

V.E.3 Combinatorial Method for Developing Cathode Catalysts for Fuel Cells

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Technical Targets

This project is focused on developing a new technique for high throughput screening of candidate catalyst systems, *in situ* at low cost. The apparatus is being used for the discovery of oxygen reduction catalysts that may meet the following DOE 2010 technical targets for electrocatalysts at the stack level:

- Durability: 5,000 hrs
- Cost: \$5/kW
- Performance: $>130 \text{ A/cm}^3$ @ 800 mV

Accomplishments

- Further development of Gen 1 screening system design.
- Explored new Gen 1 sample preparation methods.
- Prototype Gen 2 screening system developed.
- Exploration of non-Pt catalyst families using Gen 1 system.
- Detailed characterization of Pd-X catalyst systems.

Objectives

- Develop a controlled method for accurate high-throughput evaluation of new catalyst materials for fuel cells.
- Scale-up combinatorial approach: sample preparation, screening system and data processing.
- Evaluate several families of catalysts for oxygen reduction activity.
- Scale-up new, low-cost high-activity catalysts for evaluation in fuel cells.
- Develop instrument for efficient evaluation of multiple fuel cell components (catalysts, membranes, membrane electrode assemblies, etc.) for general use in process development and manufacturing quality control.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost
- (C) Performance



Introduction

Major barriers to the realization of a hydrogen economy include the high cost, durability and performance of fuel cells. A large amount of materials research has focused on the development of new oxygen reduction catalysts and catalyst structures that are lower cost, more active, have greater utilization and are more robust than the current Pt-based systems [1,2]. Unfortunately, like many complex interfacial electrocatalytic reactions, oxygen reduction is not readily predisposed to rational catalyst design and optimization. Thus a combinatorial approach that can rapidly and accurately evaluate large arrays of catalysts would likely greatly accelerate the identification and development of highly active, low-cost, catalysts to replace Pt. Such a system would be of great value in enabling the hydrogen economy based on economically viable fuel cell systems. We are developing a new approach for screening arrays of electrochemical materials *in situ*, utilizing thermal imaging and applying the technique to the discovery of new fuel cell catalysts.

The method we are developing exploits heat generation and local temperature changes related to electrochemical efficiency as a widely applicable *in situ* screening method for combinatorial arrays of fuel cell catalysts. Figure 1 illustrates a fuel cell system and how

local variations in catalyst efficiency can lead to local variations in temperature that can be directly correlated to the performance of the catalyst at that point. Assuming resistive heat generation, when a single load is applied, the most efficient catalyst would be expected to exhibit the greatest increase in temperature due to its higher current density. Chemical heat generation may also contribute to the signal. The approach allows for the evaluation of a wide range of electrochemical material arrays in an *in situ* environment, and has advantages in that a single load can be used to evaluate large numbers of samples.

Approach

For this project we focused on the development of a multi-sample fuel cell system that can be used to screen large numbers of catalysts based on their thermal signature. We performed basic electrochemical experiments to determine approximate ranges of heat generation for various fuel cell catalyst systems and used this data to do extensive thermal modeling and optimization of the designs. The goal was to achieve sufficient uniformity of performance across the fuel cell sample array. For example, uniform contact area, pressure, and fuel composition, combined with sufficient thermal resolution allows us to accurately identify the best performing catalysts within the array. Several sample preparation techniques have been developed that are compatible with the system and we are using the system to investigate the performance of a number of non-platinum families of catalysts. The best catalysts are scaled-up and evaluated in greater detail in full fuel cells and by other electrochemical methods.

Results

One focus of the work the past year has been on the further improvement of the Gen 1 “sample rod” design and the demonstration of the compatibility of alternative sample preparation methods with our system. We improved the thermal uniformity of our 25-sample rod system such that the baseline temperature from sample to sample was less than 0.1°C at an operation temperature of ~70°C by designing a new heating and insulation structure for the cell. We also began using a cooled infrared (IR) camera with greater thermal resolution to further improve our screening capability.

Electro-deposition from metal salt solutions and sputter deposition of thin solid films directly onto the graphite sample rods have been our primary forms of sample preparation. More recently we have developed a simple, controlled process for making arrays of supported catalyst materials using conventional gas diffusion layer architecture. The catalyst materials are formed by reducing metal salt mixtures applied to a carbon sheet using one of several processes including firing in H₂/Ar, washing with a solution containing a reducing agent, or microwave processing. Some advantages of this approach include: the ability to evaluate new catalyst systems, the capability to evaluate carbon supported catalysts, and increased thermal resolution from greater catalyst surface area.

