

II.J.8 SOEC Modeling, Electrode Characterization Studies, and Process Flowsheet Analysis in Support of HTE Development

Tanju Sofu (Primary Contact), Bilge Yildiz, Fee-Chul Chang, Deborah Myers, Hoydoo You, David Carter, and Richard Doctor

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
Phone: (630) 252-9673; Fax: (630) 252-4500
E-mail: tsofu@anl.gov

Grant L. Hawkes, Michael McKellar

Idaho National Laboratory (INL)
2525 N. Fremont Avenue, P.O. Box 1625
Idaho, IL 83415
Phone: (208) 526-8767; Fax: (208) 526-0528
E-mail: grant.hawkes@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

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- SOEC electrode performance and durability
- SOEC stack degradation
- HTE-VHTR system integration

Technical Targets

This project contributes to achievement of the DOE Nuclear Hydrogen Initiative Program milestones for 1) the Integrated Laboratory-Scale (ILS) Demonstrations for the High Temperature Electrolysis Experimental Development, and 2) the High Temperature Electrolysis Electrode Development.

- **Milestone 5640:** Complete analysis of SOEC stack and cell configurations to optimize hydrogen production.
- **Milestone 5644:** Complete assessment of degradation in long-duration test cells.
- **Activity 5652:** Review and provide input to INL flowsheet analyses of commercial electrolytic plants, particularly concerning equipment providing input to and treating the products of the electrolytic cell.
- **Milestone 6527:** Complete electrochemical characterization and modeling effort based on ALD-produced samples.

Objectives

- Use computational fluid dynamics (CFD) and electrochemical reaction modeling to determine optimal cell configurations and to define operating parameters to maximize solid oxide electrolysis cell (SOEC) performance while minimizing electrode degradation.
- Conduct X-ray spectroscopy studies and electrochemical measurements of SOEC electrodes to gain insight into the role of electrochemical reaction mechanisms, electrode degradation mechanisms, and materials properties on the performance and durability of SOEC electrodes.
- Conduct plant flowsheet analyses to optimize the thermal integration of the high temperature electrolysis (HTE) and very high temperature reactor (VHTR) plants to maximize overall system efficiency.

Technical Barriers

This project addresses the following technical barriers from the DOE Nuclear Hydrogen Initiative High Temperature Electrolysis Experimental Development Program:

Accomplishments

- Determined that localized degradation of the electrode activity due to Cr and/or Si poisoning severely distorts the current density and flow composition profiles, which further accelerates degradation of SOEC electrodes.
- Identified crystal orientations and changes in the chemical state of the A-site (La) in strontium-doped lanthanum manganite (LSM), which occur at the surface during DC polarization that increase the electrocatalytic activity of SOEC electrodes.
- Demonstrated that surface enhancements of dense thin-film LSM electrodes significantly improve electrochemical performance and overcome the limitations associated with bulk diffusion through the electrode.
- Determined that the cost of H₂ produced based on current INL HTE cell performance is competitive.



Introduction

HTE is one of the options being pursued as an economical means of producing H₂ using nuclear energy. One of the major issues facing the development of HTE is to increase the efficiency and to improve the durability of SOEC electrodes. To improve efficiency, a better understanding of electrochemical reaction mechanisms as well as the effect of materials properties, such as composition and crystal structure, on the electrochemical reactions is required. To improve durability, a better understanding of electrode degradation mechanisms is required. To address these issues, we are conducting computational modeling studies to aid in the design and configuration of SOECs and to define operating parameters that maximize cell performance while minimizing electrode degradation. We are also conducting *in situ* X-ray spectroscopy and electrochemical measurement studies to evaluate the role of electrochemical reaction mechanisms, electrode degradation mechanisms, and materials properties on the performance and durability of SOEC electrodes.

