Advanced Catalysts for Fuel Cells

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Project ID #
FCP-27
Overview

Timeline
• Project Start Date  01/30/05
• Project end date 09/24/06
• Percent complete 65%

Barriers
• Barriers addressed
  A. Stack Cost
  B. Reduction of precious metal content of catalysts

Budget
• Total project funding
  – DOE share $200K
  – Contractor share $0K
• Funding received in FY05 : $100K
• Funding for FY06: $100K

Partners
Collaborations( not funded):
University of Southern California : XPS
Stanford Synchrotron Research Laboratory: for XR₂D.
# Objectives

| Overall | • Reduce the cost of stack components  
• Reduce the amount of precious metal used |
|---------|--------------------------------------------------------------------------------------|
| 2005    | • Develop methods for combinatorial screening of ORR catalysts  
• Demonstrate feasibility of performing catalyst discovery |
| 2006    | • Identify catalysts capable of performing at 2500 mW/(mg of precious metal)  
• Increase the cathode potential by 0.1V at 500 mA/cm² |
Overall Approach

• Investigate corrosion resistant ternary catalysts \textbf{Pt-X-Y} (X = Ni, Co, Fe; Y = Zr, Ti, Cr) for oxygen reduction activity
• Develop a rapid characterization technique that can identify effect of composition on catalytic activity
• Prepare smooth thin films (< 10nm) of multi-component catalyst by sputter-deposition
• Rapidly screen catalyst compositions for activity using a combinatorial multi-electrode array
• Characterize the effect of composition on structure and chemistry on electro-catalytic activity
• Select promising catalysts and demonstrate in full fuel cells
# Tasks for FY ’06

## Task 1. Catalyst Preparation
- Selection of Materials
- Preparation of multi-component electrodes  
  *(60% complete)*

## Task 2. Catalyst Characterization
- Physical Characterization
- Electrochemical Characterization  
  *(50% complete)*

## Task 3. Demonstration in Full Cells
- Demonstration of new catalysts in full cells
- Demonstration of 2500 mW/mg  
  *(10% complete)*
Technical Accomplishments/Progress/Results

• Developed a combinatorial multi-electrode technique for screening of electrocatalysts for oxygen reduction
• Validated the results from multi-electrode cell
• Prepared thin film multi-electrode 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
Sputter-Deposited Thin Films

Advantages of Thin Films Prepared by Co-Sputtering

<table>
<thead>
<tr>
<th>Feature</th>
<th>Advantage</th>
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</thead>
<tbody>
<tr>
<td>Atomically Mixed</td>
<td>Bulk and surface have similar compositions</td>
</tr>
<tr>
<td>Smooth surface</td>
<td>No morphological difference between compositions</td>
</tr>
<tr>
<td>Wide Compositional Range</td>
<td>Amenable for combinatorial screening</td>
</tr>
</tbody>
</table>
Preparation of Multi-Electrode Array

- 18 electrodes on a single sheet
- Gold substrate supported on 100 µm thick PVDF
- <10 nm thick, 0.5 x 0.5 cm active areas
- Room temperature deposition in <2 minutes
Electrochemical Testing of Multi-Electrode Array

• Rotating solution can provide steady state polarization curves
• All 18 locations on the electrode array have similar polarization behavior
• Onset potential for Pt electrodes matches with literature reports
Analysis of Data on Pt Electrodes
Validation of Technique

Polarization curves for 18 Pt Electrodes

Mass Transport Corrected Tafel For Pure Pt ORR
1 M H₂SO₄ with oxygen bubble, 250 rpm stir

Tafel Slopes in the low and high current density regions for sputtered Pt films is consistent with literature, for example:


Technique has been validated
Electrochemical Evaluation of Pt-Ni Catalysts

Raw Data: 18 Ni/Pt electrodes on Au traces, in 1 M H2SO4, 0.5 mV/Sec, from 0.85V to .7 V (vs. NHE)

- Onset potential increases with increasing Ni content
- Effects of different compositions are resolved by screening technique
- Effect of nickel addition consistent with literature on supported Pt-Ni catalysts
- Pt-Ni is a good candidate for further investigation
Preparation of Pt-Ni-Zr Films

Rationale for Ni-Zr addition to Pt

• Previous studies at JPL have shown that Ni-Zr produces corrosion resistant films
  *Journal of The Electrochemical Society, 152 9 A1780-A1789 2005*

• Nickel addition has demonstrated improved oxygen reduction activity
  For example:

Conditions of Deposition

• Three 2” sputter targets used: Pt, Ni, Zr
• 7 cm separation between targets, 10 cm from plane of targets to substrate
• 40 mTorr Ar sputter gas,
• Multiple depositions performed (all with low Zr content)
Composition of Pt-Ni-Zr Catalysts

