

Advanced Catalysts for Fuel Cells

S. R. Narayanan, Jay Whitacre
and T. I. Valdez

Jet Propulsion Laboratory
May 17, 2006

This presentation does not contain any proprietary or confidential information

Project ID #
FCP-27

Overview

Timeline

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

Budget

- Total project funding
 - DOE share \$200K
 - Contractor share \$0K
- Funding received in FY05 :\$100K
- Funding for FY06: \$100K

Barriers

- Barriers addressed
 - B. **Cost:** Precious Metal Loading
 - C. **Electrode Performance:**
Increasing performance of the cathode

Partners

Collaborations(not funded):
University of Southern
California : XPS
Stanford Synchrotron
Research Laboratory: for XRD.

Objectives

Overall	<ul style="list-style-type: none">• Reduce the cost of stack components• Reduce the amount of precious metal used
2005	<ul style="list-style-type: none">• Develop methods for combinatorial screening of ORR catalysts• Demonstrate feasibility of performing catalyst discovery
2006	<ul style="list-style-type: none">• Identify catalysts capable of performing at 2500 mW/(mg of precious metal)• Increase the cathode potential by 0.1V at 500 mA/cm²

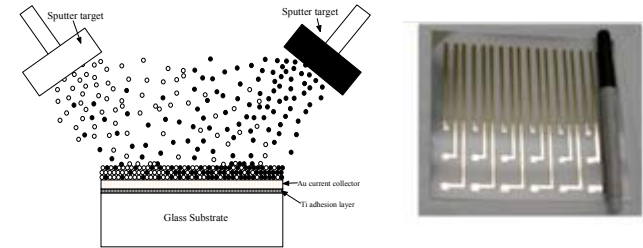
Overall Approach

- Investigate corrosion resistant ternary catalysts **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

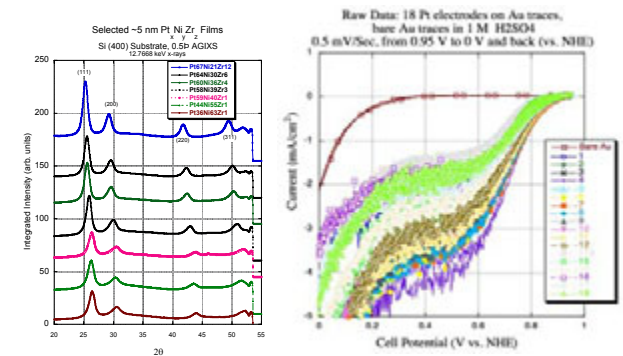
Task 1. Catalyst Preparation

- Selection of Materials
- Preparation of multi-component electrodes
(60% complete)



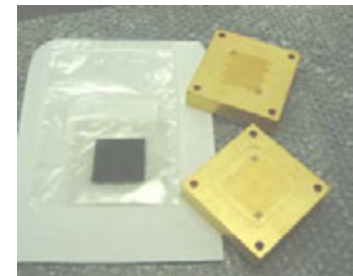
Task 2. Catalyst Characterization

- 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)

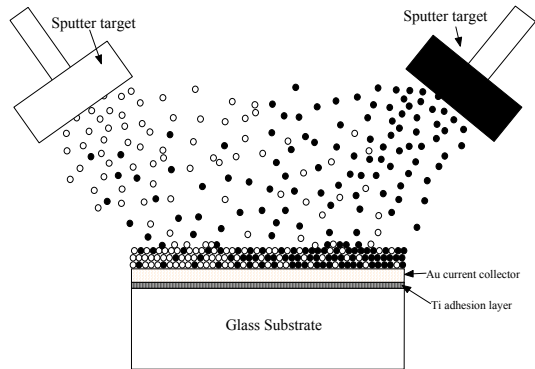


Technical Accomplishments/ Progress/Results

- 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

Schematic of Co-Sputtering Process



Sputter Chamber with Multiple Targets



Advantages of Thin Films Prepared by Co-Sputtering

Feature

Atomically Mixed

Smooth surface

Wide Compositional Range

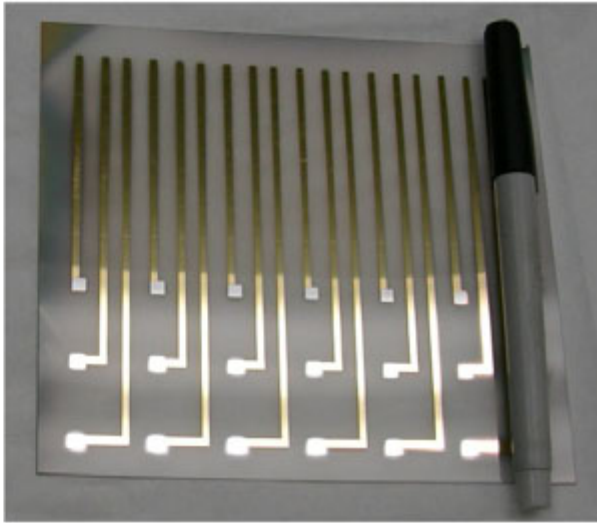
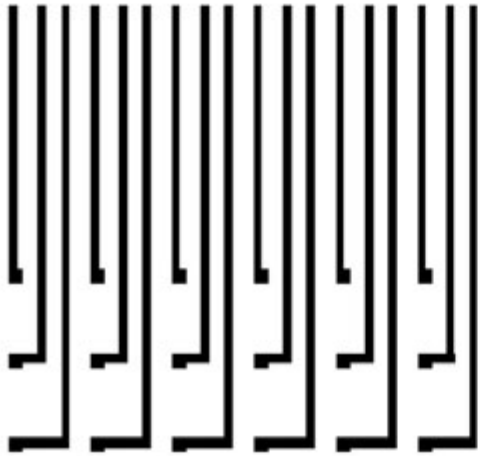
Advantage

