

## IV.A.25 Electrically Conductive, Corrosion-Resistant Coatings through Defect Chemistry for Metallic Interconnects

Anil V. Virkar

University of Utah  
Department of Materials Science & Engineering  
122 S. Central Campus Drive  
Salt Lake City, UT 84112  
Phone: (801) 581-5396; Fax: (801) 581-4816  
E-mail: anil.virkar@m.cc.utah.edu

DOE Project Manager: Ayyakkannu Manivannan

Phone: (304) 285-2078  
E-mail: Ayyakkannu.Manivannan@netl.doe.gov

### Objectives

- To synthesize and characterize coating materials with ultra-low oxygen diffusion coefficient, that are electronically conductive using site-specific doping and through fundamental understanding of defect chemistry, for application as coatings for metallic interconnects in intermediate temperature (800°C) solid oxide fuel cells (SOFCs).
- To apply the coatings on low thermal expansion, relatively inexpensive stainless steels and other alloys, and investigate oxidation kinetics in air and fuel atmospheres.
- To conduct preliminary short stack (4-cell) test, using 5 cm x 5 cm active area cells to validate ex-situ results.
- To initiate work on the development of low-cost processes for the deposition of coatings on metallic interconnects.
- To offer coated interconnect foils to Solid State Energy Conversion Alliance (SECA) vertical teams under suitable confidentiality agreements.

### Approach

- To conduct literature search on the identification of suitable perovskite and non-perovskite materials exhibiting high electronic conductivity but very low oxygen ion conductivity. Non-perovskite materials of interest include spinels and bronzes.
- To synthesize perovskite oxides with transition elements on the B-site, with site-specific doping to suppress oxygen vacancy concentration.
- To fabricate sintered bars and discs of the materials. Sintered bars are to be used for the measurement of total conductivity as a function of temperature.

Discs are to be used for measuring ionic conductivity using electron blocking electrodes.

- To deposit thin coatings of the materials on stainless steels and nickel-based alloy foils, and investigate oxidation kinetics.
- To conduct theoretical analysis of oxidation kinetics of coated and pristine alloys.
- To develop a method for the measurement of area specific resistance (ASR), and apply it to the foils oxidized under various conditions.

### Accomplishments

- Identified a number of materials with low oxygen ion conductivity (possibly lower than  $10^{-7}$  S/cm at 800°C) by taking into account ionic size effect.
- Fabricated  $\text{LaMnO}_3$  (LM) and  $\text{LaCrO}_3$ -based materials with dopant levels as high as 20% on the B-site to suppress oxygen ion conductivity.
- Measured the total conductivity over a temperature range from room temperature to 800°C; measured oxygen ion conductivity at 800°C using different sample designs.
- Sputter-deposited 1 and 3-micron coatings of various materials on Haynes 230 (H230), Inconel 718, and SS430.
- Conducted oxidation in flowing air up to 180 days at 800°C for samples having  $\text{LaMnO}_3$ -based coating.
- Conducted oxidation studies in flowing 10% $\text{H}_2$ /90% $\text{N}_2$  gas with 5% humidity up to 90 days for samples having  $\text{LaCrO}_3$  (LC) and Nb-doped  $\text{LaCrO}_3$  (LNC) coating.
- Examined the oxide scale formed and measured its thickness on coated and pristine materials.
- Developed a theoretical model for oxidation kinetics and verified experimental oxide scale thickness data with this model.
- Measured the total ASR of the coated and pristine samples after oxidation for 45 days at 800°C. It was observed that the pristine samples exhibited significant oxidation. However, even samples with as small as 1 micron coating were highly resistant to oxidation.
- Dip-coated  $\text{LaMnO}_3$  and  $\text{LaCrO}_3$ -based compositions on SS430 foils.

### Future Directions

- Conduct pressure assisted heat treatment on dip-coated perovskite coatings on SS430 foils.

- Conduct a short stack test with the best coating material, as determined by ex-situ oxidation studies.

