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DEVELOPMENT OF ADVANCED CATALYSTS FOR DIRECT METHANOL FUEL CELLS

S. R.Narayanan
C. K. Witham and Jay Whitacre
Jet Propulsion Laboratory
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Program Objectives

Overall Objective:

- Reduce catalyst cost for direct methanol fuel cells

Specific objectives:

- Reduce noble metal loading below 0.5 mg/cm^2
- Develop a new method of fabrication of MEAs
- Develop anode catalysts with enhanced activity
- Develop non-noble metal anode catalysts

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Milestones/Accomplishments

2000-2002 (Effort level: 1.75 FTE total)

- Co-sputtering can provide active thin film catalysts

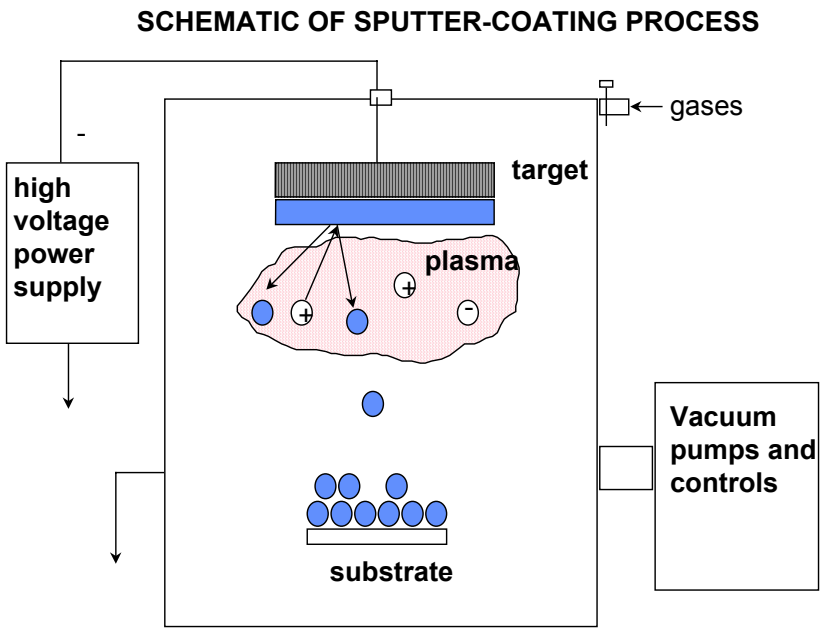
- Thin film Pt_xRu_{1-x} alloys were prepared and characterized for electrochemical activity

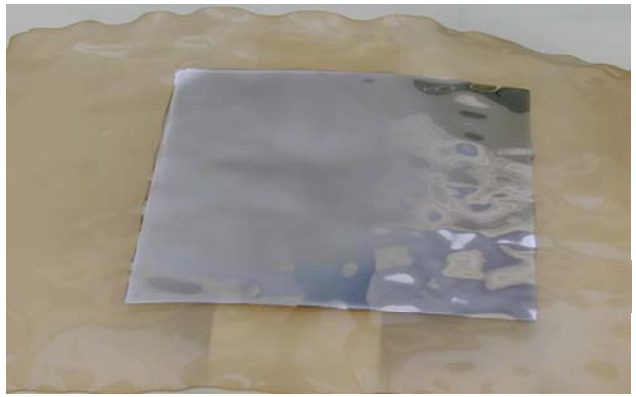
- Thin film catalysts demonstrated in Nafion MEAs

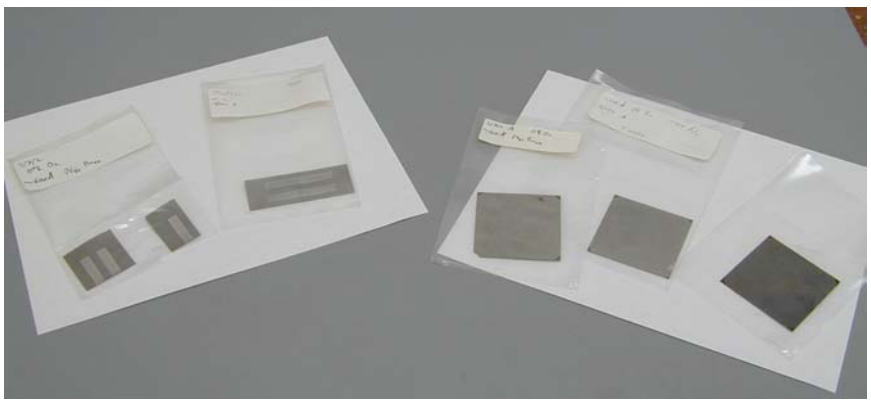
- Anode activity of 800 mW/mg at 0.1 mg/cm^2 with sputtered thin films and 2000 mW/mg at 0.03 mg/cm^2 (as opposed to 40 mW/mg with conventional ink method)

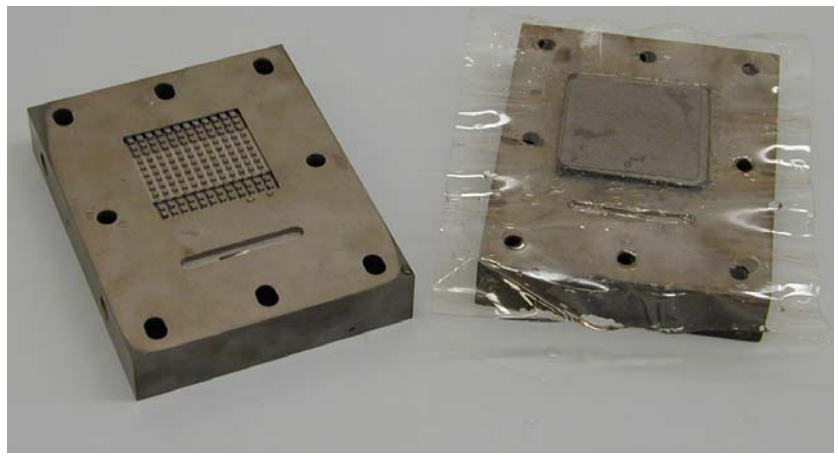
- Sputter-deposition and characterization of Pt-RuO_x layers and unique high surface area structures