Bulk and surface have similar compositions

No morphological difference between compositions

Amenable for combinatorial screening

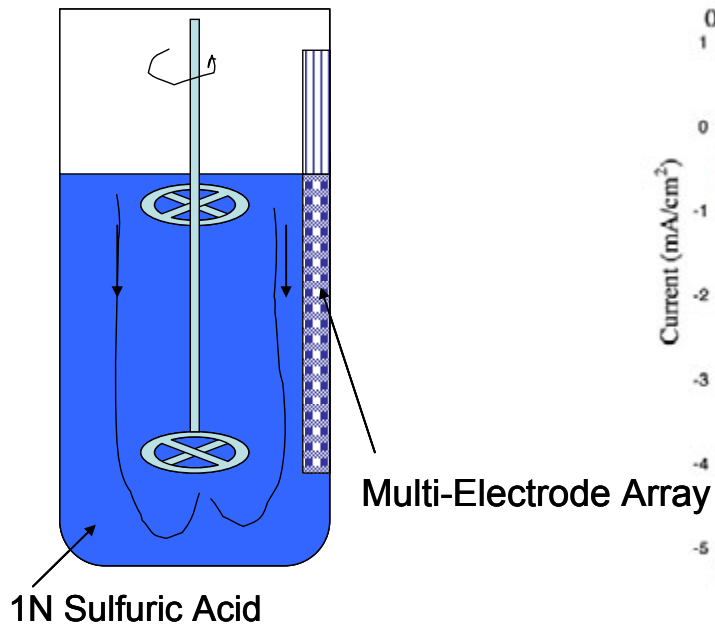
Preparation of Multi-Electrode Array



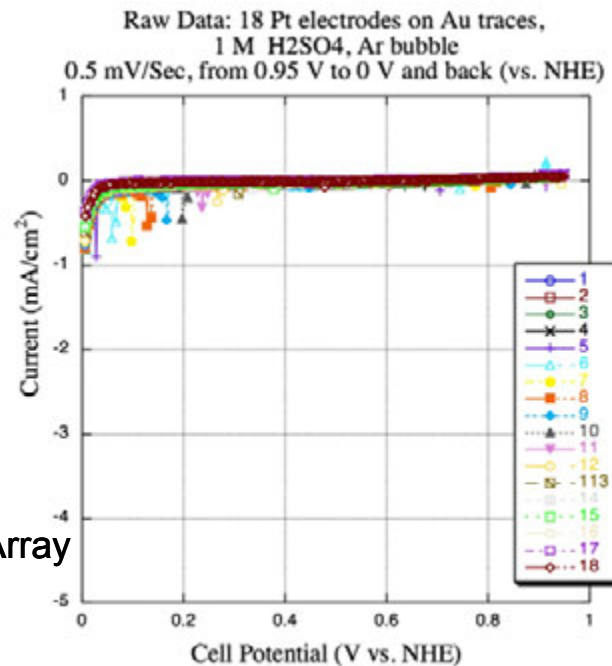
- 18 electrodes on a single sheet
- Gold substrate supported on 100 μm thick PVDF
- <10 nm thick, 0.5 x 0.5 cm active areas
- Room temperature deposition in <2 minutes

Electrochemical Testing of Multi-Electrode Array

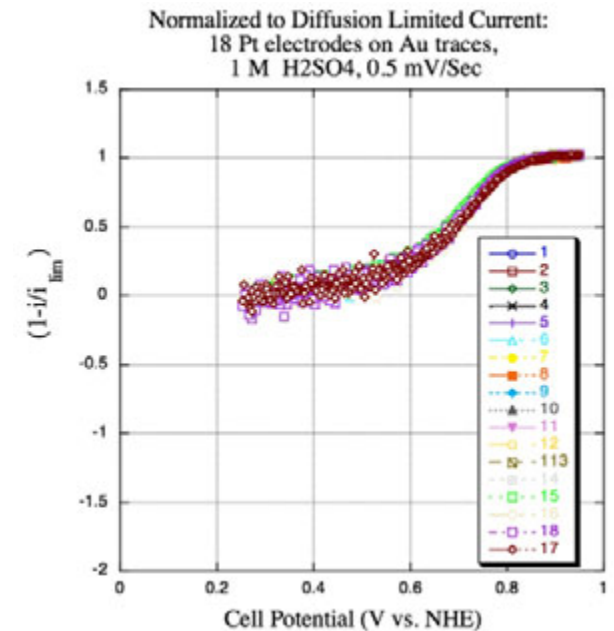
Multi-Electrode Tested in Rotating Oxygenated Solution



Gold Substrate



Platinum Electrodes



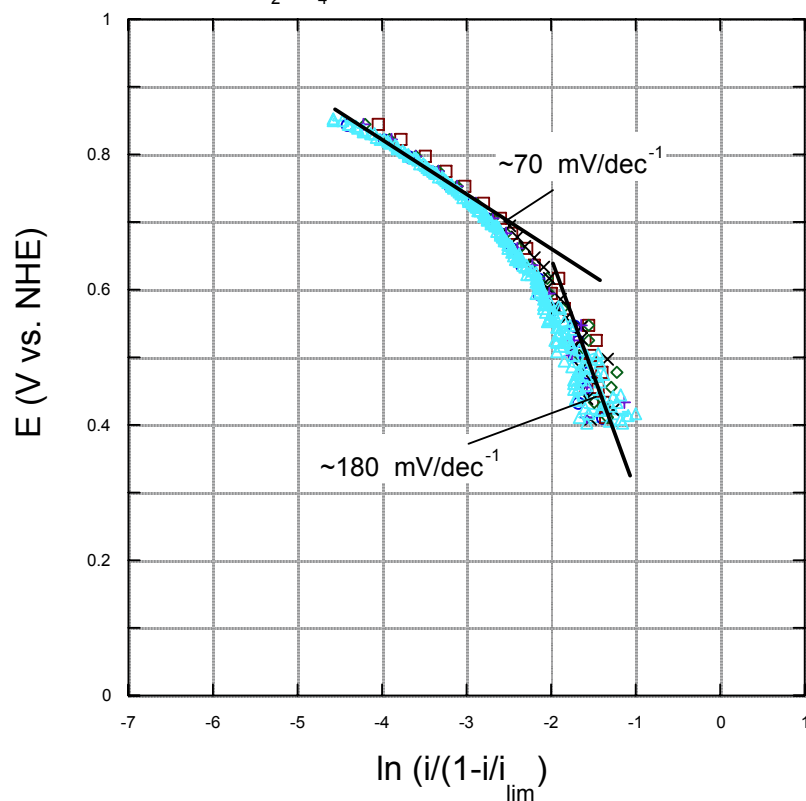
- Rotating solution can provide steady state polarization curves
- All 18 locations on the electrode array have similar polarization behavior
- Onset potential for Pt electrodes matches with literature reports

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



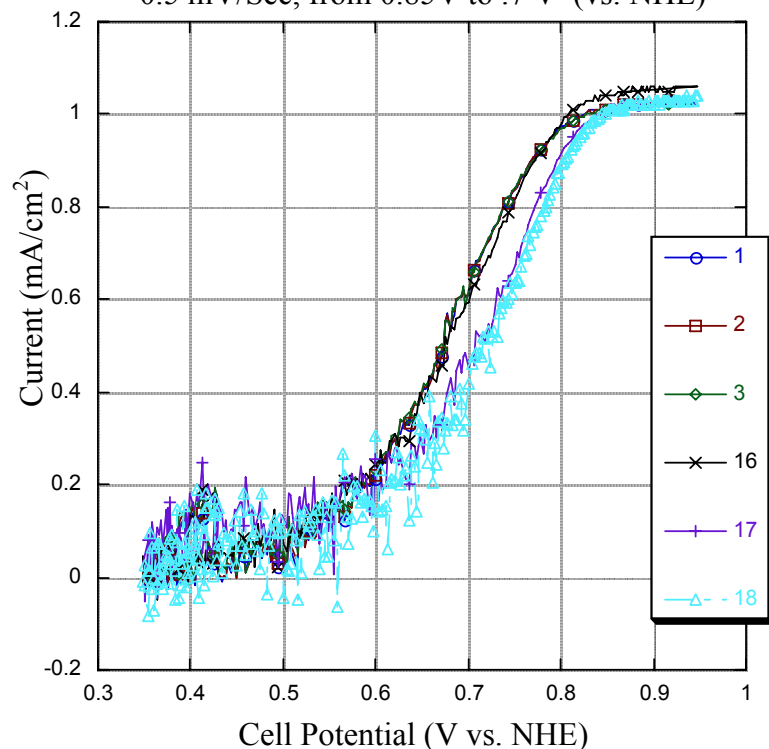
Tafel Slopes in the low and high current density regions for sputtered Pt films are consistent with literature, for example :

