V.C.11 Advanced Catalysts for Fuel Cells

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Objectives

- Develop methods for combinatorial screening of catalysts for the oxygen reduction reaction
- Demonstrate feasibility of performing catalyst discovery using combinatorial approach
- Identify advanced catalysts with reduced precious metal compared to state-of-art content catalysts capable of performing at 2,000 mW/mg of precious metal
- Increase the cathode potential by 0.1 V at 500 mA/cm^2

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost
(C) Electrode Performance

Technical Targets

Reduction in the use of noble metal catalysts with improved performance

- Near term target of 2,000 mW/mg of noble metal (0.25 mg/cm^2)
- Increase the cathode potential by 0.1 V over the state-of-art for current densities exceeding 500 mA/cm^2

Accomplishments

- Developed a combinatorial multi-electrode technique for screening of electrocatalysts for oxygen reduction
- Validated the results from multi-electrode cell for studying oxygen reduction
- Prepared thin film multi-electrode array with Pt, Ni and Zr
- Completed preliminary electrochemical and structural characterization of Pt-Ni and Pt-Ni-Zr films as electrocatalysts
- Demonstrated 60 mV higher onset potential for oxygen reduction compared to platinum
- Demonstrated potential for 40% reduction of precious metal with Pt-Ni-Zr catalysts

Introduction

The Department of Energy (DOE), under the Hydrogen, Fuel Cells and Infrastructure Technologies Program, has identified *catalyst cost* and *electrode performance* as two of the key barriers to the commercialization of hydrogen/air polymer electrolyte membrane fuel cells. Reducing the amount of precious metal used in the cell and improving the electrocatalytic activity would make fuel cells commercially viable. Reducing the amount of precious metal will reduce the cost, and improving the electrocatalytic activity will increase the energy conversion efficiency and power density. As per the technical targets set forth by DOE, the precious metal loading must be decreased to 0.1 mg/cm^2 and the cell voltage must be increased by 0.1-0.2 V.

A significant portion of the precious metal catalyst used in a hydrogen-air fuel cell is used at the cathode. Also, a large part of the voltage loss arises from the cathode. Therefore, an advanced cathode electrocatalyst that contains substantially reduced amounts of precious metal and improved electrocatalytic activity will address DOE's commercialization goals. JPL's effort has focused on a robust combinatorial approach to identifying and demonstrating new compositions of cathode electrocatalysts with reduced amounts of precious metals that will result in the desired performance improvements. This report is a description of the JPL effort in FY 2006.

Approach

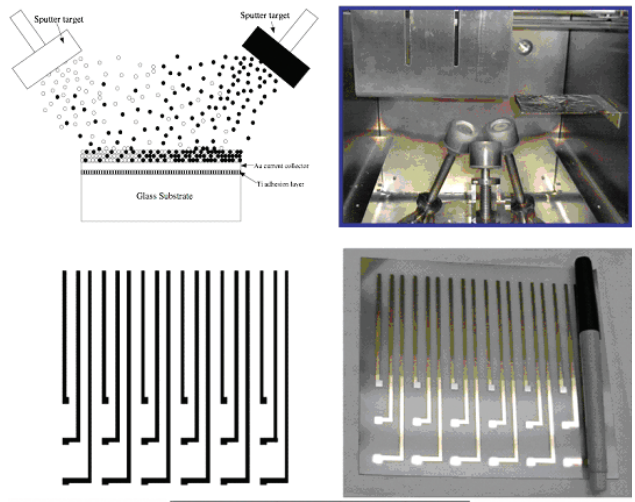
A unique combinatorial approach to preparation and characterization of thin catalyst films was developed and demonstrated as the means to identify new catalysts with reduced amounts of precious metal and increased activity. New catalyst compositions based on non-noble metals were prepared as thin films by the co-sputter deposition technique. Using this technique of preparation, any combination of elements or compounds can be prepared as thin films. The selection of catalyst materials was based on the ability of the materials to resist corrosion in acidic media and the intrinsic electronic properties of various elements to catalyze the oxygen reduction reaction. Since these films are just about 10 nanometers in thickness and are flat, the effect of composition on catalytic activity can be studied devoid of confounding effects of morphology and surface area. The thin films were deposited on to a multi-electrode array.