Sputtered thin film catalyst layers



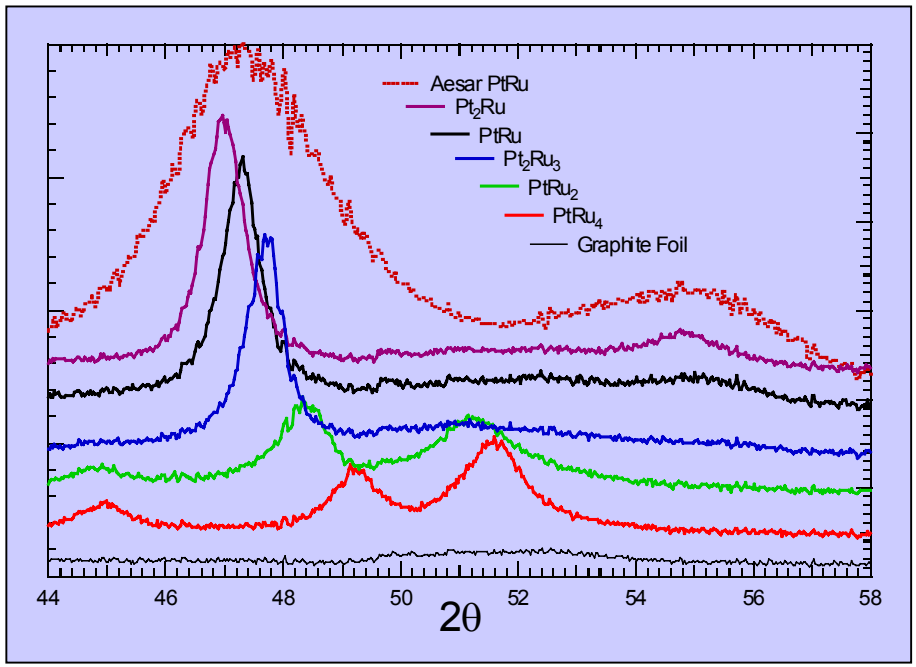




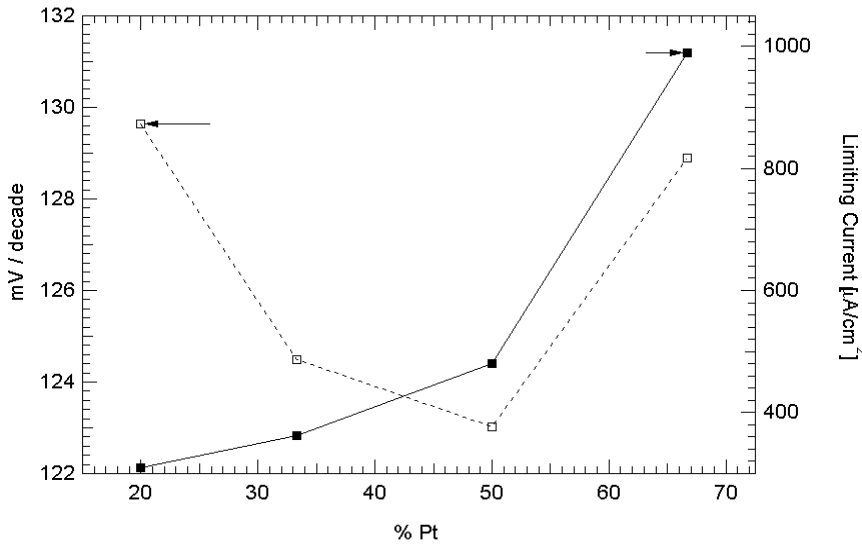


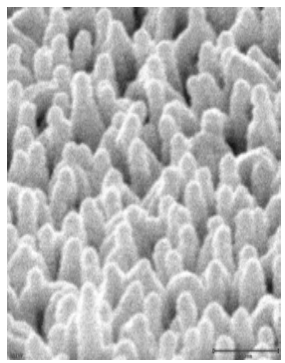
Properties of sputtered Pt-Ru films

XRD of sputtered films of Pt_xRu_{1-x}



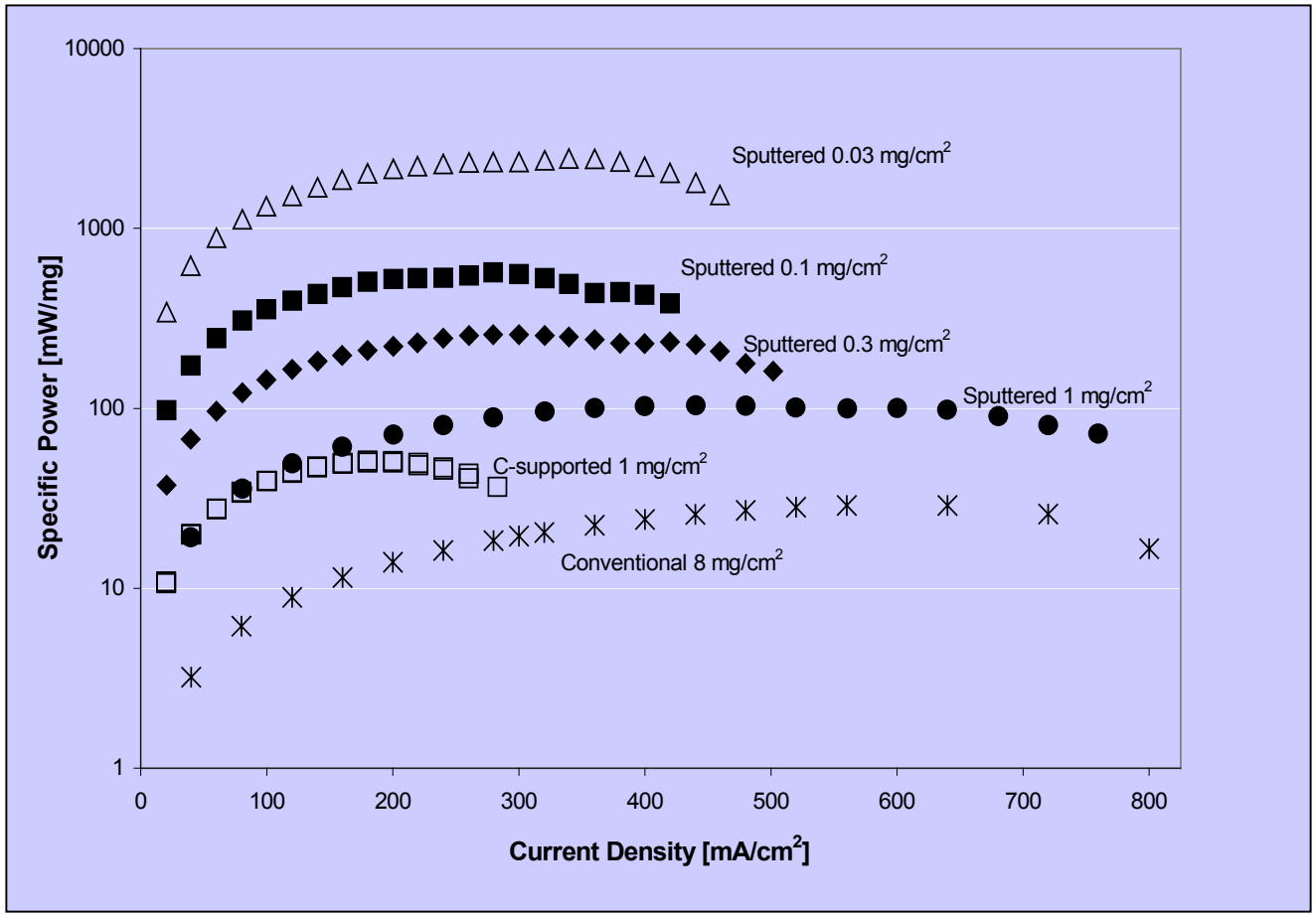
Electrochemical Activity





Unique microstructures

Utilization with thin film catalysts



800 mW/mg at 0.1 mg/cm^2, and 2000 mW/mg at 0.03 mg/cm^2

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Milestones and Accomplishments

2003 (Effort level 0.5 FTE total)

- Identification of novel corrosion-resistant non-noble nanophase thin film catalyst layers

- Sputterdeposition of electrodes and characterization under fuel cell conditions

