

High Temperature Electrochemistry Center

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Objectives

- Develop a fundamental understanding of processes that limit the performance of high temperature electrochemical systems relevant to fossil energy conversion, energy storage, gas separation and purification, electrolysis, emissions reduction and sensing.
- Create a unique research facility equipped with advanced diagnostic probes to support fundamental studies in fossil energy conversion.
- Establish collaborative research in high temperature electrochemistry with universities, industry, and other national laboratories, including the support of student internships.

Key Milestones

- Place a subcontract with Montana State University (MSU) to conduct research modeling and simulation of power system electronics, development of arc plasma source ion deposition technology, advanced x-ray characterization of high temperature electrochemical cell materials and interfaces, and transport phenomena in solid oxides (milestone completed 07/15/02).
- Complete screening studies of electrodes for the high temperature electrolysis of steam (milestone completed 09/30/02).

- Complete patterned cathode studies aimed at separating the effects of electrochemical activity and triple-phase boundary length for oxygen reduction on platinum and lanthanum manganite (milestone completed 11/30/02).

Approach

The kinetics and mechanisms of the electrochemical oxygen reduction is being studied, often one of the slowest processes common to solid oxide fuel cells, driven oxygen concentrators, and amperometric sensors. Many steps contribute to the overall rate of oxygen reduction, including mass transport to active sites, oxygen adsorption, dissociation, and charge transfer. Electrochemical impedance spectroscopy and current interrupt methods are applied to establish the contributions due to intrinsic electrocatalytic activity, interfacial microstructure (triple-phase boundary dimensions), and concentration polarization of specific cathode/electrolyte pairs. A systematic study of cathode compositions ranging from purely electronic conductors, such as platinum and lanthanum manganite to mixed conductors, such as ferrites and cobaltites is being conducted in cells with well-defined triple-phase boundary dimensions, aimed at showing how reaction rates are affected as the triple-phase boundary is expanded from a single to two dimensions. A microstructure-based Lattice Boltzmann electrochemistry model is being developed in a companion effort, and validated with experimental observations. Results will be used to guide the development of optimized oxygen reduction electrode compositions and structures.

Hydrogen can be made in a solid oxide fuel cell by running the device in reverse, potentially valuable as a means of chemical energy storage during off-peak hours. Factors that influence the magnitude of electrode overpotentials associated with steam electrolysis are being studied, which are critical because they relate directly to reaction inefficiencies. The effectiveness of substituted strontium titanate, nickel-zirconia, and noble metal-zirconia electrodes on a zirconia electrolyte are

being compared with regard to steam electrolysis as well as hydrogen oxidation. Electrode overpotentials are being established as a function of current density, partial pressures of steam and hydrogen, and temperature. Surface exchange currents will be determined by exposure of the electrolyte to D and ^{18}O -labelled tracers, followed by compositional depth profiling using secondary ion mass spectrometry and nuclear reaction analysis, and compared to values derived electrochemically. These fundamental results will guide the selection of anode material compositions that provide the best balance between electrode polarization associated with hydrogen oxidation and steam electrolysis.

Unique measurement and diagnostic capabilities are being assembled and developed to support fundamental research studies to be conducted in this facility. Electrochemical impedance spectroscopy and the complementary time-based current interrupt spectroscopy capabilities form the backbone of analytical techniques to be integrated into test stands. These techniques are particularly valuable in studying non-ohmic electrode processes that often limit performance. A suite of analytical probes to follow reaction progress and products will be incorporated into test stands including mass spectrometry, vibrational spectroscopies, and gas chromatography. Laser Raman spectroscopy is one example that shows promise as an *in-situ*, high temperature probe of reactions and structures; emission-infrared spectrometry will also be investigated as an *in-situ* probe of interfacial reactions. Four-probe conductivity equipment with controlled environment capabilities, dilatometry, thermogravimetry, differential thermal analysis/differential scanning calorimetry, analytical electron microscopy, surface profilometry, a suite of mechanical properties testing equipment, and x-ray diffraction equipment are available for use by this project.