Another issue facing the development of HTE is effective thermal integration of the HTE and the VHTR is required to optimize overall system efficiency and reduce operating costs. We are conducting process flowsheet analysis studies to develop a better understanding of the heat and mass flows in the process and their effect on overall system efficiency.

Approach

SOEC Modeling

A 3-dimensional model is being developed that simulates the performance of both planar and non-planar SOECs [1]. The model combines an Argonne-developed electrochemical code, which models the electrochemical reactions, with a commercial CFD code, STAR-CD, which calculates the mass and heat balances of gaseous flows and solid media, and the flow patterns within the cell. Input parameters are based on geometric parameters and materials properties of SOEC stacks being evaluated at INL. Simulations are performed over a range of applied cell potentials to determine cell efficiencies, current density distributions, and temperature profiles.

Characterization Studies

Electrochemical cells consisting of dense thin-films of LSM and strontium-doped lanthanum cobaltite (LSC) with thicknesses ranging from 10–150 nm were prepared and deposited on polished single crystals of yttria-stabilized zirconia (YSZ) using pulsed laser deposition techniques. Pt electrical contacts were attached to the surfaces of these electrodes along each

edge. A Pt wire was attached in the center of the cell to ensure that electrical activation of the film occurred where the X-ray beam was focused on the electrode. A Pt counter electrode was painted on the backside of the cells. The cells were then attached to an alumina support tube mounted on the six-circle goniometer. The cell was heated using a parabolic infrared heater with access openings drilled in the housing for the incoming X-ray beam and the reflected and fluorescent X-rays, as shown in Figure 1. Impedance spectroscopy, cyclic-voltammetry, and potentiostatic measurements were conducted on each cell in air at 700–800°C. X-ray reflectivity and fluorescence analyses were used for studying the structure, oxidation state, and the electron density profile of the material at the air-cathode interface, and in the bulk of the electrode. These experiments were conducted at the Materials Research Collaborative Access Team beamline at the Argonne Advanced Photon Source.

Process Flowsheet Analysis

HTE studies employed only 50% conversion of steam per pass and the stripping of oxygen product without recovering it. Current experimental efforts have pushed to much higher conversion levels of up to 90%, and these conditions will be employed in the coming year. These considerations, along with the need for steam handling and heat transfer equipment operating near 1,100 K, result in higher capital costs. For the optimal case HTE, the capital was found to be 36% higher than NorskHydro. The optimum energy balance for the conservative HTE case was 67% steam and 33% H₂ and this was also found to be the economic optimum. The cost of delivering nuclear heat from a Gen-IV reactor requires still further refinements, but assuming that it is ~30% of the cost of electricity, the high-temperature system electrolysis would be attractive

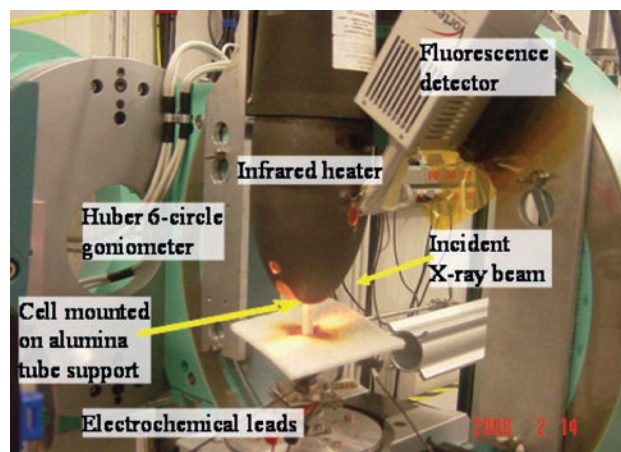


FIGURE 1. *In situ* Electrochemical Cell Set-Up for use in X-Ray Spectroscopic Studies

at the current industrial electricity cost of \$52.7/MWh (as reported by the DOE).

