

## IV.A.3 SOFC Research and Development in Support of SECA

Michael Krumpelt (Primary Contact),  
Terry A. Cruse and Brian D. Ingram  
Argonne National Laboratory  
Argonne, IL 60439  
Phone: (630) 252-8520; Fax: (630) 252-4176  
E-mail: krumpelt@cmt.anl.gov

DOE Project Manager: Lane Wilson  
Phone: (304) 285-1336  
E-mail: Lane.Wilson@netl.doe.gov

### Objectives

- Explore the effects and mechanisms of chromium migration in solid oxide fuel cells (SOFCs).
- Explore cathode formulations that mitigate the effects of chromium.

### Accomplishments

- The effects of temperature and current density on the chromium oxide deposition rates were determined.
- A cathode material with 20% improved maximum power density was found.

---

### Introduction

Chromium contamination of SOFC cathodes has been observed by several groups of researchers developing cells with metallic bipolar plates. Hilpert et al have attributed the chromium transport to the formation of a volatile oxyhydroxide species that forms when chromium-containing steels are exposed to oxygen and water at elevated temperatures [1, 2]. The volatile oxyhydroxide,  $\text{CrO}_2(\text{OH})_2$ , can form either by reaction of the surface oxide with oxygen and water, or by direct reaction of metallic chromium [3]. It has also been shown that  $\text{CrO}_2(\text{OH})_2$  is the dominant species in the gas phase when water is present [4], and that the cathode acts as a nucleation site for the deposition of chromium [5]. Quadakkers et al provide an overview of this and other issues related to metallic-based interconnects [6]. There is also work that indicates that both the cathode and electrolyte composition can play a role in chromium poisoning [7, 8].

As discussed by Hilpert and others [9, 10] the chromium oxyhydroxide is presumed to be reduced to

chromium trioxide at the triple phase boundaries in the cathode as shown:



The oxide deposits block the access of oxygen to the electrochemically active sites and cause the performance decay of the cell. However, the magnitude of the effect varies greatly between cells and stacks from various organizations. In last year's work, we showed that a steady state cell performance degradation of 5% in 1,000 hours occurs in cells with E-BRITE<sup>®</sup> interconnects at 800°C [11]. We unequivocally identified chromium oxide deposits near the electrolyte interface and manganese chromium spinel near the metal interface. Only the first is responsible for the cell potential decline. In the present work, the effects of temperature and current density on the chromium oxide deposition are quantified and results with an improved cathode are presented.

### Approach

The same experimental apparatus as discussed last year was used. Briefly, the fuel cell housing is a two-piece circular structure made of alumina (last year Macor<sup>®</sup> was used initially but proved to be unsuitable) that contains a 2.5-cm<sup>2</sup> metal current collector with five flow channels. Under the channels is a fuel cell consisting of a lanthanum manganite cathode, a zirconia electrolyte and a nickel/zirconia anode. These cells were purchased from InDEC. To define the effects of current density four cells were run at 0, 184, 367 and 735 mA/cm<sup>2</sup>, respectively. All cells had an air flow of 160 standard cubic centimeters per second and a temperature of 700°C for 500 hours; another series was tested at 800°C.

As a follow-up of last year's work, showing chromium oxide deposits at the triple phase boundaries, we tested cathodes that had various amounts of chromium added deliberately to the lanthanum manganite. Up to 22% of the manganese was substituted with chromium and the powder was screen printed onto anode supported substrates, sintered and tested.

### Results

The effects of current density at 800°C are shown in Figure 1. Without any applied current, the cell potential held steady, but when current was flowing, the potentials decline asymptotically to a steady state rate, which clearly increases with current density. Although not shown here, the effect is linear.