Tools and fixtures for preparing and laminating the samples into a single membrane electrode assembly (MEA) were developed. We used our 4-sample prototype system to evaluate different sample preparation methods before scaling up to the 25-sample system. Figure 2 shows thermal images of a prototype

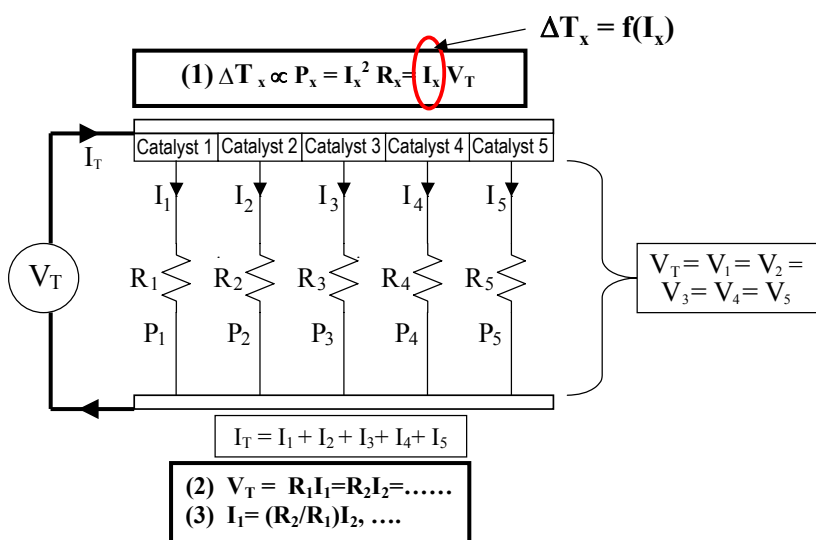


FIGURE 1. Illustration of the Relationship between the Local Temperature Increase and the Effective Resistance or Efficiency of a Sample in an Electrochemical Sample Array to which a Load is Applied

4-sample system utilizing sample gas diffusion layers with a range of Pt loadings. In this run, the temperature of operation was 50°C, the current was 50 mA/cm² with a voltage ~0.55 V. The backpressure for H₂ and O₂ gas was 20 atm with a flow rate of 30 sccm. The increase in temperature for the highest loading Pt sample (0.4 mg/cm²) was over 2°C while for the lowest loading (0.1 mg/cm²) was ~0.4°C, making them easily distinguishable. Separate measurements made of the individual currents through each sample while a 50 mA/cm² load was applied to the full cell were consistent with the thermal data.

This general sample preparation method was used to evaluate several families of non-platinum catalysts using the 25-sample Gen 1 system. Figure 3 shows a thermal image of

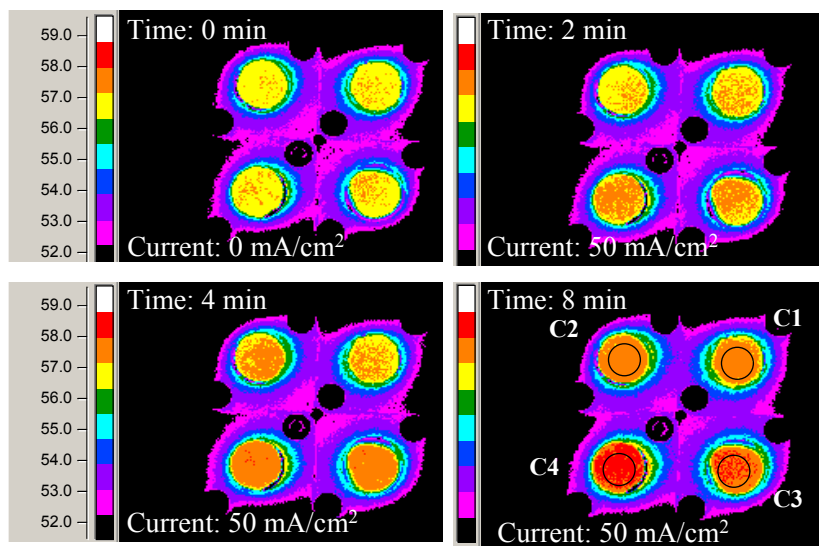


FIGURE 2. Thermal Image During Operation of a Four-Catalyst Sample Prototype Cell Used for Design and Sample Preparation Optimization; Pt Loadings: C1 = (0.1 mg Pt/cm²), C2 = (0.2 mg Pt/cm²), C3 = (0.3 mg Pt/cm²), C4 = (0.4 mg Pt/cm²)

a typical screening run. In this example, the bottom row was used to provide controlled reference based on increased loadings of platinum as indicated by the arrow. The initial temperature increase of the best catalyst compositions being evaluated was similar to that of the platinum at a similar loading, though the performance of these non-platinum phases deteriorated over a relatively

