b). This is different from that of the $\text{Co}_{0.9}\text{Fe}_{0.1}$ coatings shown in Fig. 3(a), because Co, CoFe alloy, and Fe co-exist in the $\text{Co}_{0.5}\text{Fe}_{0.5}$ coating while only Co and Fe co-exist in the $\text{Co}_{0.9}\text{Fe}_{0.1}$ coating. After oxidation at 800°C for 5 hrs, however, the microstructure is similar to that of the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coating except that some discrete, bright clusters form on the surface, as shown in Fig. 3(d). The bright clusters are characterized to be Fe_2O_3 particles by EDS mapping. Due to the low conductivity of Fe_2O_3 , the conductivity of the $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coating is compromised as shown in Table 2. Nonetheless, the dense coatings are expected to prevent oxygen gas inward diffusion, which should reduce the oxidation of the steel substrate and the formation of volatile Cr species. The thickness of all the coatings after oxidation is controlled at $\sim 6\text{ }\mu\text{m}$, which has been confirmed by the SEM cross section examination.

Fig. 3. Surface morphologies of the coatings: (a) (c) $\text{Co}_{0.9}\text{Fe}_{0.1}$; (b) (d) $\text{Co}_{0.5}\text{Fe}_{0.5}$, at as-deposited state and after oxidation at 800°C for 5 hrs respectively.

3.3. ASR measurements

ASR is an effective parameter to compare the coating layer properties since the electrical resistance of the un-oxidized steel is negligible compared with the coating layer. An important requirement for the protective coating on the interconnect is low ASR. Fig. 4 shows the ASR comparison of the bare steel and the $\text{Co}_x\text{Fe}_{1-x}$ oxide coated steels. The ASR of the bare interconnect increases from $0.9 \text{ m}\Omega \text{ cm}^2$ to $13.7 \text{ m}\Omega \text{ cm}^2$ after 100 hrs of the ASR testing. For the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coated interconnect, the ASR increases from $2.0 \text{ m}\Omega \text{ cm}^2$ to $7.6 \text{ m}\Omega \text{ cm}^2$, similar to that of the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coated interconnect ($2.0 \text{ m}\Omega \text{ cm}^2$ to $8.3 \text{ m}\Omega \text{ cm}^2$) and that of the $\text{Co}_{0.7}\text{Fe}_{0.3}$ oxide coated interconnect ($2.3 \text{ m}\Omega \text{ cm}^2$ to $10.9 \text{ m}\Omega \text{ cm}^2$). However, the ASR of

the $\text{Co}_{0.6}\text{Fe}_{0.4}$ oxide coated interconnect increases from $4.0 \text{ m}\Omega \text{ cm}^2$ to $13.8 \text{ m}\Omega \text{ cm}^2$. For the highest Fe content coating, $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide, its ASR increases from $7.5 \text{ m}\Omega \text{ cm}^2$ to as high as $31.4 \text{ m}\Omega \text{ cm}^2$. It is obvious that the ASR increases with the Fe content in the coating. The ASR of the $\text{Co}_{0.9}\text{Fe}_{0.1}$, $\text{Co}_{0.8}\text{Fe}_{0.2}$, and $\text{Co}_{0.7}\text{Fe}_{0.3}$ oxide coated interconnects are smaller than that of the bare interconnect due to their relatively small initial ASR and low increasing rates; the ASR of the $\text{Co}_{0.6}\text{Fe}_{0.4}$ oxide coated interconnect is comparable to that of the bare interconnect, but its increasing rate is still lower than that of the bare interconnect; the ASR of the $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coated interconnect is much higher than that of the bare interconnect, indicating that the Fe content limit in the $\text{Co}_x\text{Fe}_{1-x}$ oxide coating should be less than 50 at%.

Fig. 4. ASR comparison for the bare and $\text{Co}_x\text{Fe}_{1-x}$ oxide coated interconnects at 800°C for 100 hrs.

The above results can be explained from two aspects. The first is the internal conductivity of the coating. As reported, the conductivity of CoFe_2O_4 is almost one order of magnitude lower than that of Co_3O_4 . More CoFe_2O_4 in the coating results in higher ASR. Second, the

accumulated chromia scale between the coating and the substrate contributes to the total ASR. The thickness of the chromia scale is critical, which will be discussed in the next section.