## Introduction

Planar SOFC stacks are preferred over their tubular counterpart due to compact design, higher power and energy density, and projected lower cost. However, planar SOFC stacks require interconnect or bipolar plates which keep fuel and oxidants separate, and electrically connect adjacent cells. From the standpoint of cost and ruggedness, metallic interconnects are preferred. However, metallic interconnects of choice are stainless steels or nickel-chromium-based alloys, which are prone to oxidation. The oxide scale formed increases the ASR, which adversely affects the SOFC performance and efficiency, and thus in balance also adversely affects the cost. The potential remedy is the development of either baseline alloys that are oxidation-resistant, or suitable coating materials which can suppress oxidation kinetics. From the standpoint of cost and practicality, the preferred approach is the development of suitable coating materials.

To date, several coating materials have been tried, with varying degrees of success. The approach, however, has not been systematic, and has relied on trial and error. As a result, most of the coatings used to date were very thick (several or several tens of microns). This increases the potential for spalling, which is undesirable. The approach selected in this work is based on fundamental chemistry of materials, which has the potential to develop coatings that are adherent and very thin (typically less than 5 microns, and may be as thin as 1 micron), and yet can suppress oxidation kinetics to greater than 40,000 hours of operating life.

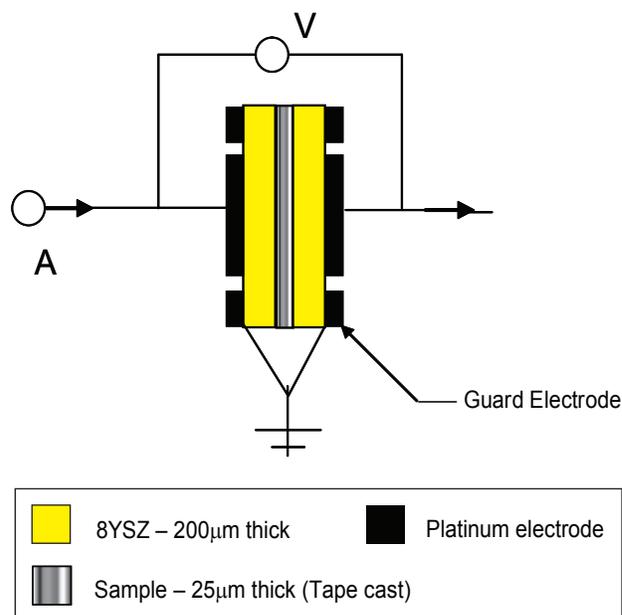
## Approach

Possible coating materials are perovskites with a transition metal, capable of exhibiting multiple valence states. An example is  $\text{LaMnO}_3$ . The approach involves doping a material such as  $\text{LaMnO}_3$  with suitable elements, which tend to suppress oxygen vacancy concentration, without significantly reducing electronic defect concentration. Powders of various coating materials, doped appropriately, are made. Samples of the materials are made by sintering. Two types of electrical tests are performed: (a) Measurement of total electrical conductivity; and (b) Measurement of oxygen ion conductivity using blocking electrodes. Thin coatings (1 to 5 microns) are then deposited on foils of various alloys. For the initial investigation, Haynes 230, Inconel 718, and SS 430 were the alloys selected. The coated and uncoated foils are subjected to air and

fuel, for various periods of time and over a range of temperatures, up to  $\sim 800^\circ\text{C}$ . Samples are oxidized for various periods of time, up to a maximum of six months. The oxide scale thickness is measured using scanning electron microscopy (SEM). The observed kinetics of oxidation is compared with the theoretical models developed. The ASR of the samples is also measured as a function of time of oxidation, with measurements conducted over a range of temperatures. Finally, a short stack will be tested using coated interconnects exhibiting the best properties.

## Results

1. Experiments were conducted on the measurement of oxygen ion conductivity using blocking electrodes at  $800^\circ\text{C}$ . Results showed that the blocking electrodes function successfully. It was decided to use a three electrode configuration (with guard electrode [Figure 1]) to eliminate the effects of surface conductivity. Lower values of conductivity were obtained for the sputter coated yttria-stabilized zirconia (YSZ)/perovskite couple as compared to the co-pressed sandwich structure. This was attributed to better equilibration to steady-state in the thinner (sputter deposited) samples. The lowest value of ionic conductivity measured was  $2.0 \times 10^{-7} \text{ Scm}^{-1}$  and was obtained for Ti-doped  $\text{LaMnO}_3$  (LMT). Measurements were also conducted on tape-cast YSZ/perovskite/YSZ sandwich structures which had stronger interfaces and thinner YSZ layers as compared to the sputtered samples.



