

## II.J.5 Materials Issues and Experiments for HTE and SO<sub>3</sub> Electrolysis

David Carter (Primary Contact), Bilge Yılız,  
Jennifer Mawdsley, and Magali Ferrandon

Argonne National Laboratory  
9700 S. Cass Avenue  
Argonne, IL 60439  
Phone: (630) 252-4544; Fax: (630) 972-4544  
E-mail: carter@cmt.anl.gov

Paul Demkowicz, Pavel Medvedev,  
and Kevin DeWall

Idaho National Laboratory  
2525 N. Fremont Avenue, P.O. Box 1625  
Idaho Falls, ID 83415  
Phone: (208) 526-3846 ; Fax: (208) 526-2930  
E-mail: Paul.Demkowicz@inl.gov

DOE Program Manager, Nuclear Hydrogen  
Research: Carl Sink

Phone: (301) 903-5131; Fax: (301) 903-0180  
E-mail: Carl.Sink@nuclear.energy.gov

Project Start Date: October 2004

Project End Date: Project continuation and  
direction determined annually by DOE

### Objectives

- Determine causes of degradation in solid oxide electrolytic cell (SOEC) stack components.
- Develop oxygen and steam-hydrogen electrode materials with improved performance and durability.
- Investigate the high temperature degradation of SOEC balance-of-plant materials.
- Identify degradation mechanisms and kinetics to determine component lifetimes and propose new materials for long-term device operation.
- Determine feasibility of SO<sub>3</sub> electrolysis to reduce temperature of the sulfur-iodine thermochemical cycle to 500-600°C.

### Technical Barriers

This project addresses the following technical barriers:

- SOEC stack degradation
- SOEC electrode performance and durability
- SOEC balance-of-plant materials degradation
- High temperature of the sulfur-iodine thermochemical cycle
- Electrode stability and activity in corrosive H<sub>2</sub>O- SO<sub>2</sub>-SO<sub>3</sub> atmosphere

### Contribution to DOE Nuclear Hydrogen Initiative Milestones

This project contributes to achievement of the following DOE Nuclear Hydrogen Initiative program milestones: 1) The Integrated Lab Scale (ILS) Demonstrations for the High Temperature Electrolysis Experimental Development and 2) Thermochemical System: SO<sub>3</sub> Electrolysis Studies.

- Milestone 5644: Complete assessment of degradation in long-duration test cells. (2Q, 2007)
- Milestone 5647: Demonstrate improved electrode materials for high-temperature steam electrolysis. (2Q, 2007)
- Milestone 5694: Complete corrosion test series #1. (1Q, 2007)

The forgoing milestones are in support of:

- Milestone 5683: Delivery of initial four-stack ILS module. (1Q, 2007)
- Milestone: Begin producing H<sub>2</sub> product with four-stack ILS module. (4Q, 2007)

In support of the sulfur-iodide thermochemical cycle:

- Milestone 5633: Complete evaluation of performance of SO<sub>3</sub> electrolysis

### Accomplishments

- Generated resistivity maps of the surfaces of stack components to identify areas of degradation. Found that the oxygen electrode degraded at the edge where hydrogen exits the stack. An evaluation of the hydrogen permeation of the seal is needed.
- Evaluated the electrode surfaces with Raman microspectroscopy and found areas of monoclinic zirconia, which can initiate stress in the electrolyte.
- Used high flux X-ray fluorescence techniques to map the deposition of chromium emanating from the bipolar plate. The chromium deposits are found preferentially near the edges of the seal and chromium diffuses toward the O<sub>2</sub>-electrode/electrolyte interface.
- Developed high temperature corrosion testing capability at Idaho National Laboratory with the ability to test in gas mixtures of N<sub>2</sub>O/H<sub>2</sub> and air/O<sub>2</sub>.
- Evaluated corrosion of Ni-Cr alloy, ferritic stainless steel and proprietary coatings using long term gravimetric tests.

- Determined that in a  $\text{H}_2\text{O}/\text{H}_2$  environment,  $\text{FeCr}_2\text{O}_4$  forms on ferritic stainless steel and a duplex layer of magnetite and chromia forms on the Ni-Cr alloy.
- Built an electrochemical test stand for the evaluation of  $\text{SO}_3$  electrodes and found that  $\text{SO}_3$  was reduced to  $\text{SO}_2$  by an apparent non-faradaic catalytic effect.



## Introduction

High temperature steam electrolysis uses waste heat and electricity from an advanced nuclear power plant to generate hydrogen from steam. The high temperature reduces the electrical energy needed to break hydrogen-oxygen bonds in the water molecule to form hydrogen. The steam electrolysis process depends on multiple cells arranged in “stacks” identical to solid oxide fuel cell designs to provide for a manageable voltage/current input as well as a manufacturable cell size.