3.4. Oxidation kinetics and Cr diffusion

After 100 hrs of the ASR testing, the microstructures of the coatings change significantly, two of which, $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide and $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide, are shown in Fig. 5. The $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coating (Fig. 5(a)) is still dense and the average grain size increases from ~ 200 nm to ~ 1 μm . The microstructure of the $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coating (Fig. 5(b)), however, is not as dense. Serious phase separation, CoFe_2O_4 and Fe_2O_3 , leads to the less dense coating. The distribution of the particles is heterogeneous. The large size particles (CoFe_2O_4) are up to 3 μm while the small size particles (Fe_2O_3) are just ~ 100 nm. The porous coating shown in Fig. 5(b) cannot prevent O_2 from reaching the steel substrate and inducing oxidation to increase the ASR, to as high as 31.4 $\text{m}\Omega\text{ cm}^2$. Moreover, some $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coating peels off from the AISI 441 substrate surface after 100 hrs of the ASR testing, which further demonstrates that the coating is less effective. These small Fe_2O_3 particles are spalled off due to the excessive Fe in the coating. Thus, low Fe content is needed in order to obtain a dense coating and low enough ASR.

Fig. 5. Surface morphologies of (a) $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide and (b) $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coatings; (c) changes of the chromia scale thickness with the Fe content in the coatings after 100 hrs of the ASR testing.

As mentioned earlier, the oxidation of the interconnect with the formation of chromia contributes to the increase of the ASR. For the bare AISI 441, Cr oxide vapors are released as volatile CrO_3 or $\text{CrO}_2(\text{OH})_2$ (depending on the presence of water vapor) to lose the passivating layer. Then Fe is oxidized. Thus, the large ASR of the bare steel shown in Fig. 4 is ascribed to the oxidation of Fe and its delamination from the substrate. For the CoFe oxide coated interconnect, the formation of the chromia scale is ascribed to two aspects. One is direct oxidation during the $\text{CoFe alloy} \rightarrow \text{Co}_x\text{Fe}_{1-x}$ oxide conversion before any electrochemical testing. In this process, a dense $\text{Co}_x\text{Fe}_{1-x}$ oxide layer has not fully formed. The activity of Co, Fe, and Cr has a relationship of $\text{Cr} > \text{Fe} > \text{Co}$, which means Cr is the easiest to be oxidized. The passivating chromia layer on the surface of AISI 441 limits the oxidation of Fe by acting as a diffusion barrier.

In order to compare the coating resistance to oxidation, the chromia scale thicknesses on the interconnect are given in Fig. 5(c) for the five coatings studied. The corresponding Cr distributions (blue) in the five coatings are also illustrated. The chromia scale thickness increases with the increase of the Fe content, from $\sim 0.84 \mu\text{m}$ for 10 at% Fe, to $\sim 0.96 \mu\text{m}$ for 20 at% Fe, to $\sim 1.24 \mu\text{m}$ for 30 at% Fe, to $\sim 1.46 \mu\text{m}$ for 40 at% Fe, and finally to $\sim 1.55 \mu\text{m}$ for 50 at% of Fe. The electrical conductivity of the chromia scale, such as Cr_2O_3 , is as low as $1.5 \times 10^{-2} \text{ Scm}^{-1}$ at 800°C [34], which is over two orders of magnitude lower than that of Co_3O_4 (6.7 S cm^{-1} at 800°C) and one order of magnitude lower than that of CoFe_2O_4 (0.85 S cm^{-1} at 800°C). The ASR can be calculated based on the parallel resistance of the coating and the chromia scale, as shown in Table 2. The calculation can be expressed as the following:

$$ASR_{\text{chromia}} = \frac{t_{\text{chromia}}}{\sigma_{\text{chromia}}} \quad (2)$$

$$ASR_{\text{coating}} = \frac{t_{\text{coating}}}{\sigma_{e,\text{coating}}} \quad (3)$$

$$ASR_{\text{Total}} = ASR_{\text{chromia}} + ASR_{\text{coating}} \quad (4)$$

where t_{chromia} is the average chromia thickness, which is shown in Fig. 5(c); σ_{chromia} is the electrical conductivity of chromia, which is $1.5 \times 10^{-2} \text{ Scm}^{-1}$; t_{coating} is the thickness of the coating, which is around $6 \mu\text{m}$; $\sigma_{e,\text{coating}}$ is the effective conductivity of the coating, which can be calculated with Equation (5) based on the Bruggeman model [35].

$$\sum_i \delta_i \frac{\sigma_i - \sigma_{e,\text{coating}}}{\sigma_i + 2\sigma_{e,\text{coating}}} = 0 \quad (5)$$

where δ_i is the volume fraction of each phase, which can be calculated from Fig. 2(c); σ_i is the electrical conductivity of each phase, 6.7 S cm^{-1} for Co_3O_4 , 0.85 Scm^{-1} for CoFe_2O_4 and $\sim 10^{-2} \text{ S cm}^{-1}$ for Fe_2O_3 . The effective conductivity for each coating is also shown in Table 2. The calculated resistance is smaller than the measured resistance, especially for the high Fe content

coating, because the Bruggeman model considers the coating as dense with all the phases homogeneously distributed. In addition, no interdiffusion is considered here which could increase the ASR.