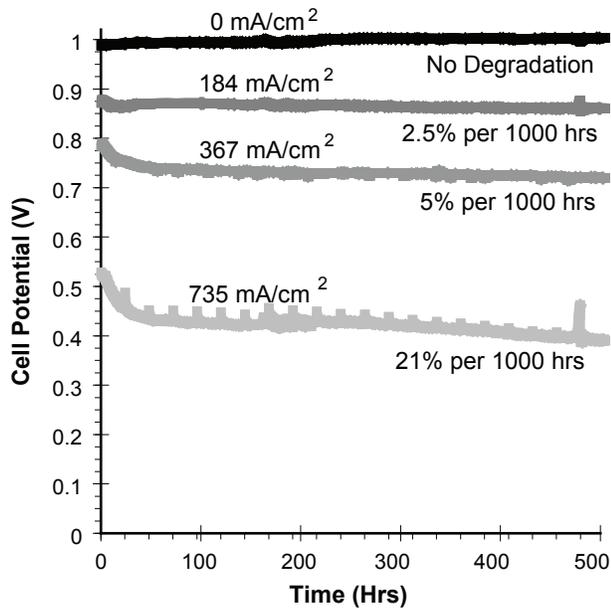


FIGURE 1. Effects of Current Density on Cell Potentials

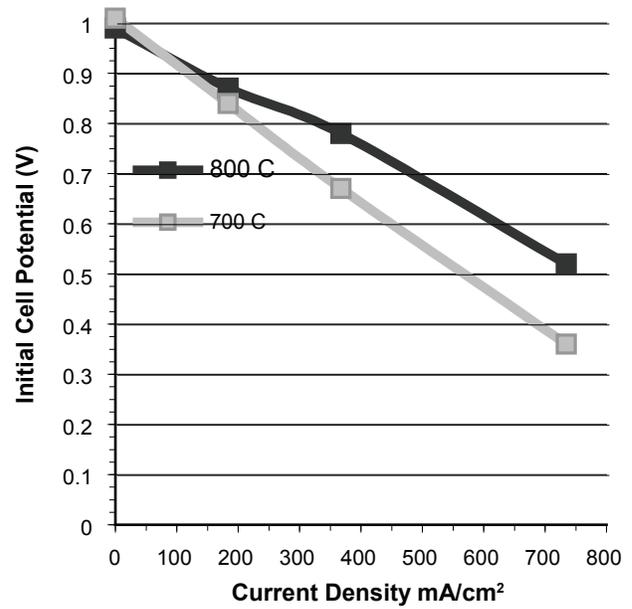


FIGURE 3. Initial Cell Potentials before Degradation

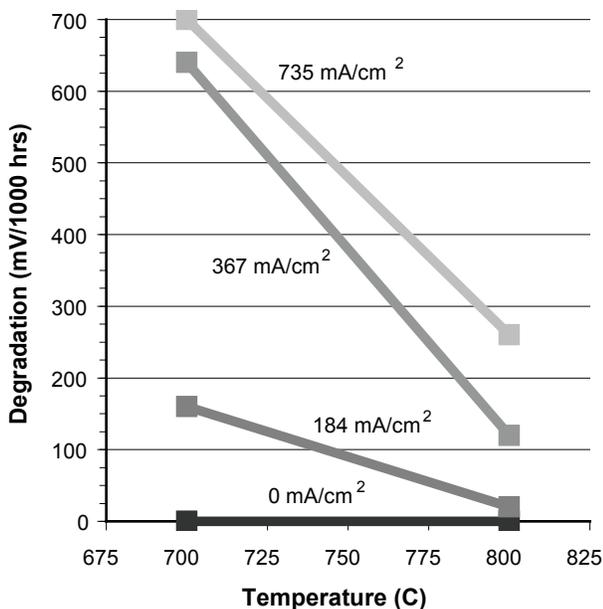


FIGURE 2. Degradation Rates at 800 and 700°C

Figure 2 gives the steady state degradation rates at 800 and 700°C. The degradation rates increase as the temperature is lowered, but the change is more dramatic than one would anticipate from the thermodynamics of the chromium oxyhydroxide formation.

An indication for the reasons can be inferred from Figure 3. Here, the initial cell potential before chromium poisoning sets in is plotted versus current density at 700 and 800°C. Consistent with thermodynamics, the cell potential is slightly higher at 700 than at 800°C at

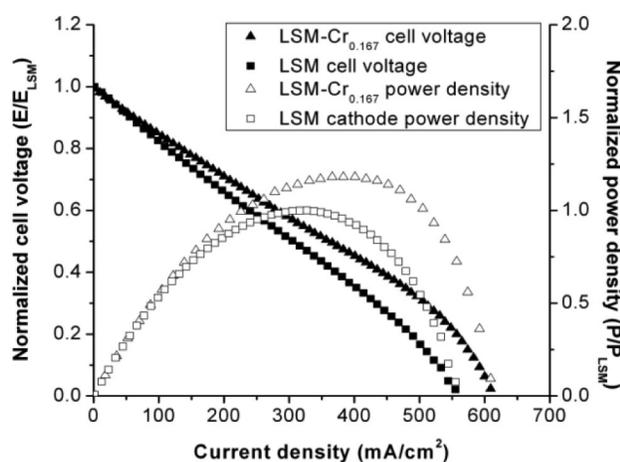
the open circuit potential. With current flowing, the cell potentials are much lower at 700 than at 800°C, indicating that the polarization resistance is much higher because the strontium doped lanthanum manganite (LSM) cathodes are considerably less active.

These effects are discussed below, but a surprising and encouraging result was obtained from testing the chromium substituted cathodes. As shown in Figure 4, the cell performance improved by 18%.

### Discussion

Current density is clearly a major factor in the deposition of chromium oxide and one needs to ask why? Either the rate of deposition of  $Cr_2O_3$  is dependent on the cell potential which changes with current density, or it is controlled by transport of the oxyhydroxide. There would appear to be at least four independent transport mechanisms for the chromium oxyhydroxide in an operating SOFC. First, it desorbs from the metal surface where it forms. Second, it diffuses through the streaming gas in the flow channel. Third, it diffuses through the pores of the inactive cathode, and forth it diffuses to the surface of the triple phase boundaries.

