



the **ENERGY** lab

PROJECT FACTS

Fuel Cells

Synchrotron X-Ray Studies of SOFC Cathodes—Argonne National Laboratory

Background

The mission of the U.S. Department of Energy (DOE) National Energy Technology Laboratory (NETL) is to advance energy options to fuel our economy, strengthen our security, and improve our environment. With the Solid State Energy Conversion Alliance (SECA), NETL is leading the research, development, and demonstration of solid oxide fuel cells (SOFCs) for coal-fueled central generation power systems that enable low cost, high efficiency, near-zero emissions and water usage, and capture carbon dioxide (CO₂).

Argonne National Laboratory (ANL) is one of various SECA Core Technology Program participants working together to provide vital research and development and testing support that addresses applied technological issues common to multiple SECA Industry Teams that are developing SOFC technology for integrated gasification fuel cell (IGFC) systems.

The performance of SOFCs is strongly influenced by the nanoscale structure and chemistry of electrode materials under operating conditions. SOFCs are operated at elevated temperatures and at near atmospheric pressure, which makes the utilization of traditional surface science techniques, typically requiring vacuum conditions near room temperature or lower, difficult. ANL is advancing the state of the art in high-pressure, high-temperature surface science by employing x-ray scattering and spectroscopy techniques to characterize the surface chemistry and structure of SOFC cathode materials at elevated temperatures (up to 900 °C), in controlled oxygen partial pressures (including air), and under electrochemical loads.

Project Description

ANL will expose model cathode thin films to synchrotron x-rays to better understand the role of cathode surface chemistry, crystallography, and electronic structure. Researchers will examine the dynamic structural and chemical changes that occur at the cathode side of a fuel cell under conditions that simulate actual operating conditions. The studies being performed in this project provide the needed understanding of in situ-ex situ correlations. The results also enable the development of molecular-level models for stimulating the rational design and development of high-performance cathode materials.

Goals and Objectives

The goal of this project is to improve the performance of SOFCs by measuring the atomic and chemical state of cathode materials under typical operating conditions, by correlating those measurements with other ex situ results, and by developing cathode modifications that will accelerate the oxidation reduction reaction and oxygen transport to the fuel cell electrolyte.

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PARTNERS

None

PERIOD OF PERFORMANCE

Start Date	End Date
10/01/1995	09/30/2012

(annual continuations)

COST

Total Project Value

\$10,230,000

DOE/Non-DOE Share

\$10,230,000 / \$0

AWARD NUMBER

FWP49071



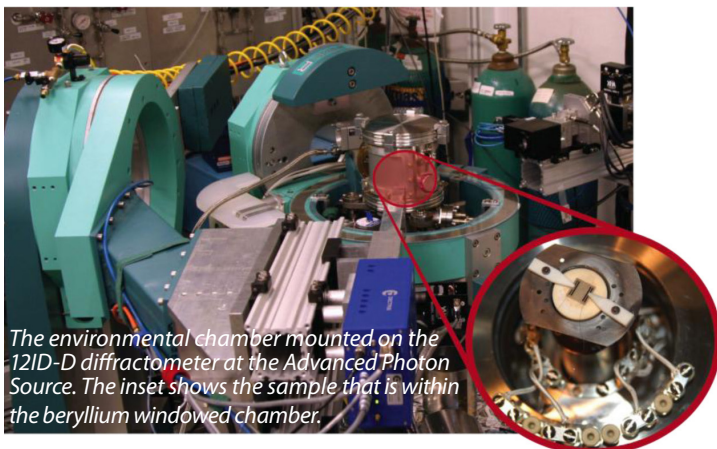
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The primary project objectives are:

- Study the chemical and atomic structure of lanthanum strontium manganite ($\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$; LSM), lanthanum strontium cobaltite ($\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$; LSC), and lanthanum strontium cobalt ferrite ($\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{FeO}_3$; LSCF), thin-film cathodes on yttria-stabilized zirconia (YSZ) electrolytes in an SOFC half-cell configuration as functions of operating temperature and electrochemical potential.
- Correlate the structure and chemical state with those determined by ex situ measurements from the literature and supplemental measurements performed at ANL, Carnegie Mellon University, and Massachusetts Institute of Technology.
- Determine the structure of, and composition gradients in, LSM, LSC, and LSCF thin films as a function of oxygen partial pressure, temperature, and substrate induced strain.
- Perform crystallographic and phase-diagram (temperature versus oxygen partial pressure [$p\text{O}_2$]) studies of recently discovered surface reconstructions to understand the chemistry of LSCF (001) surfaces.
- Utilize grazing-incidence diffraction to identify possible phase transformations and segregation on the surface of the cathodes during the electrode polarization and heating.
- Use grazing-incidence, depth-sensitive spectroscopic x-ray techniques to identify the oxidation states of LSM, LSC, and LSCF as a function of $p\text{O}_2$ and electrochemical condition.
- Perform in situ x-ray scattering measurements of the atomic scale chemistry in LSCF as a function of temperature, $p\text{O}_2$, and electrochemical potential.
- Establish the surface electrochemical potential on LSCF and LSM thin films as well as model infiltrated systems.

Accomplishments

- Determined trends for strontium surface segregation in LSM, LSC, and LSCF as a function of temperature and oxygen partial pressure. In doing so, equilibrium, high-temperature results were compared with room temperature non-equilibrium measurements.
- Demonstrated the utility of resonant x-ray scattering techniques and inelastic x-ray measurements for probing the chemical state of materials under conditions approximating those of operating SOFCs.



The environmental chamber mounted on the 12ID-D diffractometer at the Advanced Photon Source. The inset shows the sample that is within the beryllium windowed chamber.

- Completed x-ray scattering and spectroscopy experiments comparing LSM (011) on YSZ (111) that were electrochemically conditioned in situ and ex situ. Ex situ conditioned samples were found to be more electrochemically stable when subject to the same applied potential for further experiments.
- Demonstrated that surface strontium (Sr) segregation on LSM (011) on YSZ (111) is dependent on the distance from the contact wires under cathodic potential. Strontium was found to segregate in areas of the LSM thin film that is less active under potential.
- Found that LSC (011) without a gadolinium-doped ceria (GDC) buffer layer reacts with YSZ (111) forming a resistive layer. LSC (001) on a GDC (001) buffer film was found to decompose if the GDC film is less than 60 nanometers thick.
- Discovered that the LSCF (001) surface has a different crystal structure than bulk LSCF, and determined the sensitivity of the surface reconstruction to temperature and $p\text{O}_2$.
- Developed a detailed model of the surface polarization and position-dependent current for thin-film cathodes with wire electrodes. This included measuring and modeling the lateral potential drops from an LSCF on YSZ thin film when using a series of wires as current collector.
- Found that, upon high temperature annealing, Sr segregates to the surface, new phases form, and there are chemical shifts on the surfaces of LSCF films grown on YSZ (111) or gadolinium-doped ceria/YSZ (001) with a strong dependence on the distance from the electrode contact.
- Demonstrated that a thin LSM overlayer increases stability of LSCF films compared to bare LSCF films without the overlayer under similar annealing conditions.
- Determined the lattice parameter and electrical conductance of thin LSCF films as functions of temperature, $p\text{O}_2$, and electrochemical potential.
- The effects of long-term applied electrochemical potential on the surface structure and chemical state of pulse laser deposited thin-film cathodes were measured.
- A symmetric SOFC cell for ultra-small angle x-ray scattering studies was designed and constructed. The cell was used to determine the baseline porosity of sintered cathodes in preparation for atomic layer deposition infiltration studies.

Benefits

Findings and inventions under the SECA Core Technology Program are made available to all Industry Teams under unique intellectual property provisions (an exception to the Bayh-Dole Act) that serve to accelerate development. SECA will ultimately enable fuel cell-based near-zero emission coal plants with greatly reduced water requirements and the capability of capturing 99 percent of carbon at costs not exceeding the typical cost of electricity available today. Achieving this goal will significantly impact the nation given the size of the market, expected growth in energy demand, and the age of the existing power plant fleet. Federal funding support of this research is appropriate given the game changing nature of the technology accompanied by risks higher than the private sector initially can accept.