The oxygen reduction activity of thin film coated multi-electrode arrays was characterized rapidly using a newly developed combinatorial electrochemical polarization technique. Those catalyst materials that had high oxygen reduction activity and high onset potential were then identified readily from the performance curves. The thin films were also characterized to determine their microstructure and chemistry using scanning electron microscopy (SEM), x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). Specifically, combinations of platinum, nickel and zirconium were investigated this year. The electrochemical and structural data from these studies formed the basis for further optimization of the catalyst compositions. The newly-discovered materials were then to be applied on to electrodes and prepared into full hydrogen/air polymer electrolyte membrane (PEM) cell assemblies and for demonstration of performance and durability.

Results

Ternary compositions consisting of Pt, Ni and Zr were selected for optimization. This is based on earlier JPL work [1] that demonstrated that Ni and Zr can be combined to produce corrosion resistant films, and also work from Lawrence Berkeley National Laboratory that suggested that nickel addition can improve the oxygen reduction activity [2]. Multi-electrode arrays of ternary catalysts consisting of Pt, Ni and Zr were prepared by co-sputter deposition on a gold/Kynar™ substrate. Compositions of the sputterdeposited films were determined by Energy Dispersive Analysis of X-rays (EDAX). These results are shown in Figure 1.

The oxygen reduction activity of the individual elements of the multi-electrode array was determined using a combinatorial potentiostatic polarization



sample	Pt	Ni	Zr
1	36.1	63.3	0.6
2	44.3	54.6	1.1
3	42.6	56.2	1.1
4	59.3	40.1	0.6
5	52.0	47.0	1.0
6	60.9	38.3	0.8
7	46.9	50.0	3.2
8	58.5	39.2	2.3
9	68.1	30.2	1.8
10	51.6	43.4	5.0
11	60.2	36.1	3.7
12	73.0	24.3	2.7
13	56.6	36.6	6.8
14	64.2	30.2	5.6
15	75.7	20.4	3.9
16	60.8	26.7	12.6
17	65.8	22.9	11.3
18	67.8	21.5	10.6

FIGURE 1. 18-cell Multielectrode Array Prepared by Co-Sputterdeposition of Pt, Ni and Zr from Three Sputter Targets and the Compositions of the Individual Electrodes on the Array as Determined by EDAX

technique. Figure 2 shows the results of validation of the combinatorial polarization technique developed this year for studying oxygen reduction. In this method, the multi-electrode array is held snug against the walls of a beaker cell containing sulfuric acid solution. The solution was continuously saturated with oxygen gas and was rotated using a dual-impeller stirrer. This allowed a steady-state convective flux to be maintained to all parts of the array. The actual value of the convective flux to the elements varied with position but was only dependent on the stirring rate. Hence experiments with arrays where all the elements were platinum were used to map the convective flux and validate the performance of the cell. The currents were measured by methods described earlier [1]. Tafel slopes and onset potentials matched with literature data validating the measurement technique.

The electrochemical performance of the multi-electrode electrode array consisting of compositions of Pt-Ni-Zr shown in Figure 1 was measured in the cell

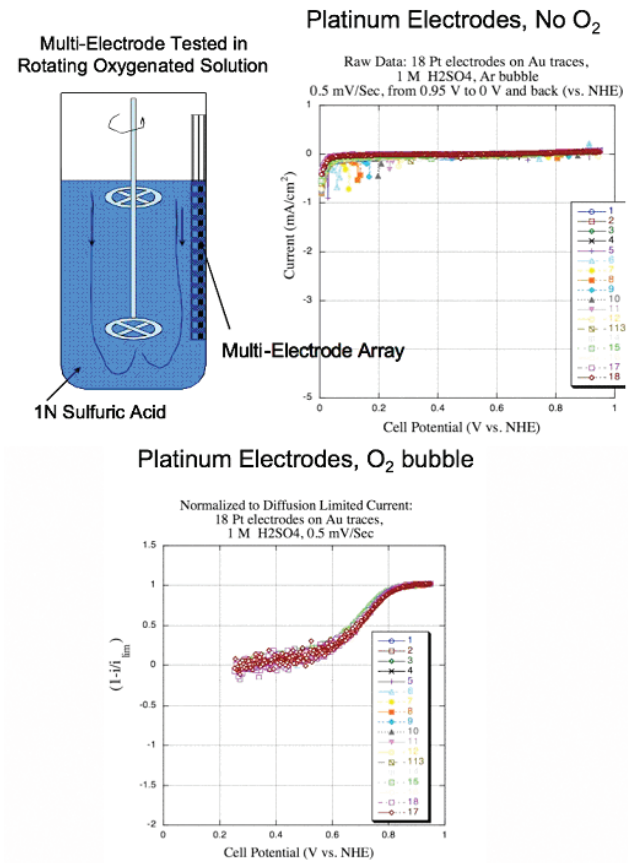


FIGURE 2. Electrochemical Testing of Gold-Substrate Blank Array and All-Platinum Array (Numbers in the legend refer to location of the electrode elements on the array.)