Results

SOEC Modeling

Modeling efforts were focused on developing a better understanding of two degradation mechanisms: Cr poisoning at the oxygen electrode and Si poisoning at the hydrogen electrode. Chromium is present in the bipolar plate and migrates from it during cell operation. It is believed that Cr poisons SOECs by inhibiting the O₂ evolution reaction, analogous to the inhibition of the reduction of O₂ observed in solid oxide fuel cells due to Cr poisoning. Silicon is present in the Ni-based cermet in the hydrogen electrode. In the high-temperature, high-steam environment present in the SOEC, Si is expected to volatilize from the seals and deposit on the hydrogen electrode, inhibiting the reactions at the electrode.

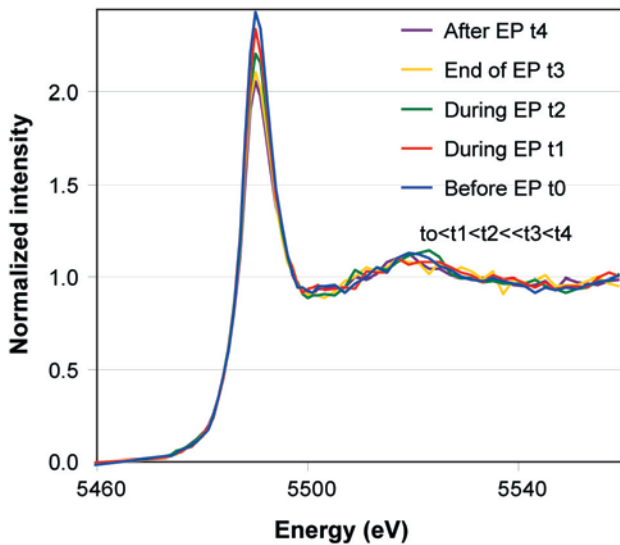


FIGURE 3. Effect of Electrochemical Polarization on X-Ray Spectra of the La L_{III}-Edge in LSM at 700°C

Our initial study considered only Cr poisoning. A model of an SOEC cell was set up that incorporated Cr distribution throughout the electrode, based on the results from a mapping study of a post-test cell [2]. An 11% decrease in oxygen electrode activity due to Cr poisoning was assumed. The model results showed that localized degradation of the electrode can lead to severe distortions in the current density profile, as shown in Figure 2. The initial study was then expanded to include Si poisoning. A 10% decrease in hydrogen electrode activity was assumed. Results showed an even greater distortion of the current density of the oxygen electrode, as shown in Figure 2. Furthermore, our results showed that these localized distortions in the current density lead to steep gradients in the current densities that further accelerate degradation of the electrode.

Characterization Studies

X-ray spectroscopy using depth-sensitive glancing angle incidence for the X-ray absorption near-edge spectroscopy (XANES) analysis was used to monitor changes in the La L_{III}-edge of samples of LSM and LCS under DC polarization at 700–800°C. Initially, no changes were observed in the total fluorescence or peak intensity of the La L_{III}-edge when the measurement was performed at angles that probed the bulk of the electrode films. However, when the incidence angle was reduced to below the critical angle (~0.5° in our experiments) so that only the air-cathode interface was probed, an increase in the total fluorescence and a decrease in the peak intensity of the La L_{III}-edge were observed with an increasing degree of current-conditioning in O₂-evolution polarization mode. In XANES analysis, the fluorescence intensity is proportional to the concentration of La and the peak intensity is related to the electronic state of the La. A plot of the consequent changes in the La L_{III}-edge spectra corresponding to the surface of the LSM electrode films when anodic and open circuit potentials were repeatedly applied is shown in Figure 3. The La L_{III}-edge spectra change with time under a polarization of 0.8 V, approaching a steady-state trace with time. This stabilization of the La spectra data correlated directly with stabilization of the area-