The first is not current density dependent since formation is not an electrochemical process. The second is largely influenced by fluid dynamics in the channel and again not significantly affected by the current density. The fourth mechanism would be expected to follow Butler-Volmer kinetics and increase with overpotential, but since the concentration of the oxyhydroxide is extremely low, at only one molecule per



**FIGURE 4.** Voltage and power density values as a function of current density for a cell operated at 800°C after 500 hours. Typical cells were used with cathodes of LSM and LSM-Cr<sub>0.167</sub> (i.e., (La<sub>0.8</sub>Sr<sub>0.2</sub>)<sub>0.99</sub>Mn<sub>0.883</sub>Cr<sub>0.167</sub>O<sub>3-δ</sub>). Values are normalized to LSM results.

ten million oxygen molecules, it will be diffusion limited and not potential driven.

Since the experimental evidence shows a linear correlation with current density, it appears that the oxyhydroxide flux is coupled to the flux of oxygen to the triple phase boundaries or through the pores of the cathode.

The effect of temperature on the chromium deposition as shown in Figure 2 is equally dramatic. Hilpert had looked at the thermodynamics of the oxyhydroxide formation and found only minor differences between 700 and 800°C. However, it is well known that lanthanum manganite cathodes lose a significant amount of their activity when the temperature is decreased below 800°C as is also evident in Figure 3. Since the effect of chromium tracks more closely with the decline in initial cell potentials rather than the thermodynamics of oxyhydroxide formation, it stands to reason that the diminished triple phase boundary area at the lower temperature is blocked more fully by the chromium oxide.

The results in Figure 4 are an exciting and unexpected finding. Since chromium oxide can react chemically with the cathode material, we were initially concerned that chromium on the surface of the manganite might adversely influence the charge transfer reaction of the oxygen. The opposite appears to be the case.

## Conclusions and Future Directions

The results presented in this report seem to raise concerns about the effects of chromium at lower temperature and higher current densities. However, we need to remember that these results were obtained with

uncoated E-BRITE<sup>®</sup> and coated material would have two orders of magnitude lower formation rates of the oxyhydroxide. More importantly, the dramatic effects of the chromium precipitation at lower temperature point to the solution to the problem. We need more active cathodes.

The results with the chromium doped manganite show already that the currently preferred cathode material can still be improved, and ferrites or mixed manganese/iron cathode would be much less affected because of the higher oxide ion vacancy concentration and mobility.

## References

- Hilpert, K., D. Das, M. Miller, D. H. Peck, and R. Wei, *J. Electrochem. Soc.*, **143**, 3642, (1996).
- Gindorf, C., L. Singheiser, and K. Hilpert, *Steel Research*, **72**, 528 (2001).
- Fryburg, G., F. Kohl, and C. Stearns, *J. Electrochem. Soc.*, **121**, 952 (1974).
- Ebbinghaus, B. B., *Combustion and Flame*, **93**, 119 (1993).
- Jiang, S. P., et al., *J. European Ceramic Society*, **22**, 361 (2002).
- Quadackers, W. J., J. Piron-Abellan, V. Shemet, and L. Singheiser, *Materials at High Temperatures*, **20**, 115 (2003).
- Matsuzaki, Y., and I. Yasuda, *J. Electrochem. Soc.*, **148**, A126 (2001).
- Kaun, T. D., T. A. Cruse, and M. Krumpelt, *Ceramic Engineering and Science Proceedings*, **25** (2004).
- Jiang, S. P., *J. Power Sources*, **124**, 390 (2003).
- Matsuzaki, Y. and I. Yasuda, *J. Electrochem. Soc.*, **148**, A126 (2001).
- T. A. Cruse, B. J. Ingram, Di-Jia Liu, M. Krumpelt, *ECS Transactions*, **5** (1) 355-346 (2007).

## FY 2007 Publications/Presentations

- M. Krumpelt, T. A. Cruse, B. J. Ingram, Chromium volatility and transport in SOFCs, 2006 Fuel Cell Seminar, Honolulu, November 19, 2006.
- B. J. Ingram, T. A. Cruse, M. Tetenbaum, and M. Krumpelt, "Effects of chromium interactions with LSM-based cathodes in solid oxide fuel cells" Materials Science and Technology Meeting and Exposition, Cincinnati, OH, October 15-19, 2006.
- T. A. Cruse, B. J. Ingram, D. -J. Liu and M. Krumpelt, "Chromium reaction and transport in solid oxide fuel cells," *ECS Transactions*, **5**(1), 335 (2007).
- M. Krumpelt, T. A. Cruse, and B. J. Ingram, "Chromium Volatility and Deposition in SOFCs," American Ceramic Society, Cocoa Beach, FL, January 22-27, 2006.