This task was to determine the major causes of long-term stack degradation and use this information to develop materials and practices to increase the durability and performance of the stack. In addition, work is being carried out to investigate the degradation of balance-of-plant materials, beginning with corrosion experiments on metallic components exposed to stack conditions elevated temperature and corrosive atmospheres.

The sulfur-iodine (S-I) thermochemical cycle is another approach to generate hydrogen, which uses waste heat from an advanced nuclear reactor. Through a series of reactions using mainly sulfuric and iodic acids, water is fed into the cycle and hydrogen and oxygen are separated out as products. One difficult step in the S-I cycle is the reduction of  $\text{SO}_3$  to  $\text{SO}_2$ . This is thermodynamically favorable at temperatures  $>800^\circ\text{C}$ . The S-I process would be simplified if the temperature of this step could be reduced below  $600^\circ\text{C}$ .

## Approach

For the identification of the degradation processes in the SOEC stack, we created maps of the surfaces of the stack components using four-point resistivity measurements, Raman microspectroscopy, X-ray fluorescence coupled with sectioning the samples and analyzing them with scanning electron microscopy and energy dispersive spectroscopy. Furthermore, we investigated the fundamental mechanisms and kinetics of corrosion of the metallic stack components using thermogravimetric techniques and scanning electron microscopy.

To determine the feasibility of reducing  $\text{SO}_3$  through electrolysis at temperatures  $600^\circ\text{C}$  and below, we built

a single atmosphere electrochemical test station and evaluated the performance of  $\text{SO}_3$  electrodes.

## Results

In the stack degradation analysis, several possible causes have been identified by our study. In the coming months, further experiments will need to be made to verify and mitigate these causes. The basic plan was to use various nondestructive analysis techniques to map out areas of the cells to identify possible regions of interest. Four-point resistivity maps of the oxygen electrode and other stack component surfaces where a simple way to begin analysis. Figure 1 shows an increase of resistivity of the oxygen electrode near the hydrogen exit of the stack. This could be due to hydrogen leakage from the seal into the electrode.

Raman microspectroscopy identified a monoclinic zirconia phase near the edges of the electrode that could be a source of crack initiation and reduced ionic conductivity. Although at this point, no cracks were observed in the electrolyte. We also found that some chromium had reacted with aluminum oxides near the edge of the electrode, but not in the open surface of the electrolyte where the seal is made.

From X-ray fluorescence maps (Figure 2) it became apparent that chromium from the metallic bipolar plate migrated into the oxygen electrode and deposited preferentially near the edges of the seal as well as near the electrode/electrolyte interface.