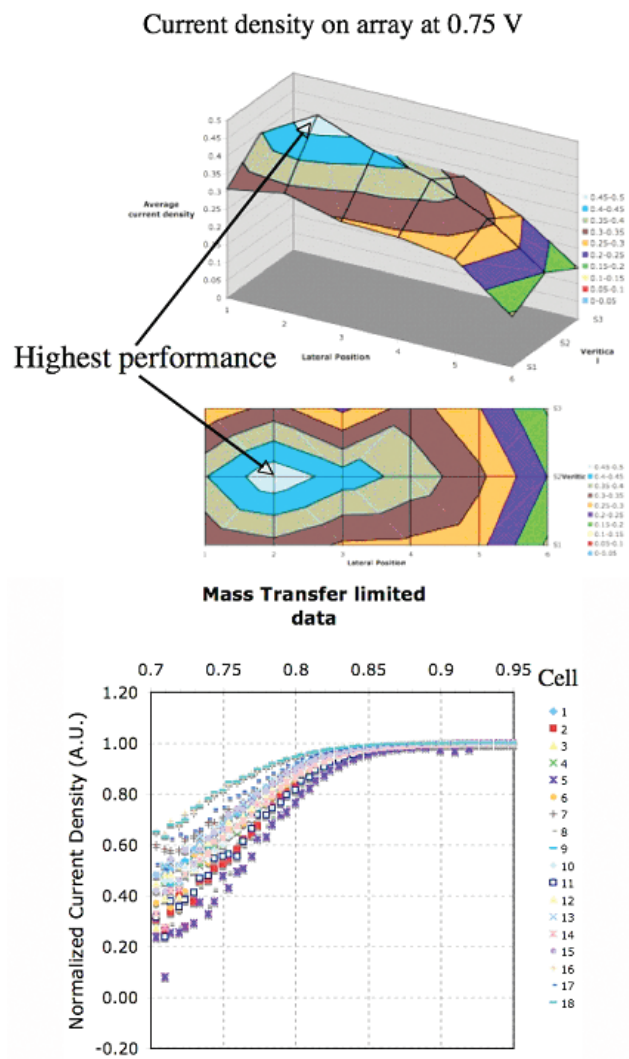


FIGURE 3. Electrochemical Performance of the Multi-Electrode Array of Pt-Ni-Zr Showing a High Performance Composition Corresponding to Pt(59%) Ni (39%) Zr (2%)

described above. These measurements allowed the identification of a ternary composition of Pt-Ni-Zr with the highest performance. The results of these tests are shown in Figure 3.

The performance of this ternary composition is compared with that of pure platinum in Figure 4.

The ternary system, Pt-Ni-Zr, generally showed higher onset potentials compared to Pt. The highest onset potential observed was at least 65 mV higher than that of Pt. The composition Pt (59%) Ni (39%) Zr (2%) was found to have the highest current density.

Structural analysis of the Pt-Ni-Zr compositions was carried out using the beam line at the Stanford Synchrotron Research Laboratory (SSRL). The XRD data showed a single phase face-centered cubic lattice, with a smooth and significant variation in the lattice constant as a function of ternary composition. The lattice constant varies from 3.65 to 3.87 Angstroms. These results are summarized in Figure 5.

The analysis of the XRD data shows that the lattice contraction is directly related with the Pt/Ni ratio. There was no discernable dependence of the lattice constant on the amount of zirconium. The onset potential for oxygen reduction was well correlated with the lattice constant variation and the maximum onset potential corresponded to a lattice constant of 3.75 Angstroms, as shown in Figure 6.

The ten times enhancement in current density achieved with Pt (59%) Ni (39%) Zr (2%) and the ~60 mV improvement in onset potential demonstrate that a new catalyst can be realized by the combinatorial approach. The results demonstrate the possibility of reducing the precious metal content by 40% reduction and also an order of magnitude improvement in catalytic activity.