Collaborative research has been established with MSU in the use of advanced synchrotron-based X-ray techniques to characterize fuel cell materials, development of large-area filtered arc plasma ion deposition technologies as a means to deposit electronic ceramics as well as in generating corrosion-resistant coatings for bipolar plates, and in studies of the electrical properties of electronic ceramics relevant to fossil fuel conversion. Additional studies at MSU focus on fuel cell power response characterization, modeling and monitoring. Research on the development of power electronics

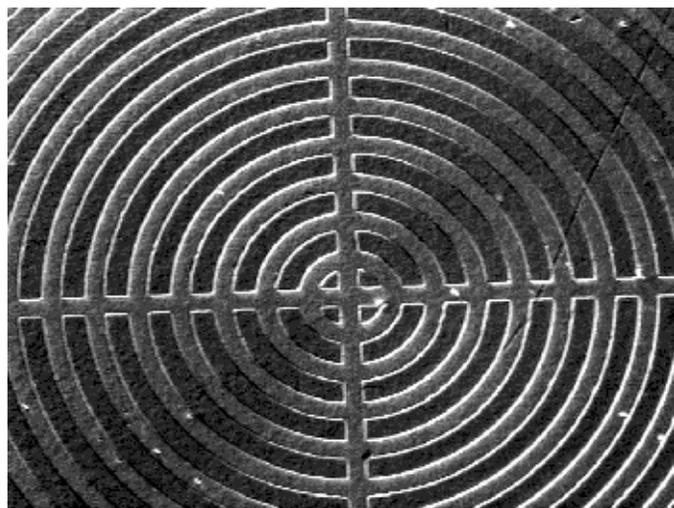
control systems suitable for high-temperature electrochemical devices, particularly fuel cells, will be conducted, aimed at improving the performance and efficiencies of fuel cell systems with multiple power sources. The unique capabilities of MSU in Filtered Arc Plasma Source Ion Deposition (FAPSID) provide a means to deposit oxide films of particularly high quality and consistency, applicable to the deposition of thin electrolyte and electrode layers as well as thin films to enhance corrosion resistance.

Results

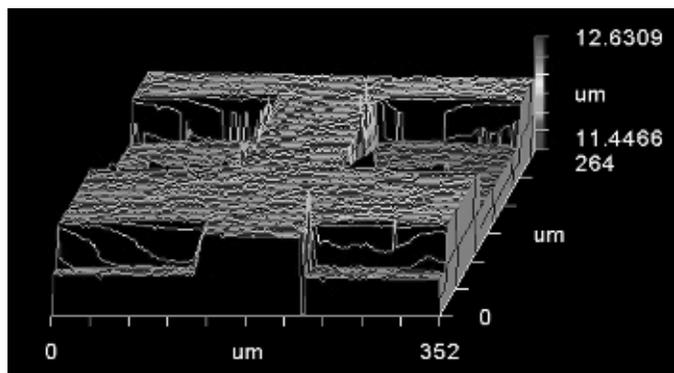
Patterned Electrode Studies: Fundamental electrochemical parameters that govern the rate of oxygen reduction at the cathode/electrolyte interface have been investigated for platinum and lanthanum manganite, both electronic conductors. A three-phase boundary (TPB) line between the electrode, electrolyte, and gas phase is usually related with the active area for the electrode reaction. The purpose of this study is to quantify relationship between the electrode reaction (thus, the overall electrode performance) and the electrode morphology or the length of the TPB, we use electrodes with a geometrically simple TPB.

Test cells consisted of a dense electrolyte formed into a rotationally-symmetric pellet carrying the working electrode at the bottom and the counter electrode at the top. The reference electrode was a platinum point, placed into a bore with the given dimensions or a Pt wire wrapped around the pellet. As shown in Figure 1a, electrodes were of a defined symmetrical geometry and, thus, known TPB length. Using an appropriate mask, a photo-resist pattern was created on a yttria-zirconia electrolyte. Next, a compact layer of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM), $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (LSC) or Pt was deposited on the pellet by vapor deposition using a corresponding oxide or Pt metal target followed by the removal of the mask. The width of the electrode circuits was in the range 50-185 microns. Typical surface image and optical profiles of the pattern LSM electrode are shown in Figure 1b, demonstrating that fairly smooth surfaces with a less than 0.03 micron thickness fluctuation and sharp horizontal edges were obtained. Electrodes had vertical edges with no slope to add to the electrode surface coverage, enabling easy geometrical calculations of the TPB.

Preliminary electrochemical impedance spectroscopy have been performed to establish electrode polarization for these patterned electrodes. The activation energy associated with oxygen reduction in the temperature range of 650 to 800°C was 1.5 eV, indicating a temperature dependence considerably sharper than that of the electrolyte (~1eV). Electrode polarization losses were also shown to decrease rapidly with increased bias potential, consistent with Butler-Volmer kinetics. Measurements on purely electron-conducting platinum and on principally electron-conducting lanthanum manganite provide a needed basis on which to compare the performance of mixed ion and electron-conducting electrodes in a similar configuration. The active portion of mixed conducting electrodes extends beyond the triple phase boundary.