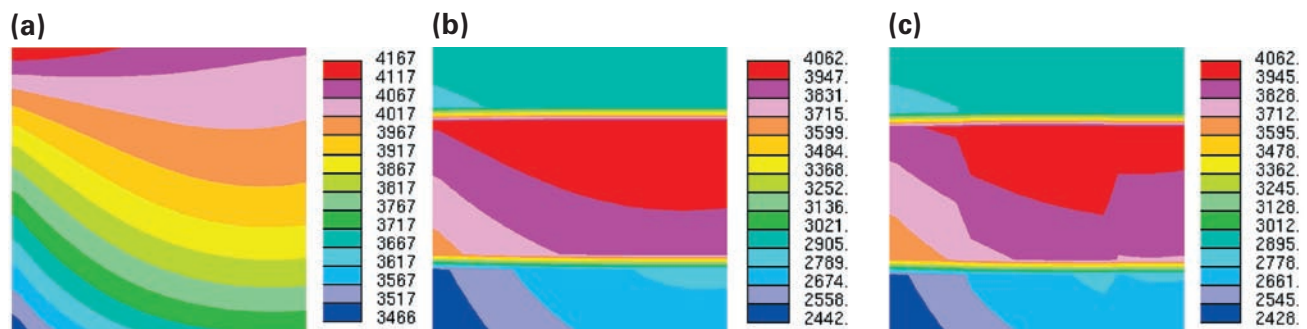


FIGURE 2. Current Density (A/m²) Profiles for an SOEC Oxygen Electrode for (a) Non-Poisoned, (b) Cr-Poisoned, and (c) Combined Cr- and Si-Poisoned

specific resistance of the electrode. This effect was seen repeatedly on several independently measured doped-LSM electrodes of 100-nm and 150-nm thicknesses.

Process Flowsheet Analysis

At \$50/MWh electric and 1,100 K heat supplied at \$15/MWh thermal, and assuming 15% internal rate of return a NorskHydro system would cost \$3.88/kg H₂, while H₂ from HTE would cost \$3.71/kg. INL is proposing process designs with far more aggressive conversion of steam per pass, recovery of oxygen, and much higher pressures. Further successful demonstrations of bench-scale and integrated HTE supporting these designs should provide significant opportunities for additional cost reductions.

Conclusions

- Localized degradation of the SOEC electrode, due to effects such as Cr poisoning, can lead to severe distortions in the current density and flow composition profiles, which can further accelerate the chemical-potential driven decomposition and degradation of the electrode.
- Specific crystal orientations and changes in the chemical state of the A-site (La) in doped LSM, which occur at the surface during DC polarization, increase the electrocatalytic activity of SOEC electrodes.

- Under very conservative assumptions for thermodynamic performance, this process is competitive. The economic uncertainties focus on the expected life-times from these cells when compared against conventional cells where the projected lifetimes are 7 years.

FY 2007 Publications/Presentations

1. J. D. Carter, B. Yildiz, D. Myers, K. C. Chang, H. You, *In Situ X-Ray, Electrochemical, and Modeling Investigation of the Oxygen Electrode Activation*. Presented at the 31st Annual Cocoa Beach Conference and Exhibition on Advanced Ceramics and Composition, Daytona Beach, FL, January 21–27, 2007.
2. J. D. Carter, A. Call, M. Ferrandon, A. J. Kropf, V. Maroni, J. Mawdsley, D. Myers, and B. Yildiz, *Post-Test Evaluation Of A Solid Oxide Electrolysis Stack*. Presented at the Annual Meeting of the American Nuclear Society, Boston, MA, June 24–28, 2007.

References

1. B. Yildiz, T. Sofu, *FY05 DOE Milestone Report on Thermal-fluid and Electrochemical Modeling and Performance Study of a Planar Solid Oxide Electrolysis Cell*.
2. B. Yildiz, T. Sofu, F.-C. Chang, *FY07 DOE Milestone Report on Results of ANL's Computational Fluid Dynamics and Electrochemical Analysis of SOEC Cells and Stacks for Higher Performance*.