Oxidation resistance and electrical properties of anodically electrodeposited Mn–Co oxide coatings for solid oxide fuel cell interconnect applications

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ABSTRACT

Co-rich and crack-free Mn–Co oxide coatings were deposited on AISI 430 substrates by anodic electrodeposition from aqueous solutions. The as-deposited Mn–Co oxide coatings, with nano-scale fibrous morphology and a metastable rock salt-type structure, evolved into a $(Cr,Mn,Co)_3O_4$ spinel layer due to the outward diffusion of Cr from the AISI 430 substrates when pretreated in air. The Mn–Co oxide coatings were reduced into metallic Co and Mn_3O_4 phases when annealed in a reducing atmosphere of 5% H_2–95% N_2. In contrast to the degraded oxidation resistance and electrical properties observed for the air-pretreated Mn–Co oxide coated samples, the H_2-pretreated Mn–Co oxide coatings not only acted as a protective barrier to reduce the Cr outward diffusion, but also improved the electrical performance of the steel interconnects. The improvement in electronic conductivity can be ascribed to the higher electronic conductivity of the Co-rich spinel layer and better adhesion of the scale to the steel substrate, thereby eliminating scale spallation.

1. Introduction

The anode-supported solid oxide fuel cell (SOFC) design, with a very thin electrolyte (<20 μm thick), allows SOFC stacks to operate at intermediate temperatures ranging from 650 to 800 °C [1–5]. The reduction of the operating temperature makes it possible to use metallic interconnects to replace expensive ceramic-based interconnects such as $LaCrO_3$. Ferritic stainless steels, as a result of their good mechanical properties, thermal and electronic conductivity, ease of fabrication and very low cost, are among the most promising materials for SOFC interconnects. However, bare ferritic stainless steels tend to form a chromia scale at the operating temperatures. Rapid growth of the chromia scale leads to a high contact resistance and, in turn, deteriorates the long-term cell performance. Volatile Cr species from the chromia scale may form in the presence of water vapor, and these species can poison the cathode or the cathode–electrolyte interface [6,7]. One approach to overcome these problems is through the application of a protective coating on the stainless steel interconnect. The materials for a protective coating ought to have high electrical conductivity and low chromium cation and oxygen anion diffusivity at the operating temperatures.

Perovskite oxides, such as $(La,Sr)CrO_3$, $(La,Sr)CoO_3$ and $(La,Sr)MnO_3$, have been extensively evaluated as coating materials during the past decade [8–20]. Generally, chromites, which exhibit a lower oxygen ionic conductivity than other perovskite compositions such as cobaltites [16–18], provide better protection to the metal substrates by inhibiting scale growth beneath the perovskite layer. However, one potential concern is the fact that the chromites will release volatile Cr species, although at a relatively low rate [21,22], which may still lead to an unacceptable degradation in cell performance. In comparison, Cr-free perovskites such as cobaltites, with higher electrical conductivity and higher ionic conductivity, offer more effective reduction in contact resistance. However, the higher ionic conductivity leads to a higher growth rate of the scale beneath the protective layer, thus offsetting the high electrical conductivity. Furthermore, fast diffusion of Cr through the non-chromium perovskite layers will eventually result in the presence of Cr at the surface of the protective layer and subsequent cell poisoning.

In addition to the perovskites, spinel oxides have also been introduced as protective coatings for ferritic stainless steel interconnects in SOFCs. A Mn–Co spinel protective layer appears to be an effective barrier to both Cr outward and O inward transport, as indicated by long-term evaluations [23]. The mechanical stability of the spinel protective layer and its effectiveness as a chromium mass barrier are not affected by thermal cycling [23]. Moreover, with a higher electrical conductivity than that of chromia and Cr-containing spinels [24,25], Mn–Co spinel protective layers drastically reduce the interfacial contact resistance. Typical preparation methods for oxide coatings are thermal spraying [26], slurry spray-

ing [23,27], screen printing [28] and sol–gel processing [29]. The first three techniques are generally not applicable to obtain conformal coatings on substrates with complex shapes, while sol–gel processing has relatively low deposition rates.

Electrochemical deposition has several distinct advantages over the techniques mentioned above for the preparation of oxide coating materials [30]. Firstly, uniform films can be deposited on substrates of complex shape with a high degree of reproducibility and film thickness can be precisely controlled by simply changing the delivered electrical charge. In addition, the low processing temperatures (often room temperature) of electrochemical deposition minimize interdiffusion. The composition and defect chemistry can be controlled through the applied overpotential and the technique setup is not capital intensive. Inspired by these considerations, anodic electrodepostion of Mn–Co oxide coatings on ferritic stainless steel substrates directly from aqueous solutions have been investigated, as described previously [31]. Co-rich and crack-free Mn–Co oxide coatings have been successfully prepared by manipulating experimental parameters, including solution composition, solution temperature and current density. The as-deposited Mn–Co oxide coatings are composed of nanocrystalline oxide particles with a defective rock salt structure [32], with a rock salt-to-spinel structural transformation occurring upon heating up to 500 °C in air [33].

The purpose of this work is to extend our previous studies on anodically deposited Mn–Co coatings to evaluate the effects of pretreating conditions, including oxidizing and reducing atmospheres, on the subsequent oxidation resistance and electrical properties of the Mn–Co oxide coatings on AISI 430 substrates.