**FIGURE 1.** Schematic of a Tape Cast Couple for Hebb-Wagner Polarization Measurement with Guard Electrodes

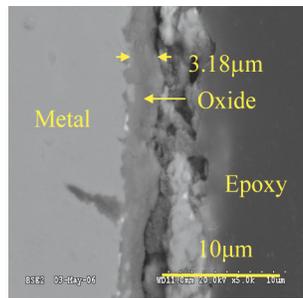
The readings were more consistent but the ionic conductivity values were higher (Table 1).

**TABLE 1.** Ionic Conductivity Values of Tape-Cast Sandwich Samples

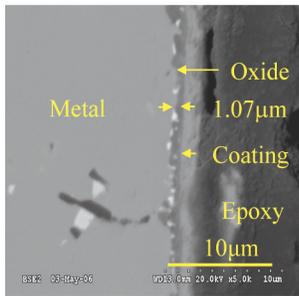
Coating Material	LMT	LM	LSM
Conductivity (S/cm)	$4.2 \times 10^{-7}$	$7.4 \times 10^{-7}$	$9.1 \times 10^{-7}$

2. Oxidation in flowing air was conducted at 800°C on the coated metal foils (LM, LMT and Sr-doped lanthanum manganite (LSM) for durations up to 4,320 hours (180 days). The oxidized samples were characterized by X-ray diffraction (XRD) and SEM. The oxidation products were identified and the oxidation kinetics ascertained by measuring the thickness of the oxide layer as a function of time. The results demonstrated that the LMT coating was the most effective and LSM least effective in suppressing the oxidation kinetics of the alloys. The results were verified by a theoretical model and demonstrated that the LMT coating was the most protective. The data were consolidated and compared with earlier work on spinel ( $Mn_2CrO_4$ ) coatings on Haynes 230 and it was found that the perovskite coatings are far superior with regard to protection against oxidation.

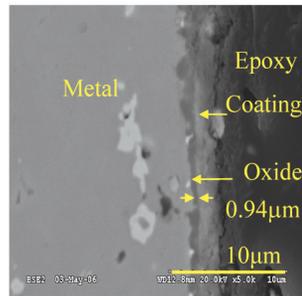
- Oxidation in flowing 10% $H_2$ /90% $N_2$  gas with 5% humidity was conducted on the coated metal foils ( $LaCrO_3$  and Nb-doped  $LaCrO_3$ ) for durations up to 2,160 hours (90 days). The oxide layer thickness was determined as a function of time. The perovskite coating significantly slowed down the oxidation kinetics of the metal foil. While an uncoated H230 foil formed an oxide layer of average thickness 3.18  $\mu m$  after 90 days, a 1  $\mu m$  coating of  $LaCrO_3$  reduced the thickness to 1.07  $\mu m$  (Figure 2).
- A spring loaded fixture was used to measure the ASR of the oxidized foils. Conductive paste was not used for these measurements as this could permeate the porous oxide layer and lead to an under-estimation of the ASR value. The ASR on the LMT-coated (1 micron) and uncoated foils showed that after 1,080 hours (45 days) in air at 800°C, the ASR of the coated foils was typically smaller by about half. The ASR for the  $LaCrO_3$  and Nb-doped  $LaCrO_3$  coated foils were also considerably lower than that for the uncoated foil over the entire temperature range (Figure 3).
- LSM and LMT were dip coated on to 2" x 2" SS430 foils. The coatings were cured at 1000°C for 1 to 5 hours. The samples were characterized by SEM. The coatings were about 5 to 10  $\mu m$  thick and showed excellent adherence. In some samples, load was applied on the dip coating by means of a spring at the time of heat curing. The application of load resulted in a more compact and less porous coating (Figure 4).