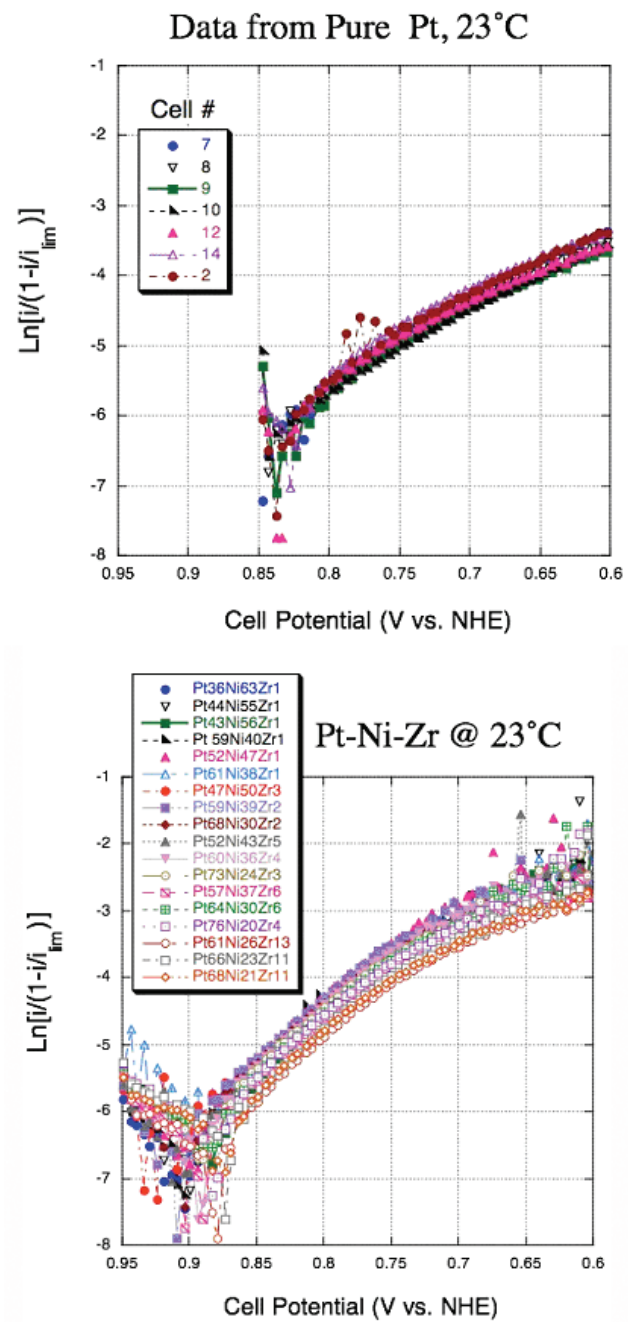


FIGURE 4. Comparison of the Performance of Pt and Various Ternary Compositions of Pt-Ni-Zr