S. Gojkovic, S. Zecevic, R. Savinell, J. Electrochem. Soc. **145** (1998) 3713

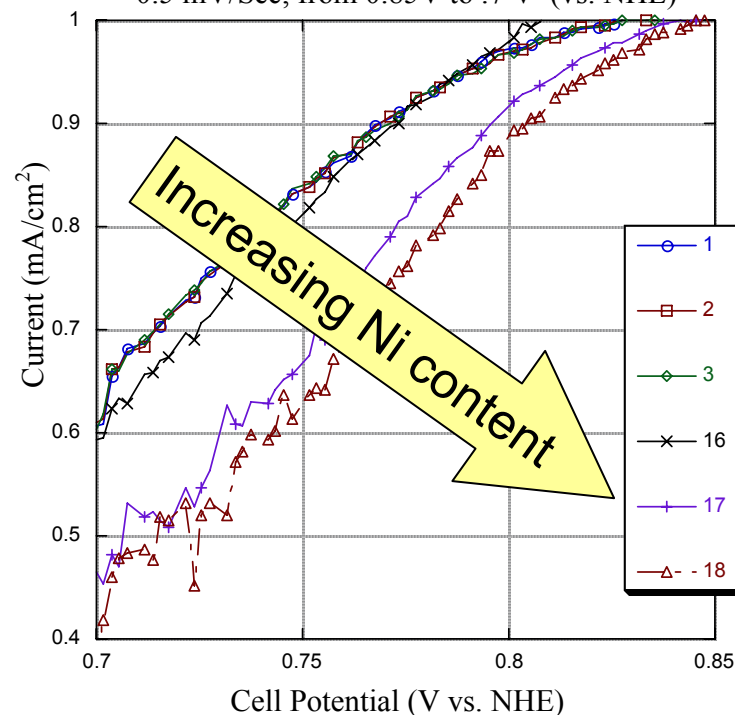
Technique has been validated

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)



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:

Stamenkovic V, Schmidt T.J., Ross P.N., Markovic N.

J. Electroanal. Chem. 554(2003) 191



Conditions of Deposition

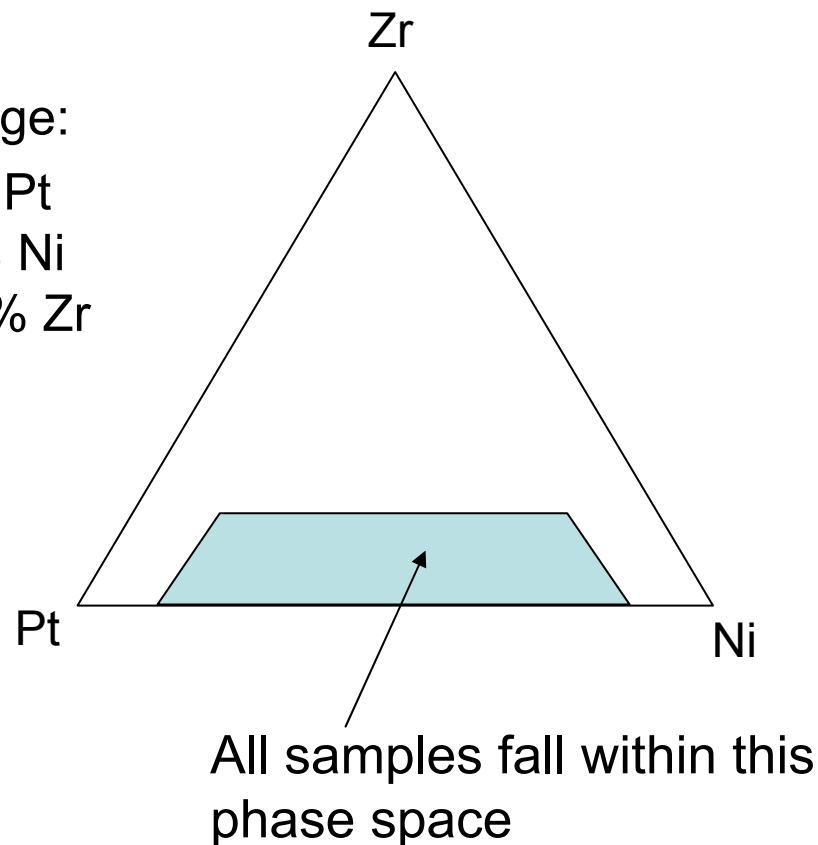
- Three 2" sputter targets used: Pt, Ni, Zr
- 7 cm separation between targets, 10 cm from plane of targets to substrate
- 40 mTorr Ar sputter gas,
- Multiple depositions performed (all with low Zr content)

Composition of Pt-Ni-Zr Catalysts

% element by EDAX

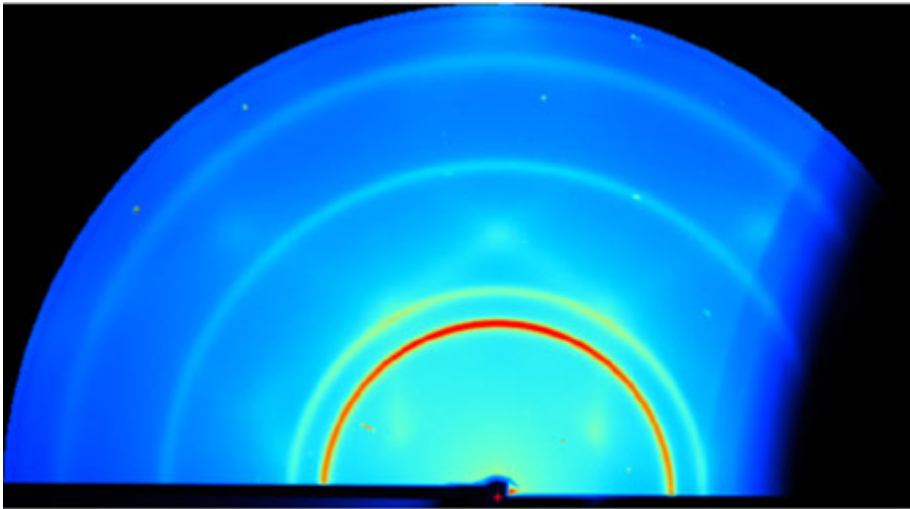
sample	Pt	Ni	Zr
1	36.1	63.3	0.6
2	44.3	54.6	1.1
3	42.6	56.2	1.1
4	59.3	40.1	0.6
5	52.0	47.0	1.0
6	60.9	38.3	0.8
7	46.9	50.0	3.2
8	58.5	39.2	2.3
9	68.1	30.2	1.8
10	51.6	43.4	5.0
11	60.2	36.1	3.7
12	73.0	24.3	2.7
13	56.6	36.6	6.8
14	64.2	30.2	5.6
15	75.7	20.4	3.9
16	60.8	26.7	12.6
17	65.8	22.9	11.3
18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