Uncoated H230

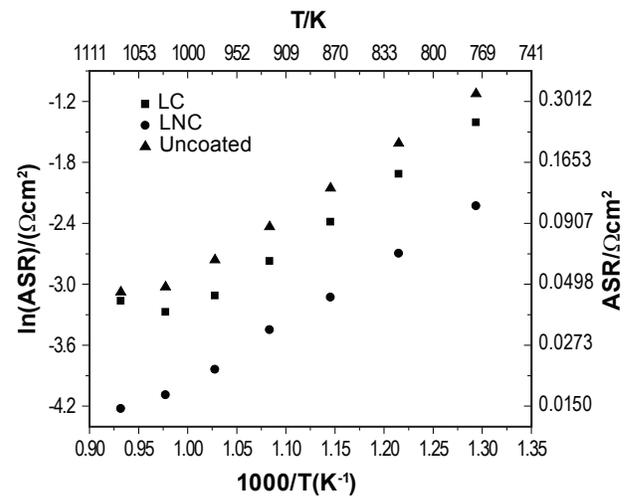


H230 coated with 1µm LC

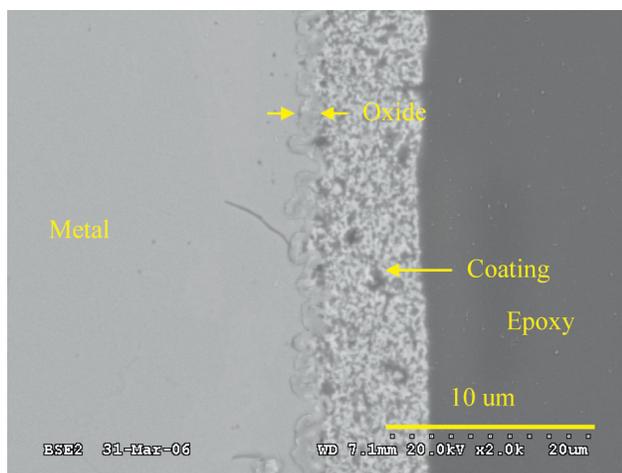


H230 coated with 1µm LNC

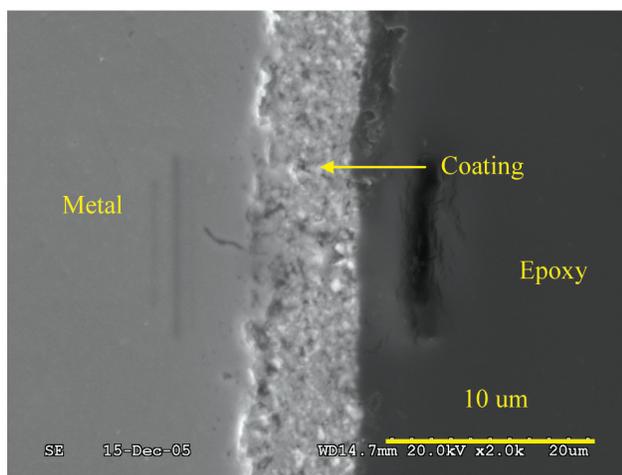
**FIGURE 2.** SEM Micrographs (Edgewise) of Uncoated, LC-coated (1  $\mu m$ ) and LNC-coated (1  $\mu m$ ) H230 Foils Oxidized for 2,160 Hours in Reducing Atmosphere at 800°C



**FIGURE 3.** Plots of ASR vs. 1000/T for Uncoated and Coated H230 Metal Foils with 1  $\mu m$  Coatings of LNC and LC, Oxidized in Reducing Atmosphere at 800°C for 336 Hours



Annealed without application of pressure



Annealed with application of pressure

**FIGURE 4.** SEM Micrographs of Dip-coated SS430 Foils with LSM0.85 Coating, Annealed at 1000°C for 2 Hours in Air

## Conclusions

Defect chemistry plays a major role in oxygen ion transport through oxides, and thus determines the suitability of a given material as a coating. Coating materials based on  $\text{LaMnO}_3$  and  $\text{LaCrO}_3$  were successfully made. It was demonstrated that perovskite coating is an order of magnitude superior to spinel coating.

1. Electronic and ionic conductivities of coating materials are in accord with defect chemistry, and that defect chemistry provides a scientific basis for the design of oxidation-resistant coatings.
2. High quality, strongly adherent coatings can be sputter deposited. The resulting foils exhibit improved oxidation resistance over the baseline foils. Even after 45 days at 800°C, the coating continues to remain well-bonded.
3. Coated foils also exhibit much lower ASR as compared to pristine foils.
4. Initial trials suggest that it is possible to coat larger metal sheets cost effectively by a combination of dip technique and pressure assisted curing at elevated temperature.