Table 2. Comparason of the calculated and measured ASR for the $\text{Co}_x\text{Fe}_{1-x}$ oxide coated interconnects.

Fe	Calculation				Measurement
concentration	$\text{ASR}_{\text{Chromia}}$	$\sigma_{\text{e, Coating}}$	$\text{ASR}_{\text{Coating}}$	$\text{ASR}_{\text{Total}}$	$\text{ASR}_{\text{Measured}}$
(at%)	($\text{m}\Omega\cdot\text{cm}^2$)	($\text{S}\cdot\text{cm}^{-1}$)	($\text{m}\Omega\cdot\text{cm}^2$)	($\text{m}\Omega\cdot\text{cm}^2$)	($\text{m}\Omega\cdot\text{cm}^2$)
10	5.6	4.38	0.1	5.7	7.6
20	6.4	2.28	0.3	6.7	8.3
30	8.3	1.06	0.6	8.9	10.9
40	9.7	0.76	0.8	10.5	13.8
50	10.3	0.75	0.8	11.1	31.4

The reason for the increase of the chromia scale is oxygen diffusion in the $\text{Co}_x\text{Fe}_{1-x}$ oxide coatings. The chromia scale is not desired and its growth should be limited in order to maintain the desirable conductivity. The coatings with low Fe contents are dense and can prevent O_2 from reaching the steel. These coatings keep the thin passivated chromia scale in place, which protects Fe from being oxidized. Based on the microstructures in Fig. 5, a dense coating layer with less Fe content contributes to low ASR.

The elemental distributions of Fe, Cr, and Co along the cross section of the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide and $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coating layers after 100 hrs of the ASR testing are shown in Fig. 6. For the

$\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coated interconnect shown in Fig. 6(a), an intense Cr peak is located in the dark thin layer between the AISI 441 substrate and the coating. It demonstrates the Cr accumulation on the AISI 441 surface and the effectiveness of the coating in preventing its evaporation after the long-term operation. The process can be understood as follows. During the high temperature testing, oxygen diffuses inward through the oxygen vacancies in the coating layer to oxidize the substrate. Due to the higher activity of Cr than Fe, Cr is oxidized prior to Fe. When there is no outer coating layer, Cr_2O_3 layer would increase fast and a thick chromia layer might even detach from the steel substrate. If the $\text{Co}_x\text{Fe}_{1-x}$ oxide layer is porous, Cr_2O_3 can also be oxidized further into volatile CrO_3 (dry air was used as stated earlier), which is the Cr species that poisons the cathode. Since almost no Cr is detected in the coating layer, it means that the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coating is effective in inhibiting the Cr solid state diffusion. Meanwhile, a significant amount of Fe is detected in the middle of the coating. A high concentration of Co is also distributed along the coating. This means that the $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide coating is intact. For the $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coated interconnect shown in Fig. 6(b), the chromia scale grows thicker to $1.55\text{ }\mu\text{m}$, indicating that more oxygen diffuses inward due to the porous nature of the coating. A Co peak is detected in the steel substrate, confirming that Co diffuses into the metallic substrate after more Cr oxidation, which has been reported before [14, 21, 36-38]. Still, almost no Cr is detected in the coating layer, which means that the $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coating continues to be effective in inhibiting the Cr solid state diffusion, even with its porous nature. High concentration of Fe and low concentration of Co are distributed uniformly along the coating.

Fig. 6. Cross section view of (a) $\text{Co}_{0.9}\text{Fe}_{0.1}$ oxide and (b) $\text{Co}_{0.5}\text{Fe}_{0.5}$ oxide coatings and their elemental line scans after 100 hrs of the ASR testing.