Composition Range:
36 to 76 atomic% Pt
20 to 60 atomic % Ni
Max of 13 atomic% Zr

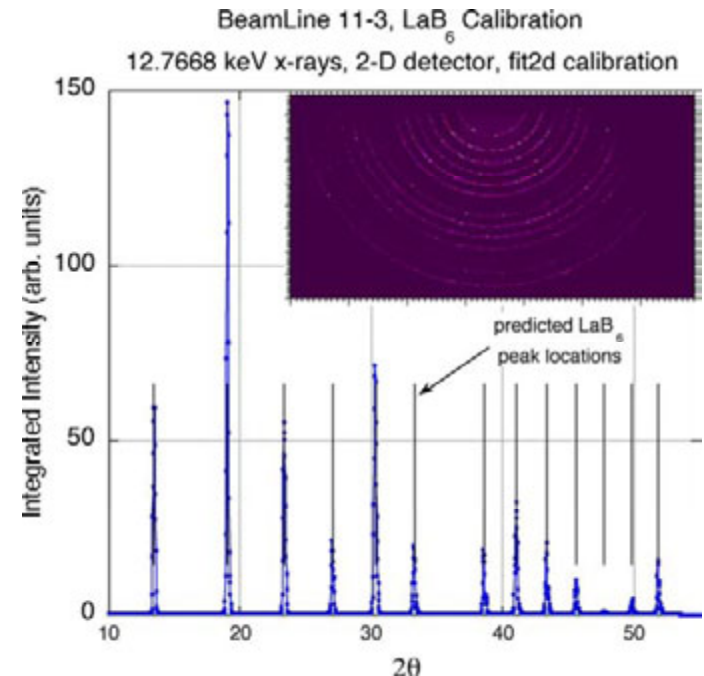


Synchrotron Diffraction for Determining the Structure of Pt-Ni-Zr Thin Films

2D diffraction pattern from <10 nm PtNiZr on Si



Sample data

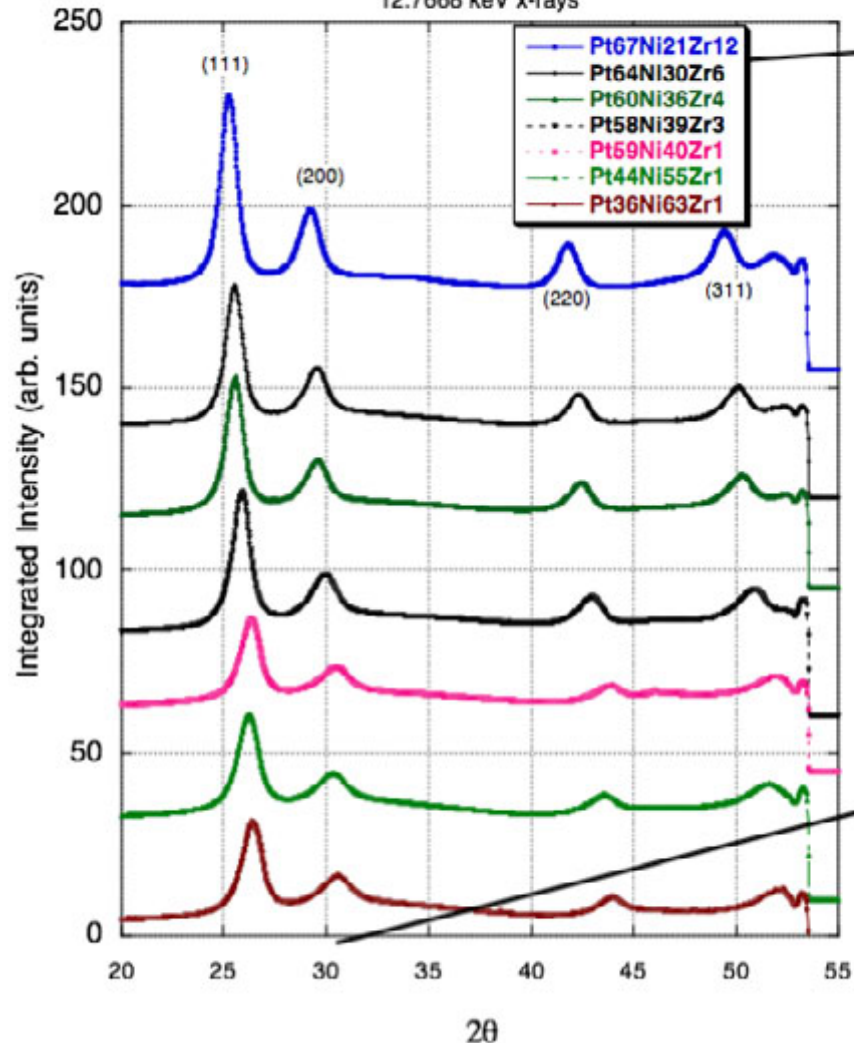


- SSRL, new beamline 11-3: 12.7 keV (0.91 Å)
- Use asymmetric grazing incidence x-ray scattering (GIXS) geometry, incident angle of 0.5°
- Use large area detector with 100 μm resolution to collect data from large range of reciprocal space at the same time
 - Total collection time is <5 minutes for samples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