Non-Noble Metal Thin Film Catalyst layers

Motivation

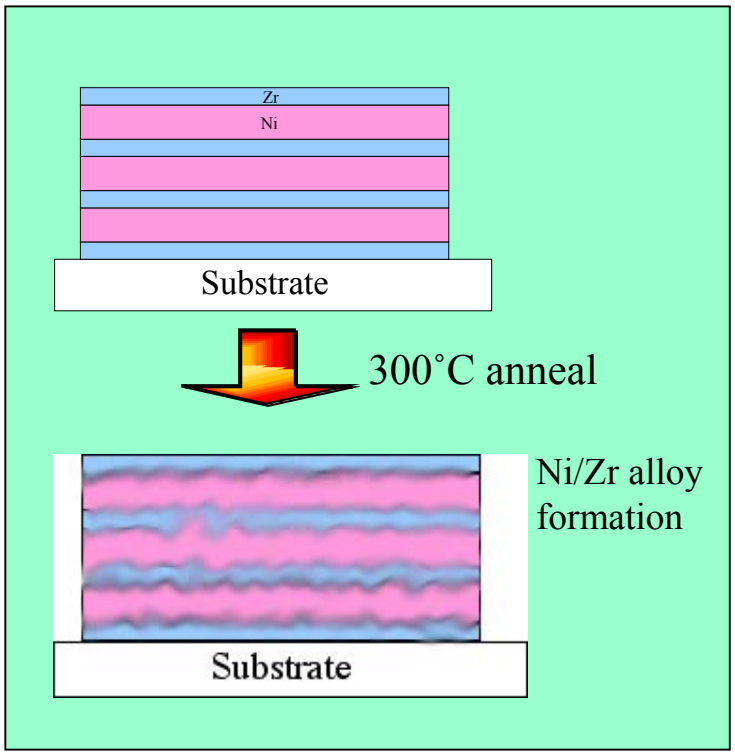
- Identifying alternates to precious metal catalysts
- Developing noble metal and non-noble metal combinations to reduce precious metal loading and enhance activity

Approach

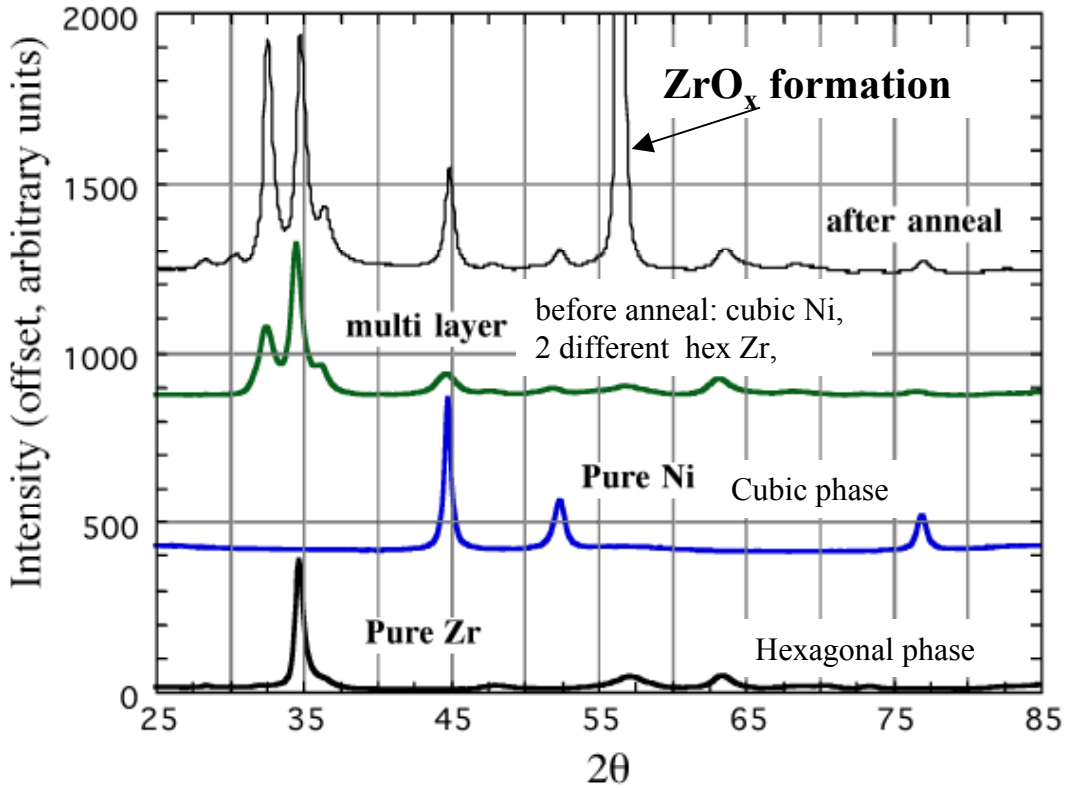
- Take advantage of sputter-depositon to identify a corrosion resistant non-noble metal system
  - non-equilibrium phases, unique nanophase structure, morphology and electronic properties.
- Ni/Zr system as proof-of-concept
- Characterization:
  - Corrosion studies in sulfuric acid, XRD,SEM
  - Fuel Cell studies with Ni-Zr/Pt-Ru catalyst layers