3.5. Interconnect coating effects on the SSCF cathode

In this work, $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coated interconnect is taken as an example to study the coating effect on the half-cell performance. The ohmic resistances and polarization resistances for the SSCF cathode with the coated and bare interconnects are shown in Fig. 7. Ohmic resistance, R_{Ω} , is the from the cathode, the Pt wires, the Pd paste, the contact between the interconnect and the cathode, and the electrolyte; The high frequency resistance, R_H , corresponds to O^{2-} incorporation into the electrode and its transport in the cathode; and the low frequency resistance, R_L , is attributed to oxygen adsorption and dissociation as well as its surface diffusion [39]. The ohmic resistance R_{Ω} for the coated interconnect increases from $1.1 \, \Omega \, \text{cm}^2$ to $1.5 \, \Omega \, \text{cm}^2$ and is smaller than that with the bare interconnect ($2.0 \, \Omega \, \text{cm}^2$ at stabilized state after ~ 20 hrs of testing). This means that less or no low conductivity phase, such as SrCrO_4 , is deposited on the cathode for the former. The high frequency polarization resistance R_H gradually increases to $3.1 \, \Omega \, \text{cm}^2$ for the coated interconnect half-cell after 100 hrs of the thermal treatment, which is still smaller than

that with the bare interconnect ($4.1 \Omega \text{ cm}^2$). This is because without Cr poisoning the path for O^{2-} incorporation and transport is more available. The low frequency polarization resistances R_L are initially smaller except for the stabilized value ($0.3 \Omega \text{ cm}^2$), which is comparable to that of the half-cell without the coating on the interconnect ($0.2 \Omega \text{ cm}^2$). This means that the oxygen adsorption and dissociation are almost unchanged by the coating.

Fig. 7. Electrochemical performance of the SSCF cathode with the (a) bare (b) $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coated interconnects.

Our previous work shows that SrCrO_4 forms on the cathode side next to the interconnect when bare interconnects are applied [27, 40]. In this study, after 100 hrs of the thermal treatment, the XRD pattern of the SSCF cathode with the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coated interconnect is shown in Fig. 8(a). No SrCrO_4 peaks are detected and the SSCF cathode is stable after 100 hrs of the thermal treatment. This further proves that the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coating is effective in inhibiting the Cr diffusion and evaporation. SrCrO_4 phase is a poor electrical conductor (1.8×10^{-5} and $1.8 \times 10^{-4} \text{ S cm}^{-1}$ at 700°C and 800°C respectively [41]). If it forms on the cathode, the SSCF cathode ohmic resistance will eventually increase. In addition, SrCrO_4 formation leads to fewer two phase boundaries between the cathode and the gas phase, thus the rate of ORR will be

lowered. This explains why the high frequency polarization resistance R_H decreases for the coated interconnect half-cell.

XPS depth profiling is used to detect the Cr concentration on the SSCF cathode after 100 hrs of the thermal treatment with the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coated interconnect. When an XPS scan is conducted on the top surface, a small Cr2p3 peak is detected as shown in Fig. 8(b). The Cr concentration is calculated to be 1.54 at%, which is much less than that with the bare interconnect (6.8 at% on the top surface and 9.39 at% after 0.60 μm of sputtering). When another XPS scan is conducted after 0.66 μm of sputtering, no Cr peak is detected. Even three more scans are conducted after deeper sputtering, still no Cr is detected. This means that only a small amount of Cr accumulates on the surface of the SSCF cathode after 100 hrs of the thermal treatment. The $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coating can effectively inhibit the Cr diffusion and evaporation during 100 hrs of the thermal treatment.

Fig. 8. (a) XRD pattern and (b) XPS scans (cathode surface and after 0.66 μm of sputtering) of the SSCF cathode thermally treated with the $\text{Co}_{0.8}\text{Fe}_{0.2}$ oxide coated interconnect.

4. Conclusions

In this study, five coatings ($\text{Co}_{0.9}\text{Fe}_{0.1}$, $\text{Co}_{0.8}\text{Fe}_{0.2}$, $\text{Co}_{0.7}\text{Fe}_{0.3}$, $\text{Co}_{0.6}\text{Fe}_{0.4}$, and $\text{Co}_{0.5}\text{Fe}_{0.5}$) are created by electrodeposition followed by oxidation at 800°C for 5 hrs. Coatings with lower Fe (<30 at%) contents have smaller ASR and are more effective in limiting the growth of the chromia scale on the AISI 441 substrate. EIS testing also demonstrates the effectiveness of the coatings. Low Fe content coatings improve the electrochemical performance of the SSCF cathode compared with the SSCF cathode with the bare interconnect. Very little Cr is detected on the SSCF cathode surface after the EIS testing and no Cr is detected in the SSCF cathode. Thus, low Fe-containing CoFe oxide coatings ($\text{Fe} \leq 30$ at%) are effective in protecting the interconnect oxidation and the Cr diffusion and evaporation and are desirable coatings for SOFCs.

Acknowledgments

The authors acknowledge the financial support from Office of Naval Research under grant number ONR N00014-14-1-0466.

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