Structure of Pt-Ni-Zr Films

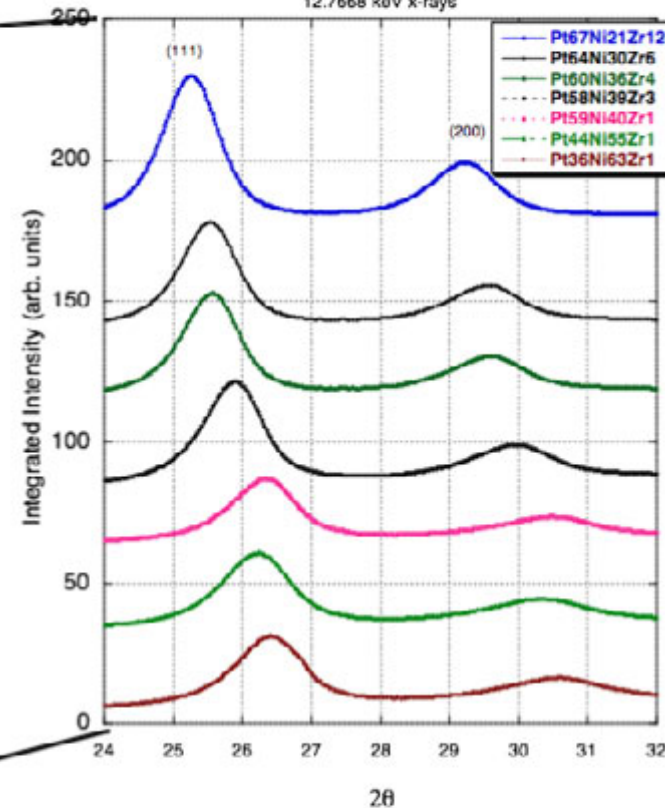
Selected ~5 nm Pt Ni Zr Films

Si (400) Substrate, 0.5° AGIXS
12.7668 keV x-rays



Selected ~5 nm Pt Ni Zr Films

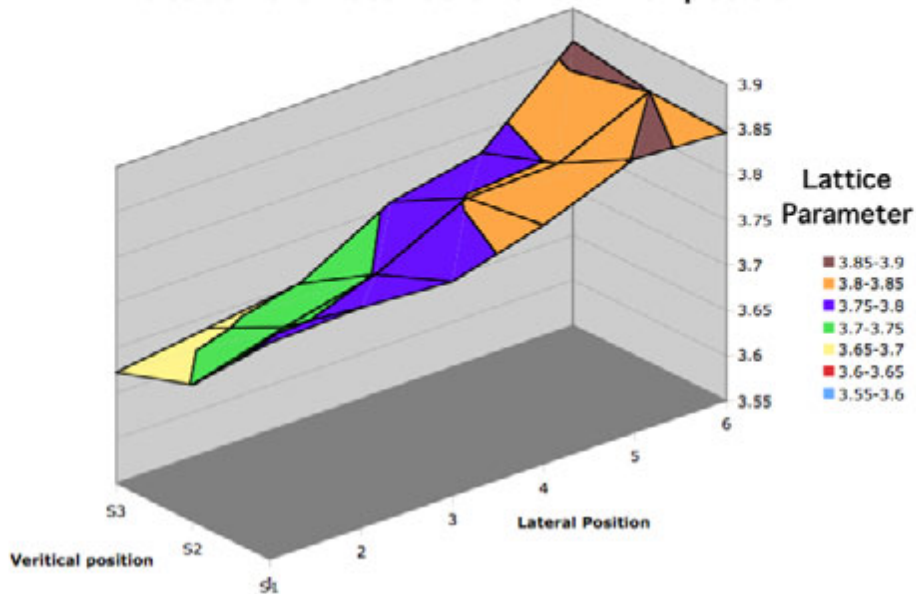
Si (400) Substrate, 0.5° AGIXS
12.7668 keV x-rays



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

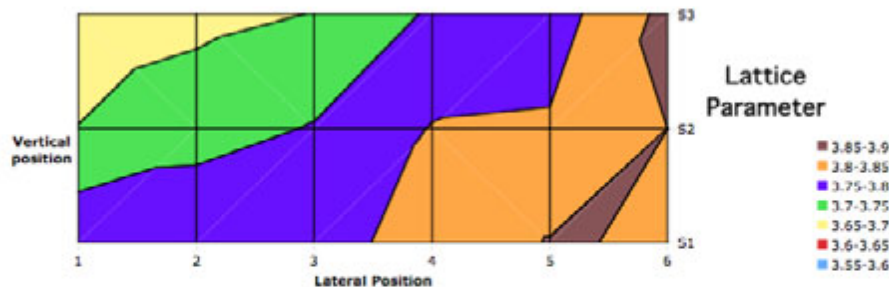
Lattice Parameter of Pt-Ni-Zr films

Lattice Parameter as a function of position

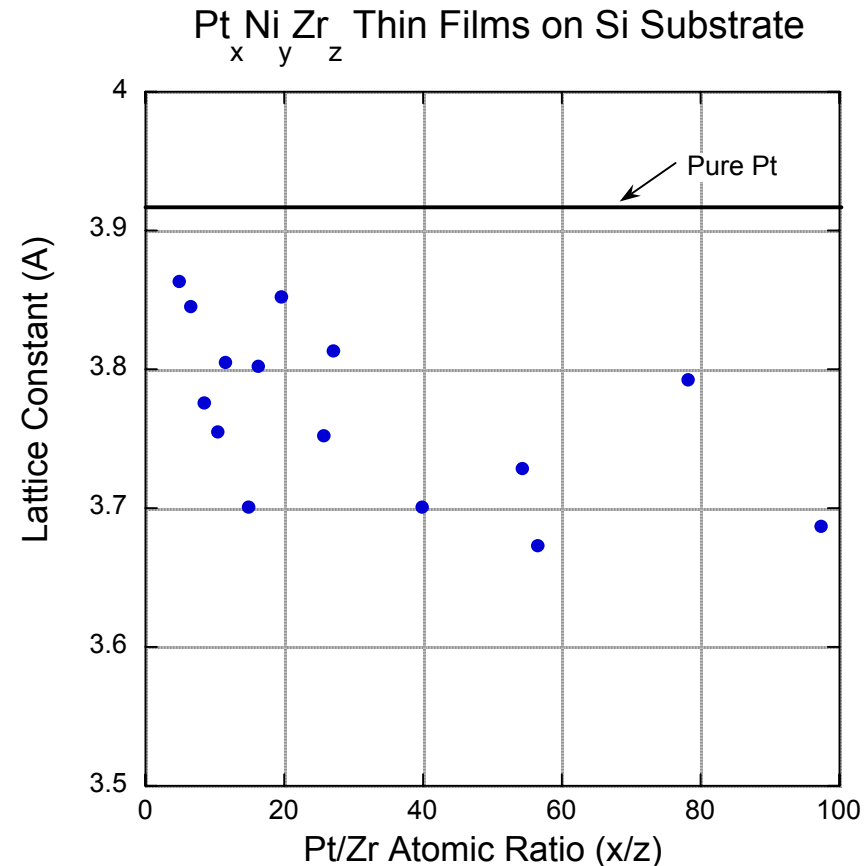
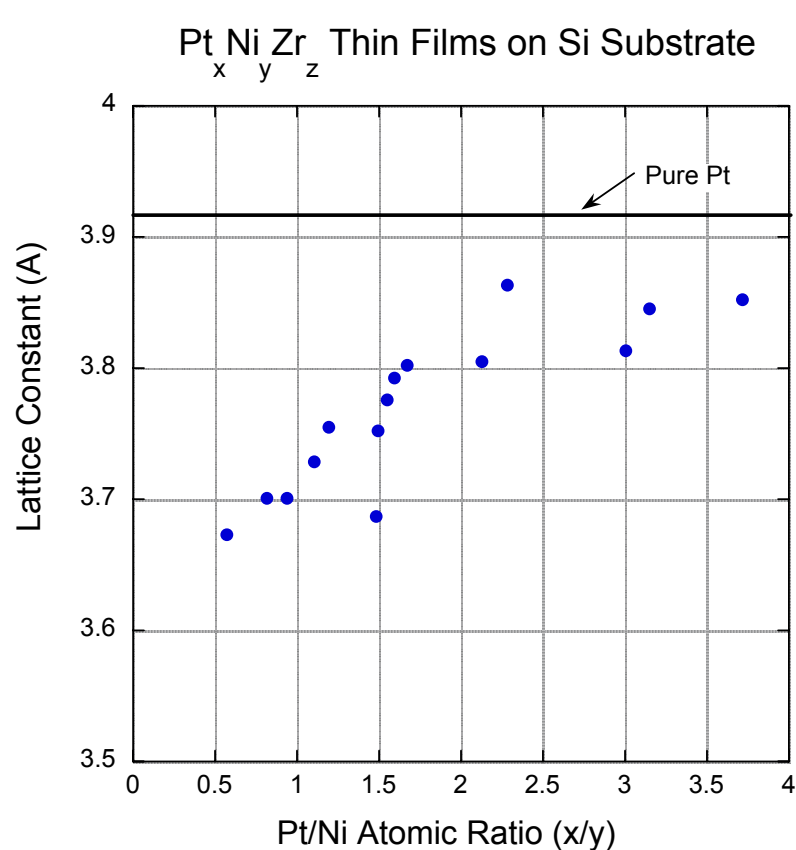