Multilayer Ni/Zr films

Concept

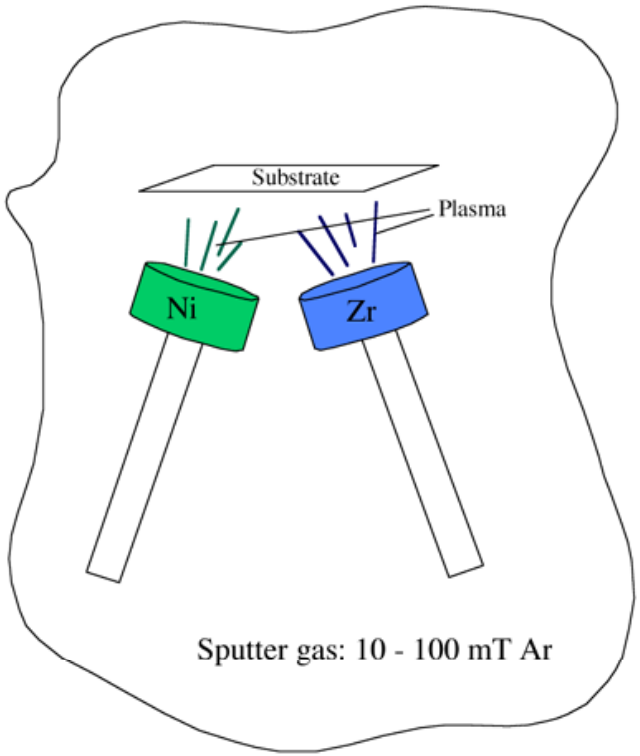


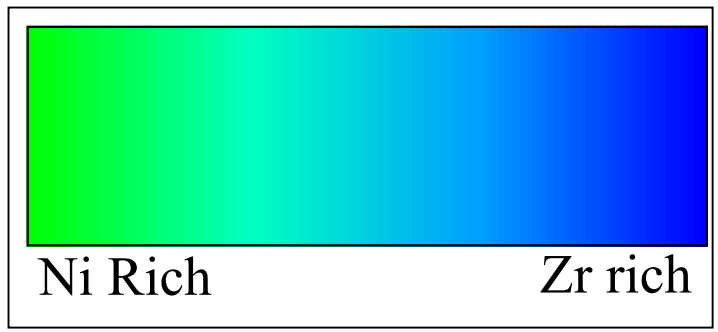
XRD of 50/50 NiZr films



- Polycrystalline films with grain diameters of ~50 nm
- 300°C annealing produces secondary phases: ZrO_x and Ni
- Multiphase composition not ideal for corrosion resistance

Co-sputtering of Ni/Zr

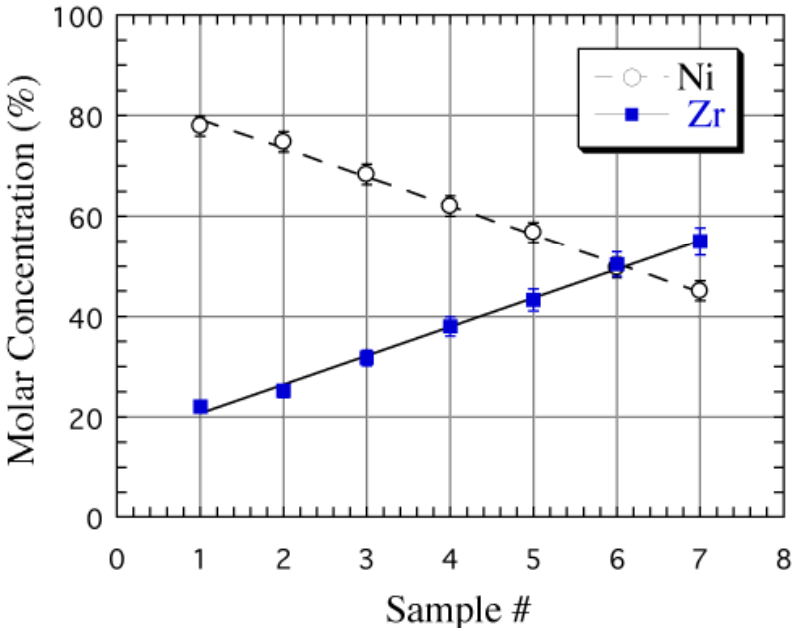




- Simultaneously use two sources
- Create a compositional gradient
- Produce multiple samples in one deposition experiment

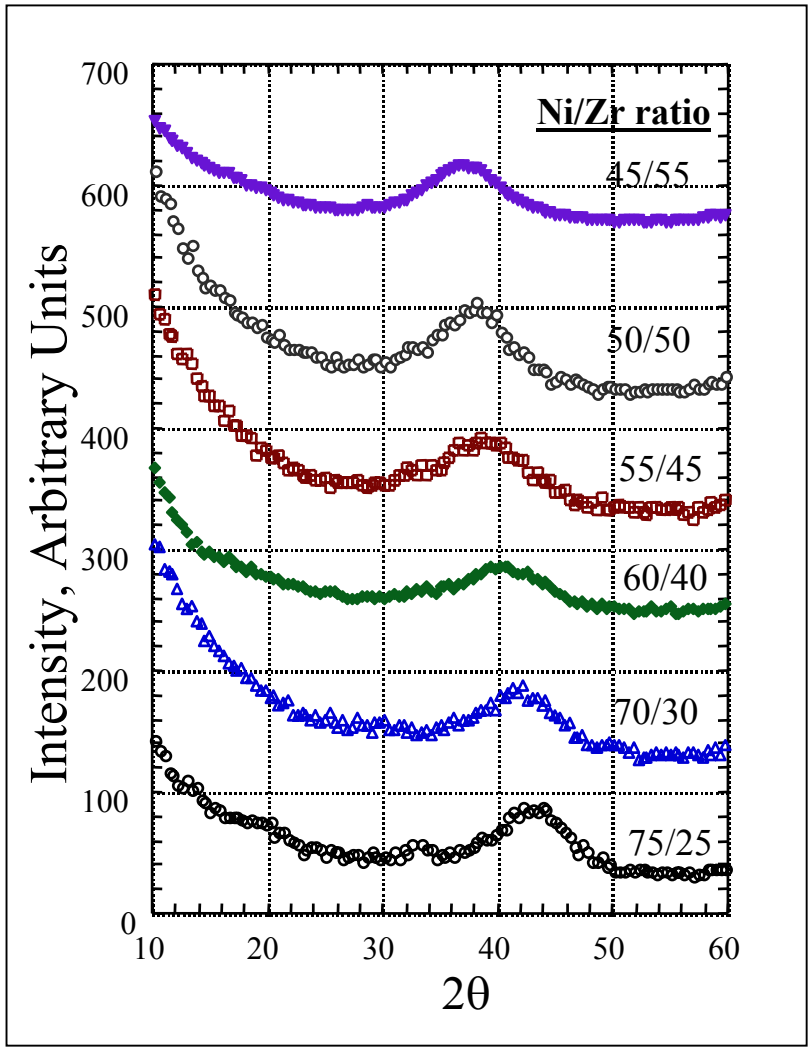
Composition and Structure of co-sputtered Ni/Zr films