2. Experimental procedure

2.1. Electrochemical synthesis

Mn–Co–O coatings were anodically electrodeposited on AISI 430 substrates with dimensions of 20 mm × 10 mm × 1 mm using a Gamry PC4/750 potentiostat/galvanostat. The solution consisted of 0.2 M EDTA disodium, 0.29 M $CoSO_4 \cdot 7H_2O$ and 0.01 M $MnSO_4 \cdot H_2O$. EDTA disodium salt was added to stabilize the solutions. The three-electrode cell configuration consisted of a Pt counter electrode placed horizontally 20 mm above a horizontal AISI 430 working electrode. A saturated calomel electrode (SCE) was used as the reference electrode and all the potentials quoted are with respect to it. Before anodic deposition, the stainless steel substrates were ground with 600-grit SiC grinding paper, degreased in an alkaline solution at 80 °C and cleaned ultrasonically in deionized water. The steel substrates were anodically activated at a current density of 30 mA cm^{-2} for 2 min in 0.2 M H_2SO_4 solution and then cathodically activated at a current density of 30 mA cm^{-2} for 6 min in 0.1 M HCl solution. The deposition current density, electrolyte pH value, electrolyte temperature and deposition time were adjusted to be 5 mA cm^{-2}, 6.0, 90 °C and 90 min, respectively. During electrodeposition, agitation was introduced with a magnetically driven Teflon® coated stirring bar at a speed of 300 rpm. After electrodeposition, the working electrodes were rinsed with deionized water and dried in air.

2.2. Materials characterization

Selected Mn–Co coated samples were pretreated at 800 °C in air and forming gas (5% H_2–95% N_2) for 10 h before oxidation and electrical property analysis. Deposit microstructure, composition and morphology were analyzed in a Hitachi S-2700 scanning electron microscope (SEM), equipped with an ultra-thin window (UTW) X-

ray detector, and a JAMP 9500F Auger microprobe. A JEOL 2010 transmission electron microscope (TEM), equipped with a Noran ultra-thin window (UTW) X-ray detector, was used to study the microstructure on a finer scale. Crystal structure analysis was performed using selected area electron diffraction (SAED). A Rigaku rotating Co anode XRD system, with a thin film camera attachment, was also employed for phase identification of annealed Mn–Co oxide coatings. Chemical state analysis was carried out by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra X-ray photoelectron spectrometer. A monochromatic Al source, operating at 210 W with a pass energy of 20 eV and a step of 0.1 eV, was utilized. All XPS spectra were corrected using the C 1s line at 284.6 eV. Curve fitting and background subtraction were accomplished using Casa XPS Version 2.3.13 software.

2.3. ASR measurements

The area-specific resistance (ASR) of uncoated coupons and Mn–Co oxide coated specimens, pretreated at 800 °C in air and forming gas for 10 h, were compared. The setup is similar to that described in a previous study [34]. Pre-oxidation of uncoated samples was performed at 800 °C in air for 24 h in order to prevent alloy-to-alloy adhesion. The Mn–Co–O coated specimens, with Pt wires welded on the backsides, were arranged face-to-face. No contact materials, which may affect the oxidation mechanism, were applied between the two coupons. A static load of 4.9×10^4 Pa was applied on the surface of the samples to ensure a reliable electrical contact between the samples. A constant current density of 200 mA cm^{-2} was applied and the voltage was recorded every 600 s using a PC4/750 potentiostat/galvanostat. In order to subtract the resistance contribution from the connections, Pt wires and the alloy substrates, two Pt wires were spot-welded to the sides of a single AISI 430 coupon and the resulting resistance was subtracted from the original results. All the ASR measurements mentioned above were run at 800 °C in air.

3. Results and discussion

3.1. As-deposited Mn–Co oxide coatings

The morphology and crystal structure of the as-prepared Mn–Co oxide coatings were analyzed using SEM and TEM. Plan view secondary electron (SE) images, shown in Fig. 1a, indicate that the Mn–Co oxide coatings have a rough but crack-free morphology. The high resolution SE micrograph (inset of (Fig. 1a) confirms that the oxide coatings are composed of nano-scale fibers entangled with one another. A cross-sectional backscattered electron (BSE) image of an as-deposited Mn–Co oxide coating is shown in Fig. 1b. It is apparent that the as-deposited coating is continuous and uniform with an average thickness of about 6.0 μm. The Co/Mn ratio in the as-deposited oxide coatings was determined to be 53:47 using EDX analysis. Fig. 1c shows a dark field (DF) TEM micrograph and a corresponding SAED pattern taken from an as-deposited Mn–Co–O coating. The DF TEM image reveals that the nano-scale fibers are not individual oxide crystals, but are composed of equiaxed oxide nanocrystals with a diameter less than 10 nm. The continuous SAED ring pattern also confirms their nanocrystalline nature. The d-spacings measured from the SAED pattern (inset of Fig. 1c) are consistent with face-centered cubic (FCC) MnO (JCPDS card No. 07-0230) with a space group of $Fm\bar{3}m$. The diffracted rings were indexed as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), respectively, as shown in the inset of Fig. 1c. The structural information is in agreement with our previous study [32].