Variation across 18 (3x6) electrode array:

- Smooth variation of of lattice parameter
- Lattice parameter ranges from 3.65 to 3.87 Å

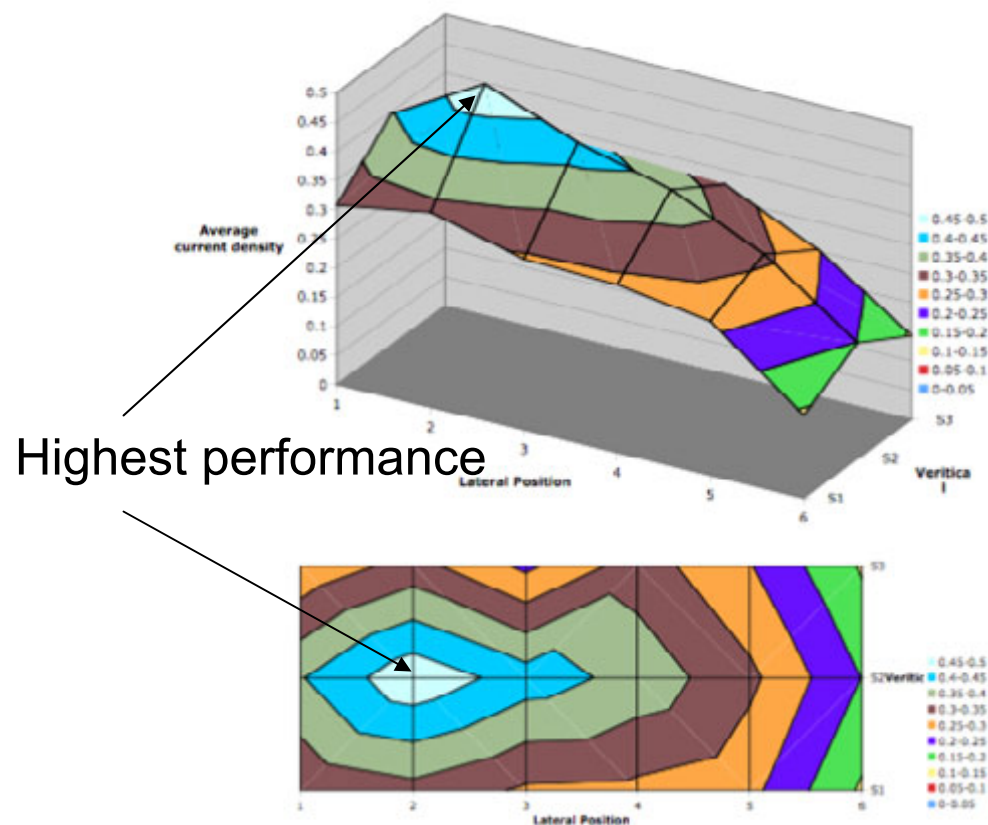
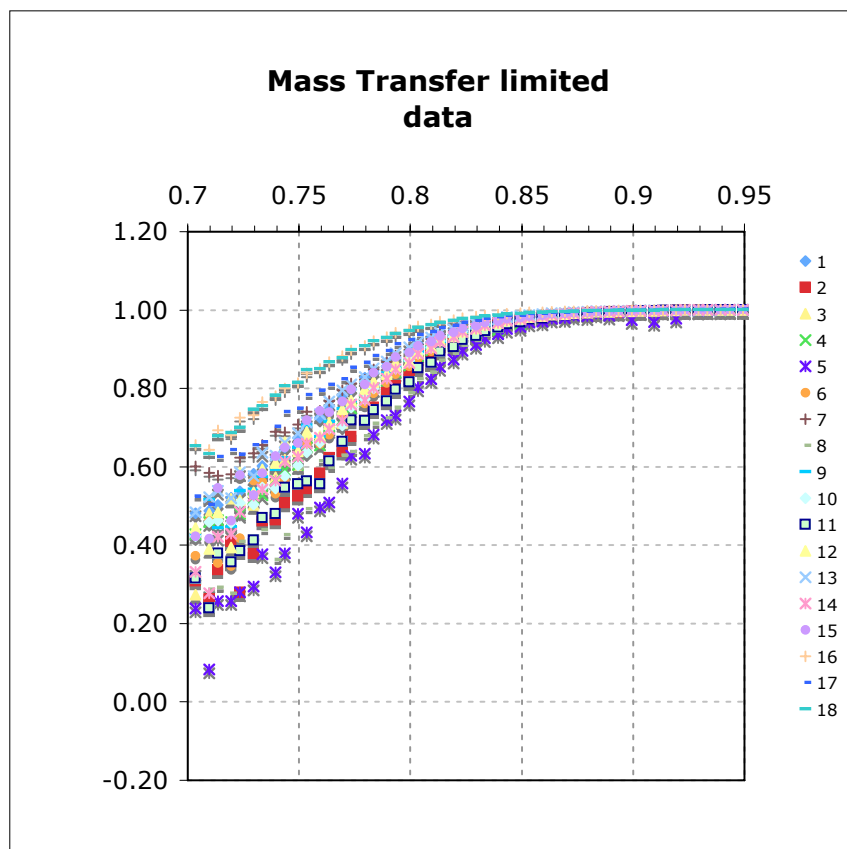