EDAX Results of composition



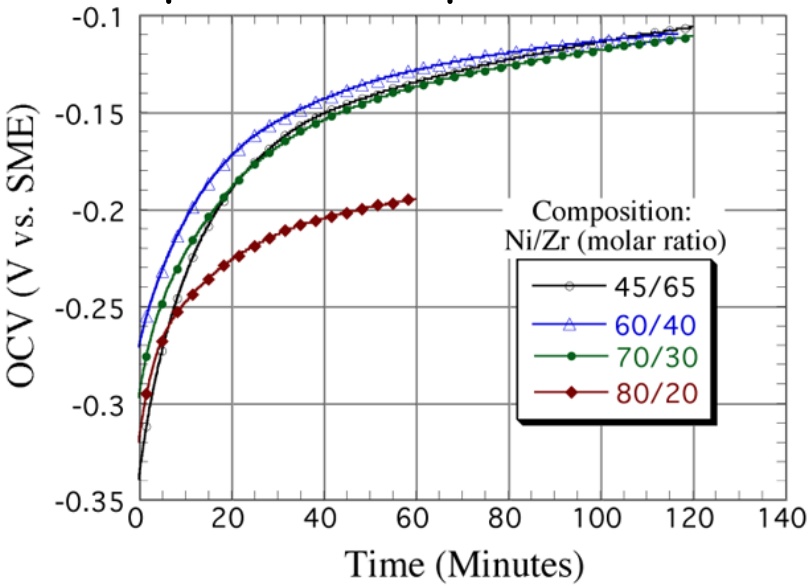
- Ni/Zr 45/55 to 75/25
- Amorphous to nanocrystalline
- Grain diameter 1.5 nm

XRD Results

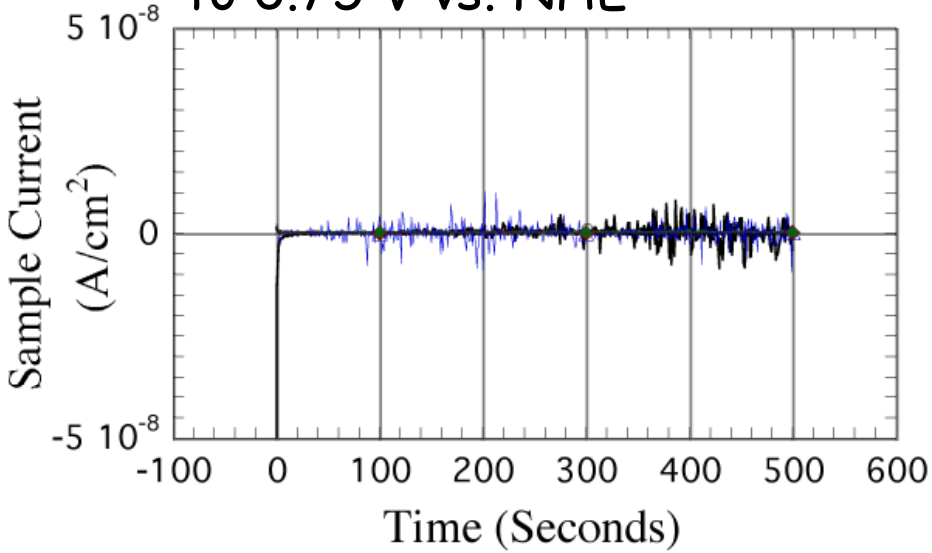


Polarization Studies in sulfuric acid solution

Open circuit potential



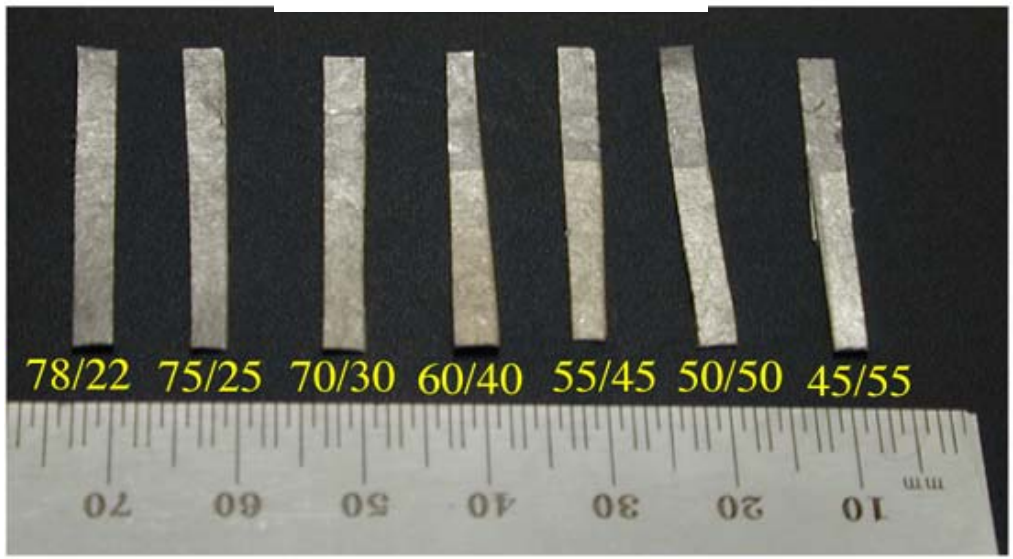
Potential scanned from 0.05 to 0.75 V vs. NHE