% element by EDAX

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<th>sample</th>
<th>Pt</th>
<th>Ni</th>
<th>Zr</th>
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<tr>
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<td>36.1</td>
<td>63.3</td>
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<tr>
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<td>40.1</td>
<td>0.6</td>
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<td>5</td>
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<td>47.0</td>
<td>1.0</td>
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<tr>
<td>18</td>
<td>67.8</td>
<td>21.5</td>
<td>10.6</td>
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Composition Range:
- 36 to 76 atomic% Pt
- 20 to 60 atomic % Ni
- Max of 13 atomic% Zr

All samples fall within this phase space
Synchrotron Diffraction for Determining the Structure of Pt-Ni-Zr Thin Films

- SSRL, new beamline 11-3: 12.7 keV (0.91 Å)
- Use asymmetric grazing incidence x-ray scattering (GIXS) geometry, incident angle of 0.5°
- Use large area detector with 100 µm resolution to collect data from large range of reciprocal space at the same time
  - Total collection time is <5 minutes for samples 50Å thick
- “Fit 2D” computer program used to calibrate and integrate data
Structure of Pt-Ni-Zr Films

- f.c.c. structure
- single phase, solid solution
- significant variation in lattice constant

Selected ~5 nm PtNiZr Films
Si (400) Substrate, 0.5° AGIXS
12.7688 keV x-rays

Integrated Intensity (arb. units)

2θ
Lattice Parameter of Pt-Ni-Zr films

Variation across 18 (3x6) electrode array:

- Smooth variation of lattice parameter
- Lattice parameter ranges from 3.65 to 3.87 Å
Composition and Lattice Constant for Pt-Ni-Zr Films

- Lattice constant strongly correlated to Pt/Ni ratio
- No clear trend of dependence of lattice constant on Zr content
Electrochemical Performance of Pt-Ni-Zr films

- Significant variation of onset potential across the array
- “Sweet spot” in Pt-Ni-Zr composition has been identified
Example Summary Slide

Project Summary

Relevance: Help to answer fundamental questions necessary for energy-efficient PEM fuel cell implementation.

Approach: Develop and apply intra-FC diagnostics to characterize transient performance characteristics.

Technical Accomplishments and Progress: Demonstrated dynamic temperature, humidity and species distributions throughout an operating PEM fuel cell.

Technology Transfer/Collaborations: Active partnership with Plug Power and others, new partnership with GM, presentations, publications and patents.

Proposed Future Research: Apply intra-FC diagnostics to identify performance barriers and pathways for performance.

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U. S. DEPARTMENT OF ENERGY

Project ID# FC42
Comparison of Performance of Pt and Pt-Ni-Zr Catalysts

- Pt-Ni-Zr exhibited higher onset potentials compared to Pt.
- Tafel Slopes were similar for Pt-Ni-Zr and Pt.
- Pt(59%)Ni(39%)Zr(2%) showed the highest current density.
Onset Potential and Lattice Parameter

Onset Potential measured at current > 1.5% limiting current density

Onset potential shows a maximum as a function of lattice constant
Onset potential highest for Pt(59)Ni (39)Zr(2); lattice constant = 3.75 Å:
Onset potential of Pt(59)Ni (39)Zr(2), 65 mV higher than Pt
Effect of Zr Content on Current Density

Zirconium content higher than 4% resulted in decrease of current density
Summary

• A rapid combinatorial screening technique based on multi-electrode thin film array has been developed and validated for identifying catalysts for oxygen reduction; focus shifted from methanol oxidation in FY05 to oxygen reduction in FY06
• Multi-electrode arrays of thin film catalysts of Pt-Ni and Pt-Ni-Zr have been deposited
• Pt-Ni and Pt-Ni-Zr films have been characterized electrochemically and structurally.
• Pt-Ni-Zr and Pt-Ni films show higher current density and onset potential compared to Pt
• Electrocatalytic activity and onset potential are 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 65mV* higher onset potential than Pt

* These findings are extremely significant for meeting the DoE 2010 targets
Publications List


Future Work

• Screen more new catalyst compositions based on Pt-M-Zr catalysts, where M=Ni,Co,Fe,Cr
• Prepare MEAs based on down-selected catalysts and establish performance
  – Current-Voltage Curves and Stability
• Focus on further increases to onset potential and activity
Reviewer’s Comments

Program was not reviewed in FY 05 because of a late start.

FY 04 Review:

Reviewer Comment 1: Shift focus from methanol oxidation catalysts to oxygen reduction catalysts

Response: All work in FY05/06 has been directed towards oxygen reduction catalysts