Composition and Lattice Constant for Pt-Ni-Zr Films



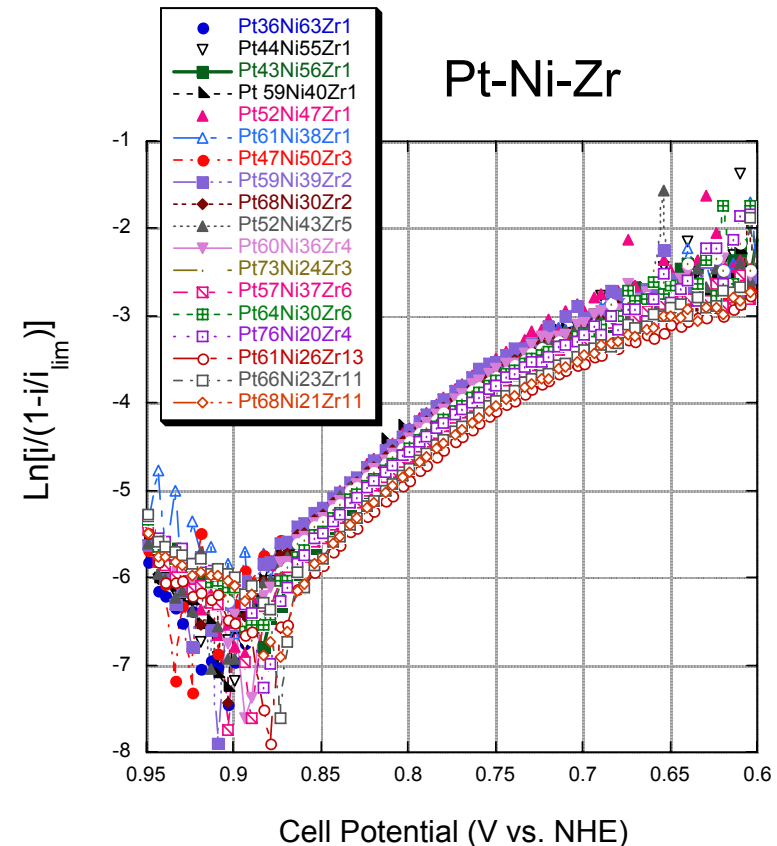
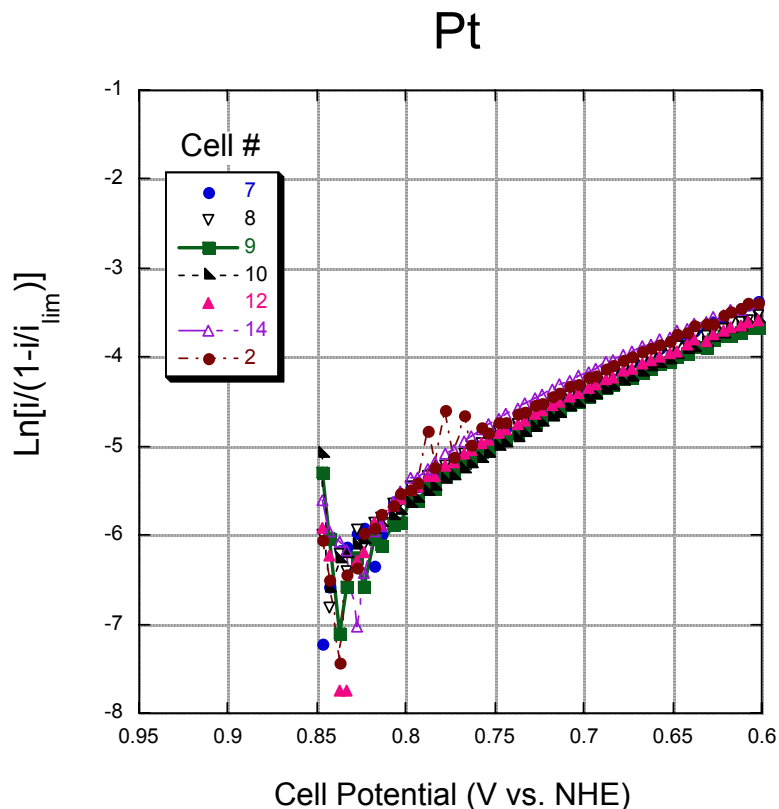
- Lattice constant strongly correlated to Pt/Ni ratio
- No clear trend of dependence of lattice constant on Zr content

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

Comparison of Performance of Pt and Pt-Ni-Zr Catalysts

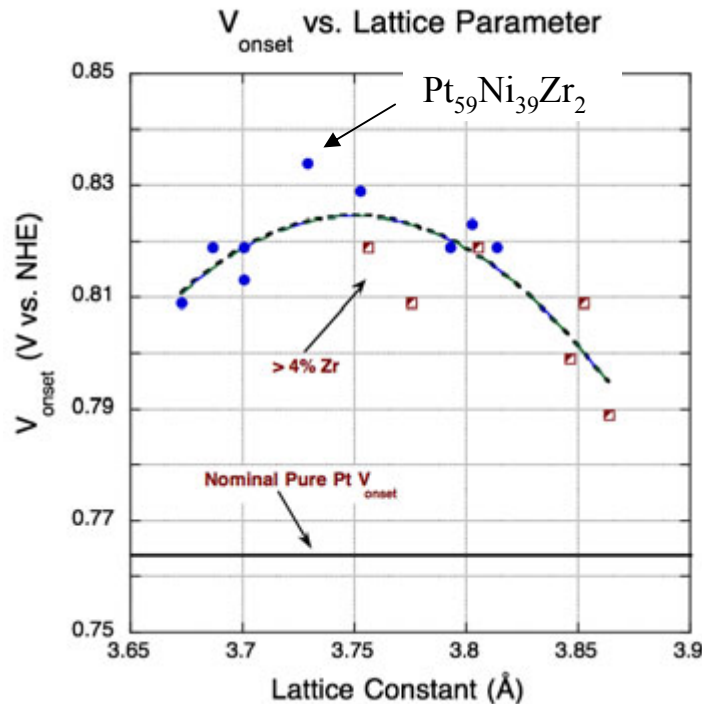


- Pt-Ni-Zr exhibited higher onset potentials compared to Pt
- Tafel Slopes were similar for Pt-Ni-Zr and Pt
- Pt(59%)Ni(39%)Zr(2%) showed the highest current density