- Films with < 70% Ni had similar high open circuit potential of about +0.55V vs. NHE, indicative of passivation.
- Faradaic current of the order of 1 nanoampere/cm^2 over wide potential window: Good corrosion resistance

Corrosion Resistance of Ni/Zr samples in sulfuric acid

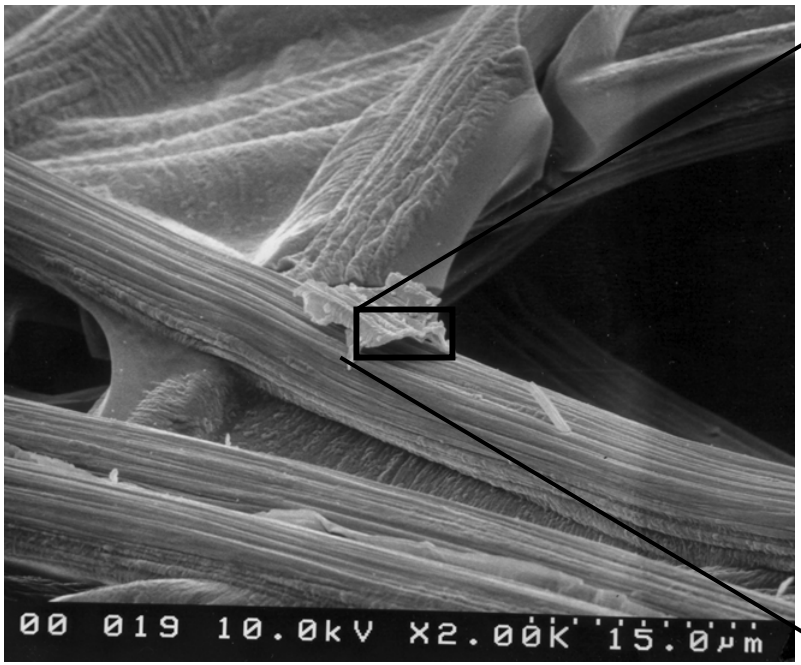
Samples with different Ni/Zr ratio



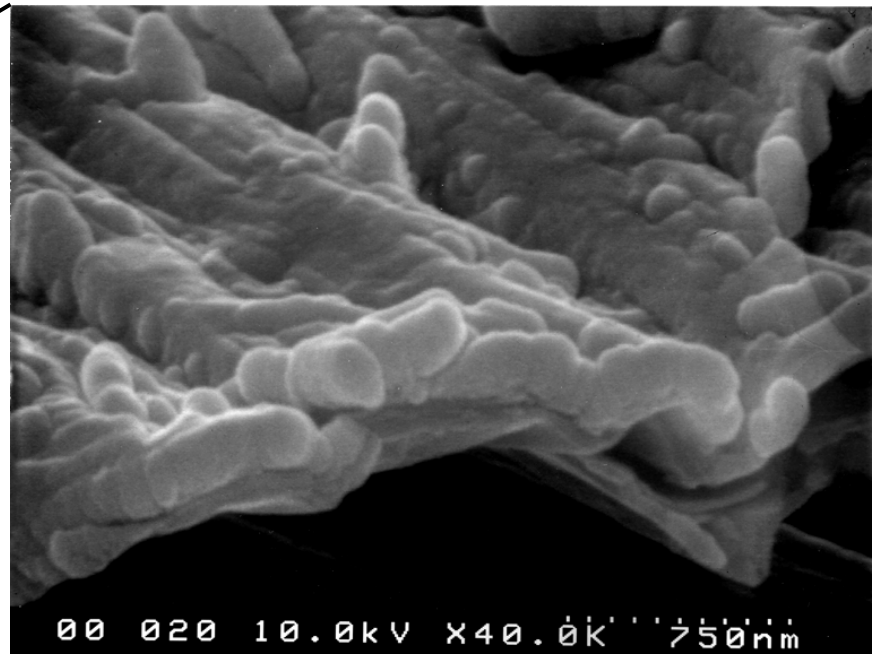
- Samples with nickel content <70% show no visible evidence of corrosion
- Samples with nickel content >70% tend to dissolve in sulfuric acid over extended period of time
- Consistent with positive open circuit potential values.