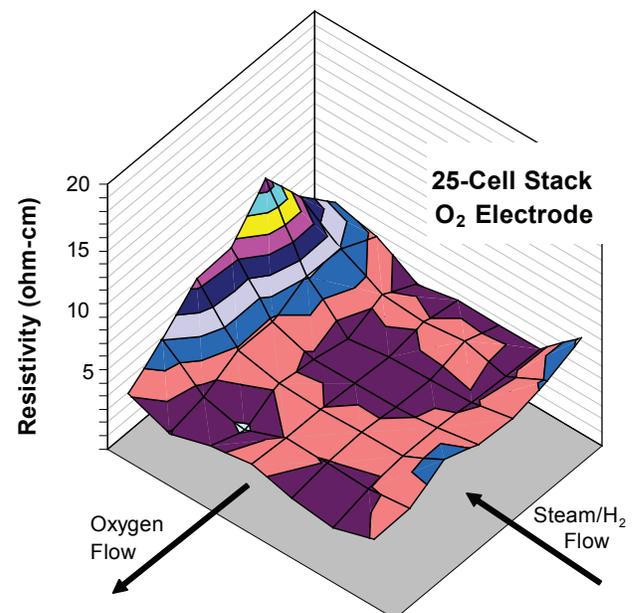


FIGURE 1. Resistivity Map of the Oxygen Electrode

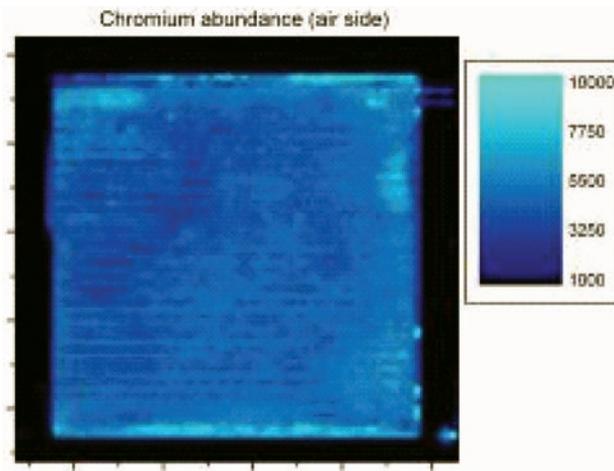


FIGURE 2. Chromium Abundance in the Oxygen Electrode

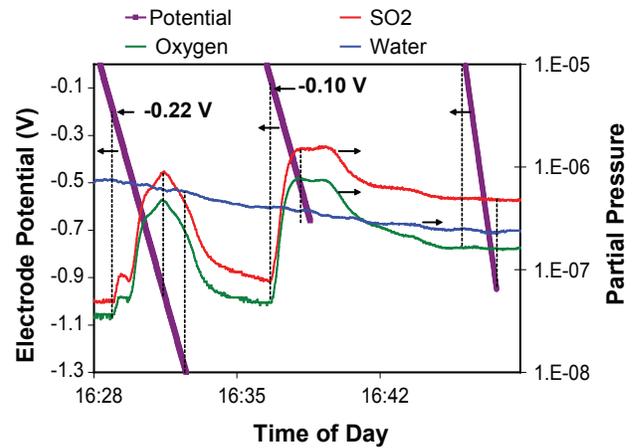


FIGURE 4. Electrode Potential and Partial Pressure of Gases as a Function of Time of Day

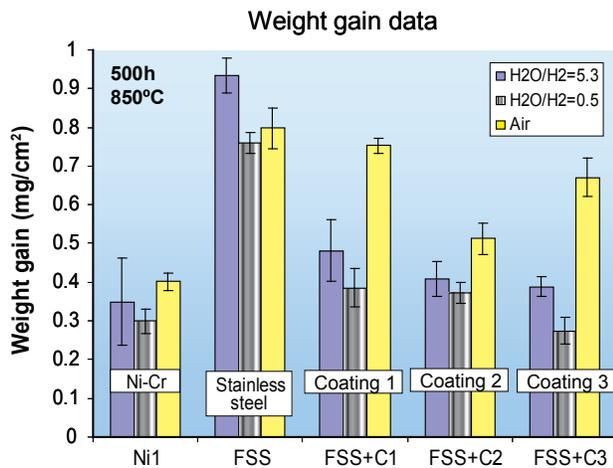


FIGURE 3. Gravimetric Test Results for the Corrosion of Metals in Air and  $H_2O/H_2$

In the task of improving electrode activity and durability, we found that  $Pr_2NiO_4$  has high activity as an oxygen electrode, and when it is deposited on a ceria interlayer, we achieved a low area specific resistance (ASR) of 0.07 ohm-cm<sup>2</sup> at 800°C.

Gravimetric experiments in  $H_2O/H_2$  and air (Figure 3) show that Ni-Cr alloy is more corrosion resistant in air and  $H_2O/H_2$  than stainless steel, and that the proprietary Ceramtec coatings are effective in corrosion resistance in  $H_2O/H_2$  but less effective in air.

In the  $SO_3$  electrolysis demonstration, we found that there are few materials that can be used as electrodes for the reduction of  $SO_3$ . However, we did find that a vanadium-based electrode mixed with

gold to make a conductive cermet was able to catalyze the reduction reaction. Figure 4 shows the results of an electrochemical test where the oxygen and  $SO_2$  concentrations increase with the application of an electric potential.

### Conclusions

- Stack degradation analysis showed that degradation occurred at the edges of the oxygen electrode near the exit of  $H_2$  from the stack. Chromium was seen to migrate from the bipolar plate into the oxygen electrode, depositing increased concentrations near the seals and the electrode/electrolyte interface.
- Corrosion testing on metals used for the bipolar plate and the balance-of-plant showed that the Ni-Cr alloy was more stable than ferritic stainless steel and that the Ceramtec coatings were effective in  $H_2O/H_2$  environments, but not as effective in air.
- The  $SO_3$  electrolysis demonstration showed that vanadium-based oxides exhibited an electrocatalytic effect on the reduction of  $SO_3$ .

### FY 2007 Publications/Presentations

- J.D. Carter, A. Call, M. Ferrandon, A.J. Kropf, V. Maroni, J. Mawdsley, D. Myers, and B. Yildiz, *Proceedings of the International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management*, June 24-28, 2007, Boston, MA.
- P. Demkowicz, P.I. Medvedev, K. DeWall, and P. Lessing, *Proceedings of the International Topical Meeting on the Safety and Technology of Nuclear Hydrogen Production, Control, and Management*, June 24-28, 2007, Boston, MA.