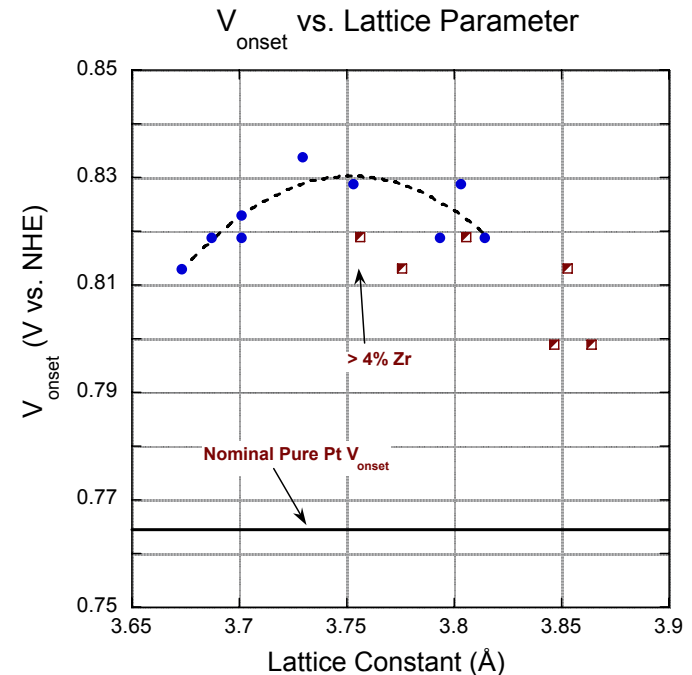
Onset Potential and Lattice Parameter

Onset Potential measured at current > 1.5% limiting current density

Fit including Zr content catalysts



Fit without high Zr content catalysts

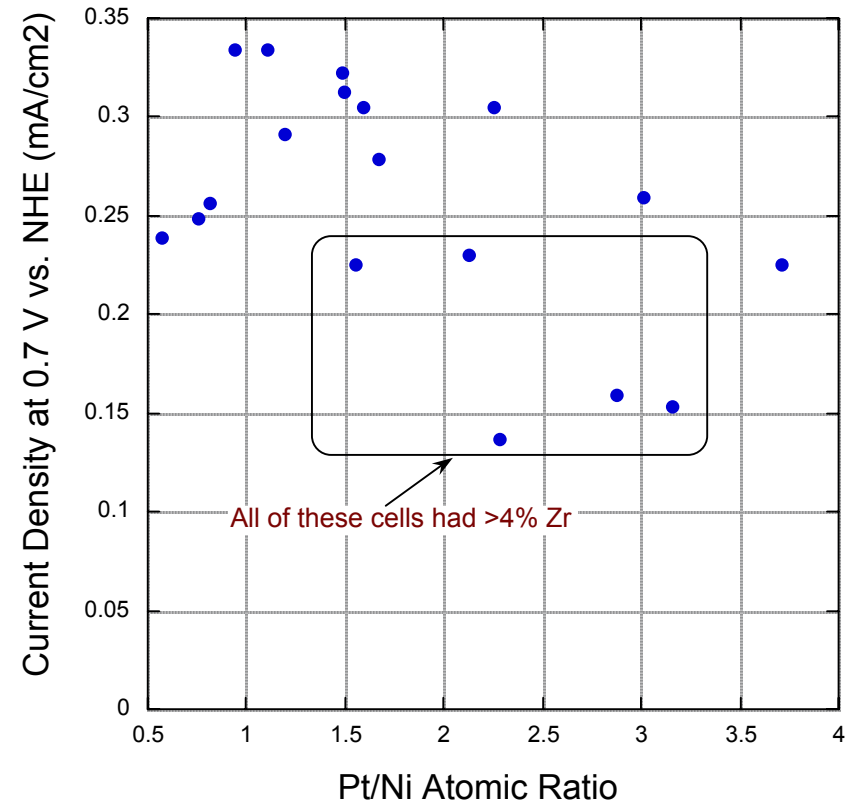
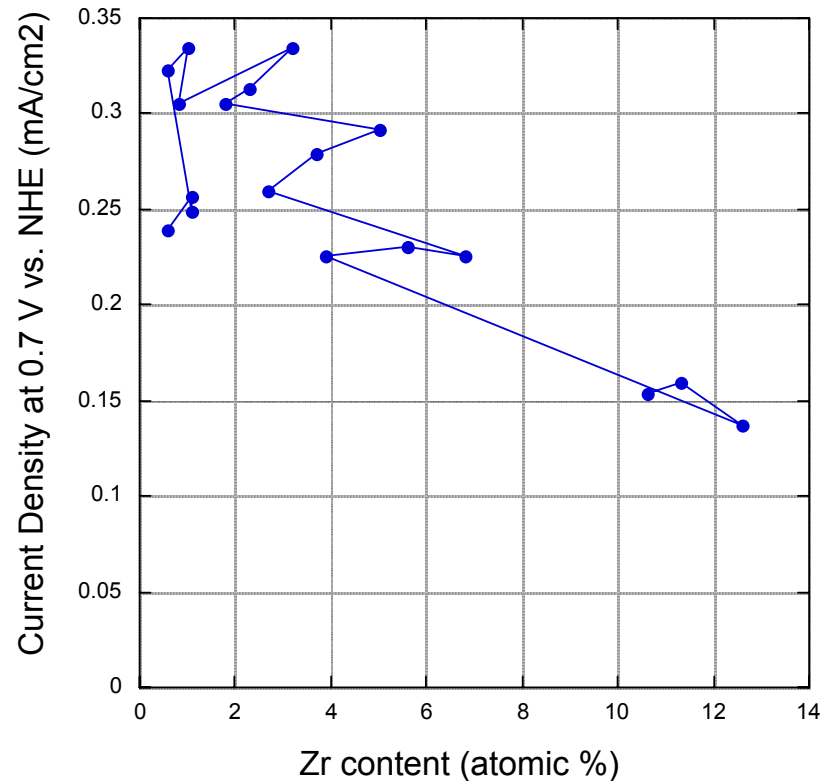


Onset potential shows a maximum as a function of lattice constant

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

- **Investigation of Direct Methanol Fuel Cell Electrocatalysts Using a Robust Combinatorial Technique**, Jay F. Whitacre, T. Valdez, and S. R. Narayanan *Journal of The Electrochemical Society*, **152** 9 A1780-A1789 2005
- **Robust Combinatorial Catalyst Discovery for Methanol Fuel Cells**, Jay Whitacre, T. Valdez and S. R. Narayanan, *Invited Talk at 46th Battery Symposium, November 2005, Nagoya, Japan.*
- **PEM Fuel Cell Cathode Catalyst Discovery via Multi-Electrode Electrochemical Screening of Thin-Film Test Structures**, J. F. Whitacre, T.I Valdez, and S.R. Narayanan, *Presentation at ECS Meeting, Denver, May 2006.*

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