Nanoscale Morphology of Ni/Zr films

Ni-Zr films on Toray paper

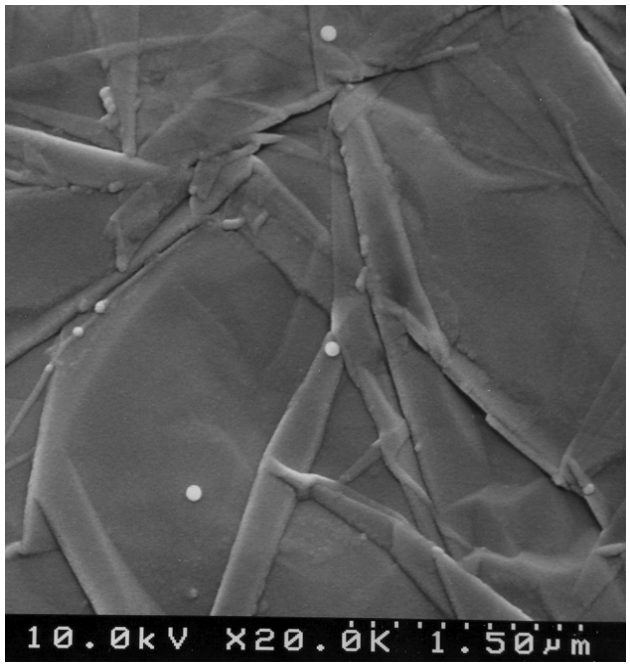


Magnified view of film



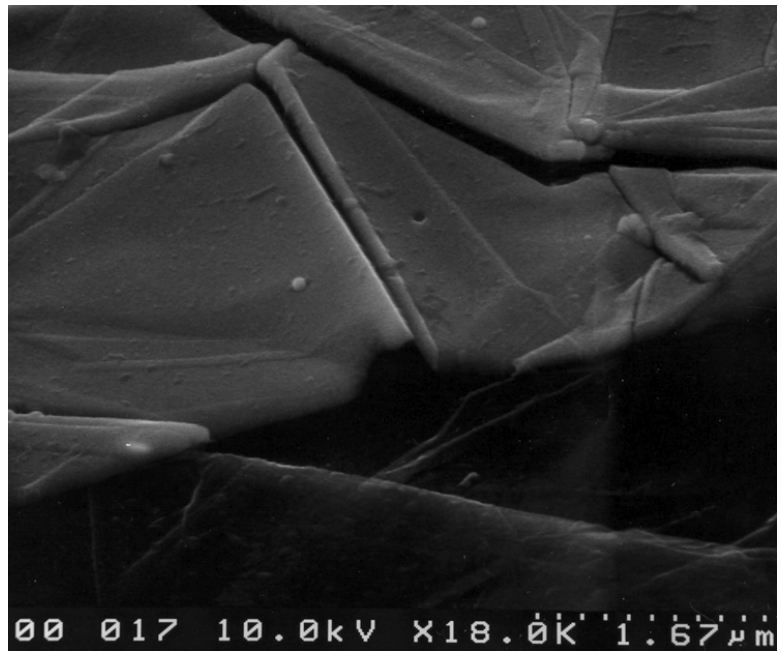
Rough nano-scale morphology can result in high surface area and active sites for catalysis

Morphology of films after exposure to 2 M sulfuric acid



- Smooth films that conform to graphite foil substrate before acid exposure

Ni/Zr 50/50



After 48 hours of exposure Pristine surface, no visible change

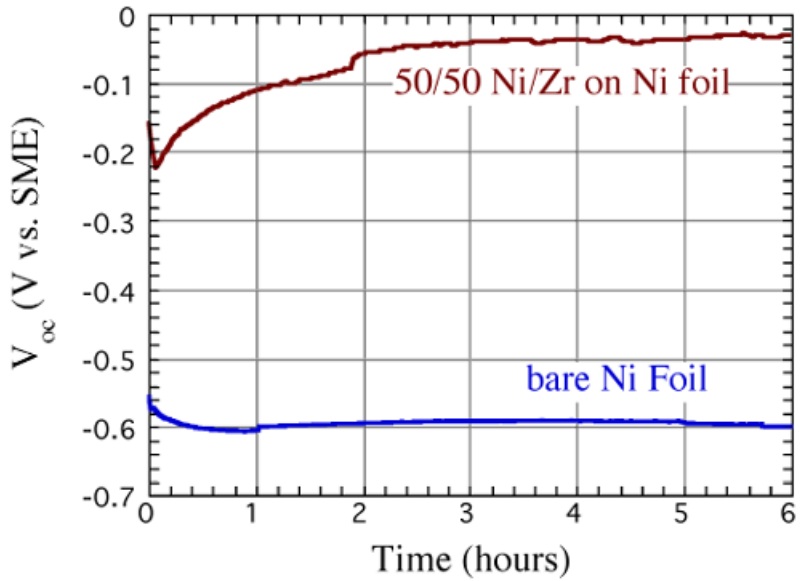
Coated Ni Foil exposed to sulfuric acid

Ni/Zr coated

Epoxy coated

Bare Ni

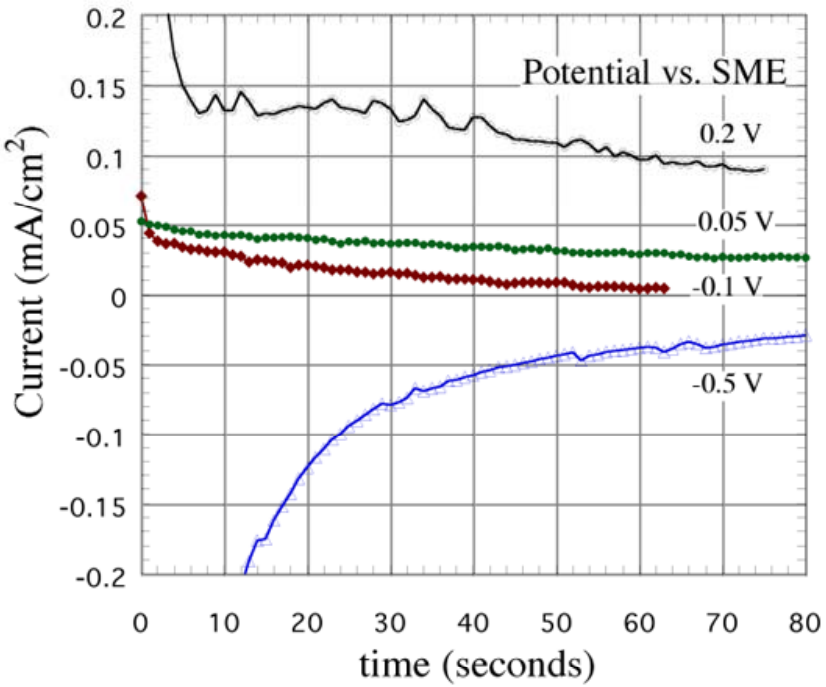
Open circuit potential measurements



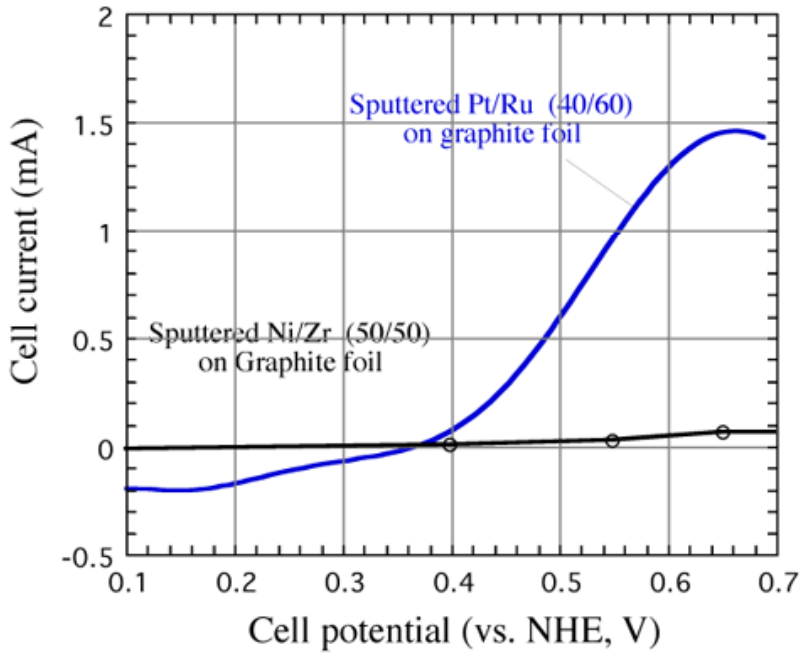
- Ni/Zr is a corrosion resistant coating for base metals.
- Protective coating for metal biplates and fuel cell hardware