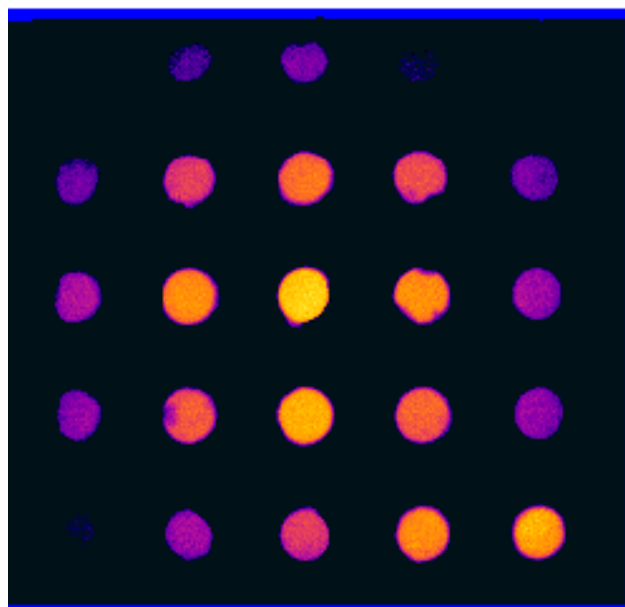


FIGURE 3. Thermal Image of 25-Sample Catalyst Array For A Binary Catalyst System after 1 Hour Operation at 55°C (The temperature range of the image is 4°C. The bottom row comprises control samples based on an increased loading of Pt catalyst, as indicated by the arrow. The best binary catalyst exhibited a delta T similar to that of Pt at a similar loading.)

short period of time (<1 hr) relative to the long-term stability of the Pt samples.

One of the best systems we had identified earlier and selected for more detailed evaluation was the Pd-Co systems. A number of methods were used to evaluate carbon supported Co-Pd catalysts. Though all of the prepared electrocatalyst exhibited significant activity, the CoPd₃ catalysts showed the best activity, with the lowest activation energy, a low Langmuirian Tafel slope, a competitive onset potential and rate constant that is at least an order of magnitude higher than the other electrocatalysts. Also, as shown in Figure 4, the CoPd₃ MEA performance was comparable to a commercial Pt electrocatalyst under identical experimental conditions.

The ORR mechanism was evaluated on the CoPd₃ and it was found that the rate-determining step is a chemical step following a fast first electron transfer and most likely involves a breaking of the O-O bond in the adsorbed PdCo-OOH species.

Conclusions and Future Directions

- We have developed an easily scalable method of combinatorially screening materials for electrochemical systems based on their efficiency related thermal signature.
- While DOE funding for the project has ended, we will continue to use this system for the internal

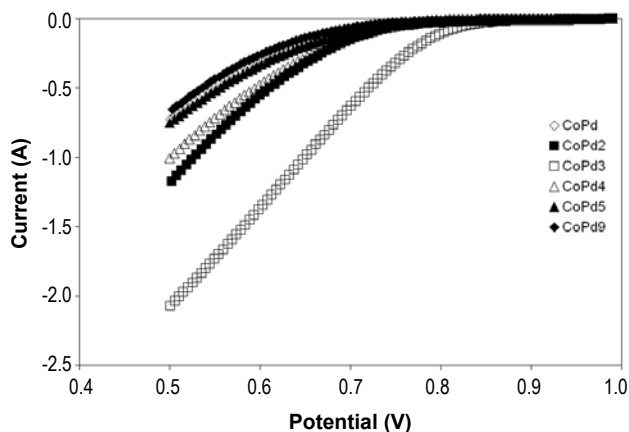


FIGURE 4. Polarization Curves of Cells Built Using Carbon Supported Pd-Co Catalysts of Different Compositions showing the Best Performance for the Pd₃Co Material

development of catalysts with a focus on oxygen reduction activity.

- Materials with the greatest potential will be further characterized and optimized by conventional methods.
- Future directions include development of the Gen 2 system and demonstration of the system on a larger scale.

Special Recognitions & Awards/Patents Issued

1. Patent filed: USPTO 11/801,847.

FY 2007 Publications/Presentations

1. “Thermal Imaging for In-situ Combinatorial Characterization of Fuel Cell Catalyst Arrays” Keith D. Kepler, Yu Wang, Hongjian Liu, Lianxi Yang, William Mustain, Jai Prakash, Presentation at The Electrochemical Society Meeting, Chicago, 2007.

2. “CoPdx Alloys as Oxygen Reduction Electrocatalysts for Polymer Electrolyte Membrane Fuel Cells”, William E. Mustain, Keith Kepler, and Jai Prakash, *Electrochimica Acta*, 52-5 (2007) 2102.

3. “Investigations of Carbon-Supported CoPd₃ Catalysts as Oxygen Cathodes in PEM Fuel Cells” W. E. Mustain, Keith Kepler, Jai Prakash, *Electrochemistry Communications*, 8-3 (2006) 406.

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2. Benny C. Chan, Renxuan Liu, Krishnakumar Jambunathan, Hong Zhang, Guoying Chen, Thomas E. Mallouk, and Eugene S. Smotkin; *J. Electrochem. Soc.*, Volume 152, Issue 3, pp. A594-A600 (2005).