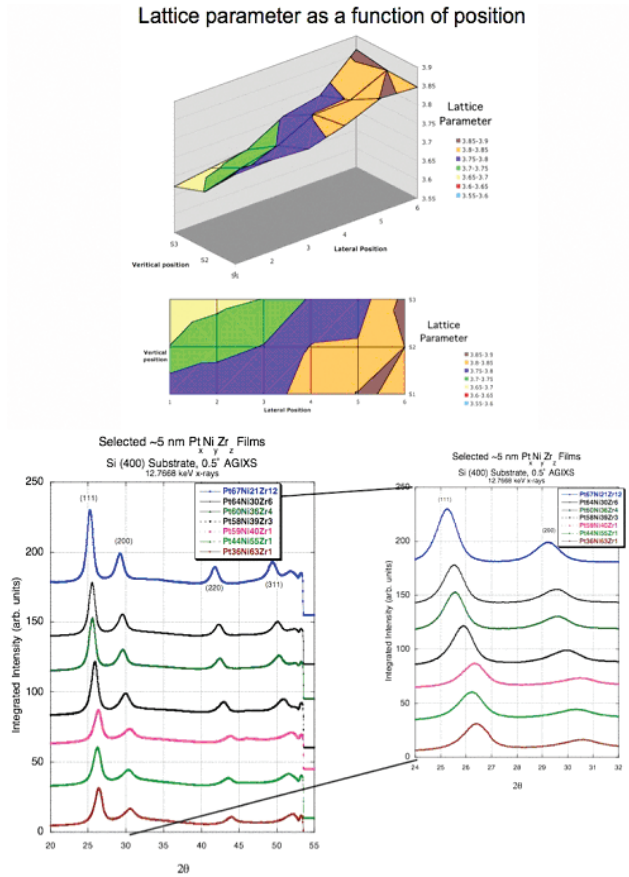


FIGURE 5. X-Ray Diffractograms for Pt-Ni-Zr films and the Variation of Lattice Parameter with Position on the Multi-Electrode Array

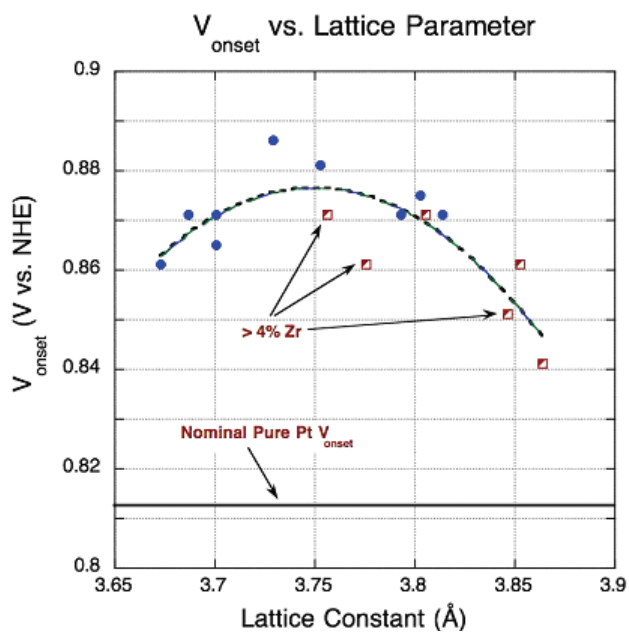


FIGURE 6. The Dependence of Onset Potential on the Lattice Constant for Ternary Pt-Ni-Zr Catalysts

Conclusions and Future Directions

A rapid combinatorial screening technique based on multi-electrode thin film array was developed and validated for identifying catalysts for oxygen reduction. Multi-electrode arrays of thin film catalysts of Pt-Ni and Pt-Ni-Zr were deposited. Pt-Ni and Pt-Ni-Zr films were characterized electrochemically and structurally. Pt-Ni-Zr films showed a higher current density and onset potential compared to Pt. The electrocatalytic activity and onset potential were found to be strong function of the lattice constant. Thin film Pt(59)Ni(39)Zr(2) can provide 10 times the current density of thin film Pt. Thin film Pt(59)Ni(39)Zr(2) also shows 60mV higher onset potential than Pt. In order to fully exploit these advances, it is necessary to sputterdeposit the new materials on high surface area substrates such as the ones developed by 3M [3]. Further work is underway to optimize other compositions with Co, Fe, and Mn, and transitioning the findings with Pt-Ni-Zr catalysts into actual membrane-electrode assemblies and performing full cell tests to establish durability.

Special Recognitions & Awards/Patents Issued

1. NASA-New Technology Report "Multi-Electrode Test System for Rapid Electrochemical Screening of Oxygen Reduction Catalysts"; Contributors: Jay Whitacre and S. R. Narayanan; Accepted as NPO 43220 in May 2006.

FY 2006 Publications/Presentations

1. Jay Whitacre, Thomas Valdez, and S. Narayanan, "PEM Fuel Cell Cathode Catalyst Discovery via Multi-Electrode Electrochemical Screening of Thin-Film Test Structures" Abstract 1106, Presented at the Electrochemical Society Meeting, Denver, May 2006.

References

1. Jay Whitacre, T. I. Valdez and S. R. Narayanan, *J. Electrochem. Soc.*, **152** (2005) A1780.

2. Stamenkovic V, Schmidt T.J., Ross P.N., Markovic N., *J.Electroanal.Chem.* 554(2003) 191.

3. 2005 Progress reports for DoE Fuel Cells program. "Advanced MEAs for Enhanced Operating Conditions", Mark K. Debe, 3M Company, available at http://www.hydrogen.energy.gov/annual_progress05_fuelcells.html.