Methanol oxidation activity of Ni/Zr (Preliminary Studies)

Ni/Zr 50/50

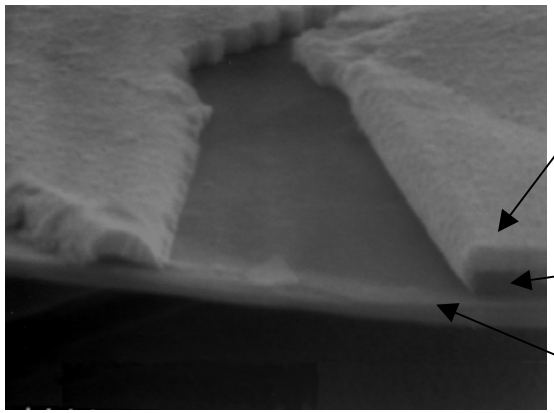


Polarization in 1M methanol/ 1M sulfuric acid, 25°C.



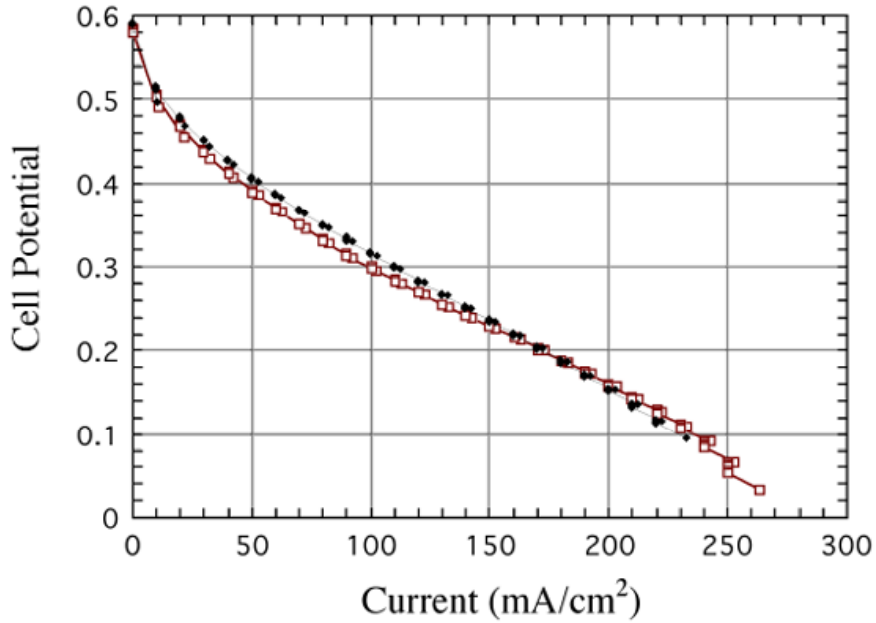
Methanol oxidation on NiZr(50/50) about 1 order-of-magnitude lower than sputtered Pt-Ru

Pt-Ru coatings on Ni/Zr



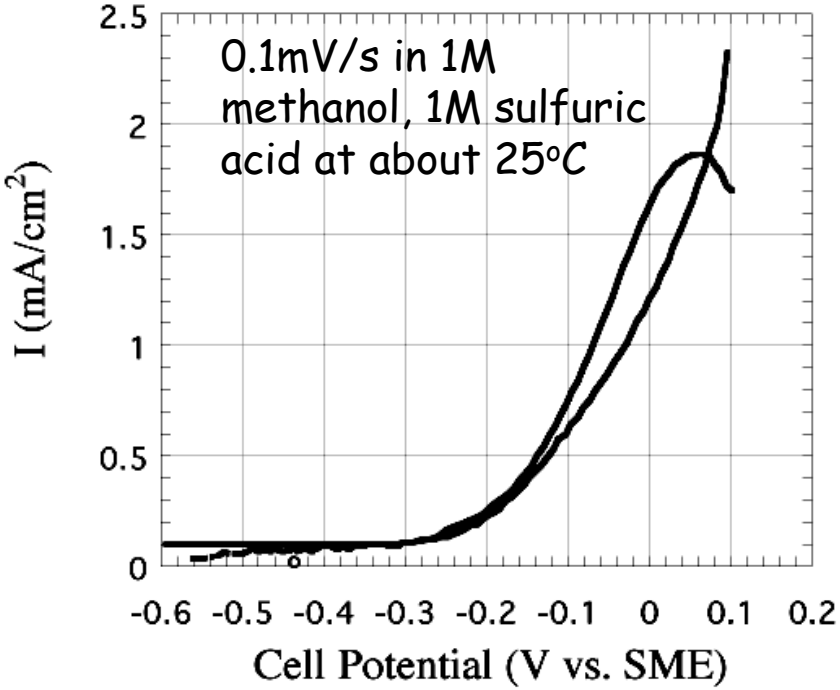
Fuel Cell Studies:

0.1 mg/cm^2 PtRu/NiZr
Nafion 117, Standard Pt cathode, 1 M methanol, 90°C



Stable operation during 4 days of testing;Ni/Zr underlayer is stable in fuel cell environment

Half cell studies



Summary of 2003 Progress

- A non-noble metal system with corrosion resistance with potential catalytic activity has been produced
- Sputter-deposition has been demonstrated to provide unique non-equilibrium nanophase materials for fuel cell applications
- Co-sputtered Ni/Zr coatings with Ni content less than 70% have desirable properties for fuel cells.
- Ni/Zr underlayer with Pt/Ru catalyst layer has shown stable performance in fuel cells.
- Ni/Zr coatings have demonstrated to protect base metals such as Ni.
- Quaternary compositions based on Ni-Zr-Pt-Ru have been prepared.

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Future Studies

•Continue to study composition, morphology and electrochemical performance Ni/Zr coatings.

• Evaluate quaternary compositions of Ni-Zr-Pt-Ru; potentially lower the amount of Pt-Ru and provide opportunity for tuning electronic interactions

• Evaluate Co-Zr sputtered layers for methanol oxidation activity ; Co has higher catalytic activity compared to Ni for many organic transformations

•Correlate electronic properties of materials from EXAFS and XPS with catalytic properties.