(a)



(b)

Figure 1. Geometry (a) and optical profile (b) of a patterned lanthanum manganite electrode. This special electrode geometry enables the role of intrinsic electrocatalytic activity to be distinguished from contributions, due to triple phase boundary length in determining overall electrode reaction kinetics.

Exceptionally Active Oxygen Reduction

Electrodes: New oxygen reduction electrode materials have been developed that show exceptional electrocatalytic activity at low temperatures. The electrode materials were created by doping lanthanum ferrite with transition metal oxides having favorable reduction potentials in the temperature range of interest. Potential applications for such electrodes include fuel cells, gas sensors, and oxygen separation devices.

Cathodic overpotentials for a transition metal-doped lanthanum ferrite compare favorably with those determined for $\text{La}_{0.80}\text{Sr}_{0.20}\text{FeO}_3$, a very active electrocatalyst for oxygen reduction, as shown in Figure 2. These overpotentials were established using current interrupt techniques to separate ohmic contributions, such as those due to the zirconia electrolyte, from non-ohmic electrode polarization. Both electrode compositions were applied by screen printing over a 5 micron-thick samaria ceria buffer layer to minimize deleterious interfacial reactions. Electrode performance was shown to be very sensitive to sintering conditions, which affects the character of the triple-phase boundary as well as possible chemical interactions at the interface. Further research is needed to understand the role that added transition metal oxides play in determining electrocatalytic activity, in addition to investigations related to stability and lifetime.

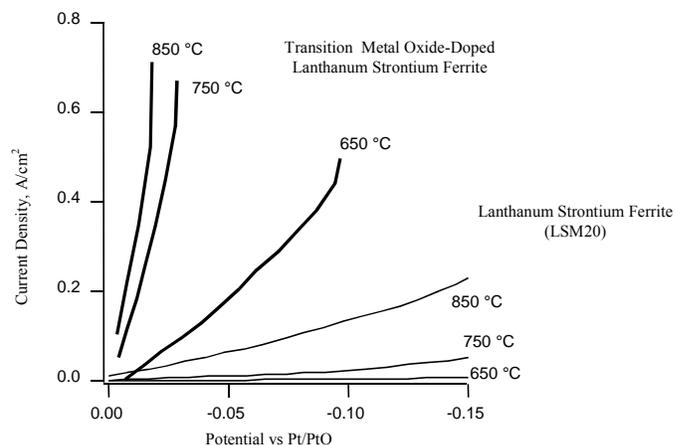


Figure 2. Oxygen reduction overpotentials for a lanthanum strontium ferrite and a transition metal oxide-doped lanthanum strontium ferrite, determined by current interrupt methods. Doped ferrites yielded much improved polarization losses

Conclusions

Patterned electrodes show promise as a means of separating the role of intrinsic electrocatalytic activity and microstructure in determining the overall effectiveness of the oxygen reduction electrode. Though photolithography and sputtering techniques, electrodes have been prepared with a precisely controlled geometry. This approach will be used to study differences in oxygen reduction kinetics on electrodes with varying levels of mixed electron and ion conductivity.

Through transition metal oxide doping of lanthanum ferrites, exceptionally active oxygen reduction electrodes have been produced. The electrode activity is most pronounced at low operating temperatures. Future research will focus on identifying additional dopants to enhance electrocatalytic activity, on microstructural control, and on lifetime and durability issues.

Factors that control electrode overpotentials in a reversible solid oxide fuel cell, where steam is electrolyzed to produce hydrogen, will be identified. Characteristic overpotentials resulting from the use of substituted strontium titanate, nickel-zirconia, and noble metal-zirconia electrodes on a zirconia electrolyte will be established as a function of current density, partial pressures of steam and hydrogen, and temperature. Surface exchange currents will be determined from Butler-Volmer kinetics and by exposure of the electrolyte to D and ^{18}O -labelled tracers, followed by compositional depth profiling using secondary ion mass spectrometry and nuclear reaction analysis. These fundamental results will guide the selection of anode material compositions that provide the best balance between overpotentials associated with hydrogen oxidation and steam electrolysis.

Research at Montana State University will focus on dynamic load/fuel cell characterization and modeling, deposition of thin ceramic films by filtered arc plasma source ion deposition, advanced x-ray characterization of electroceramic surfaces and interfaces, and fundamental studies of conduction processes in solid electrolytes.