

JPL

DEVELOPMENT OF ADVANCED CATALYSTS FOR DIRECT METHANOL FUEL CELLS

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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



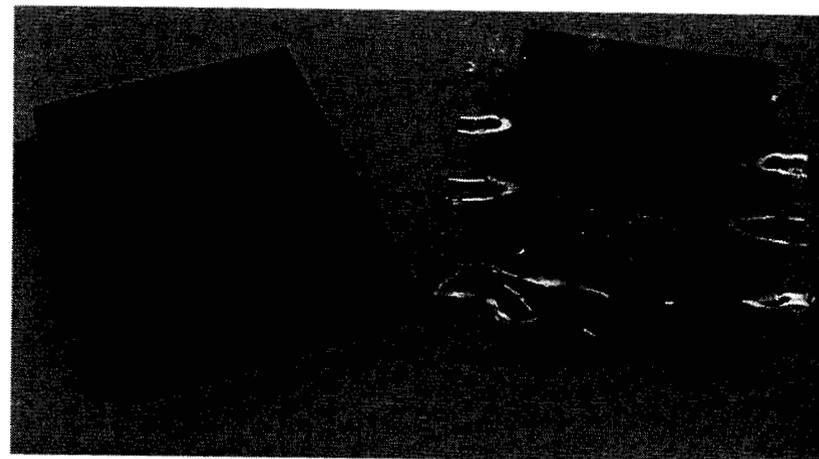
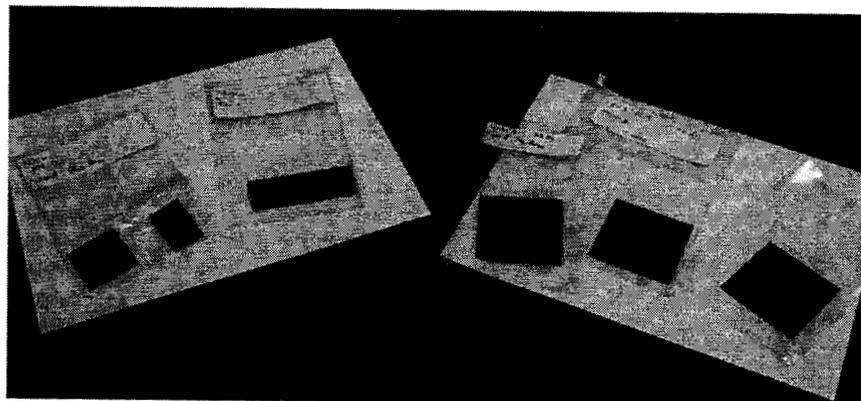
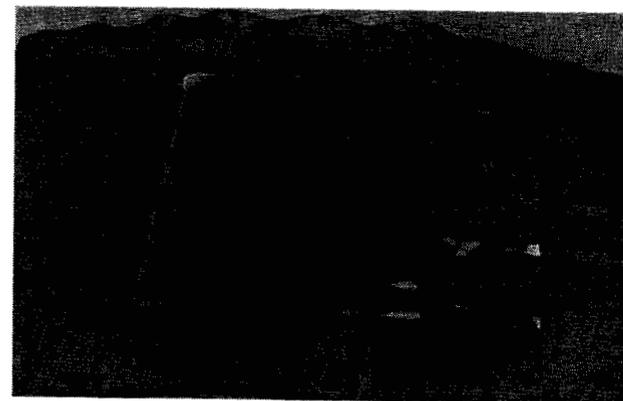
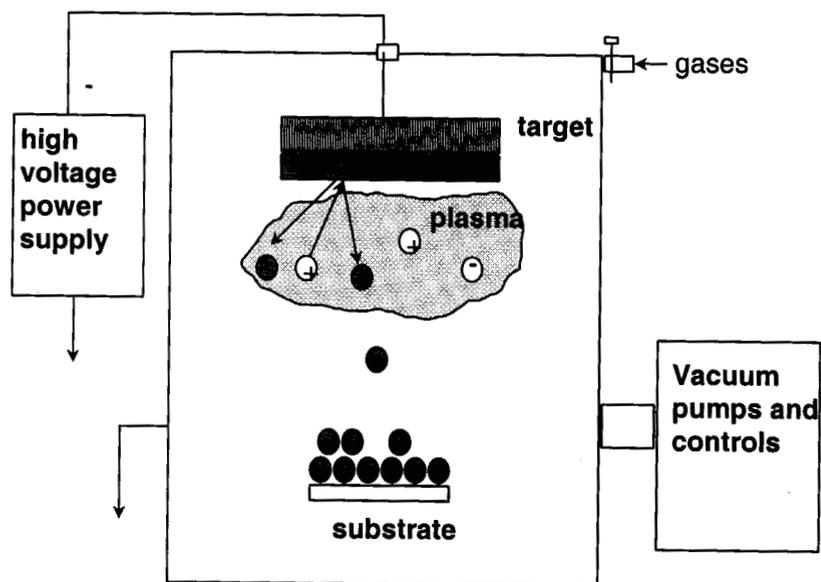
Milestones/Accomplishments

2000-2002 (Effort level: 1.75 FTE total)

- Co-sputtering can provide active thin film catalysts
- Thin film $\text{Pt}_x\text{Ru}_{1-x}$ 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/cm² with sputtered thin films and 2000 mW/mg at 0.03 mg/cm² (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

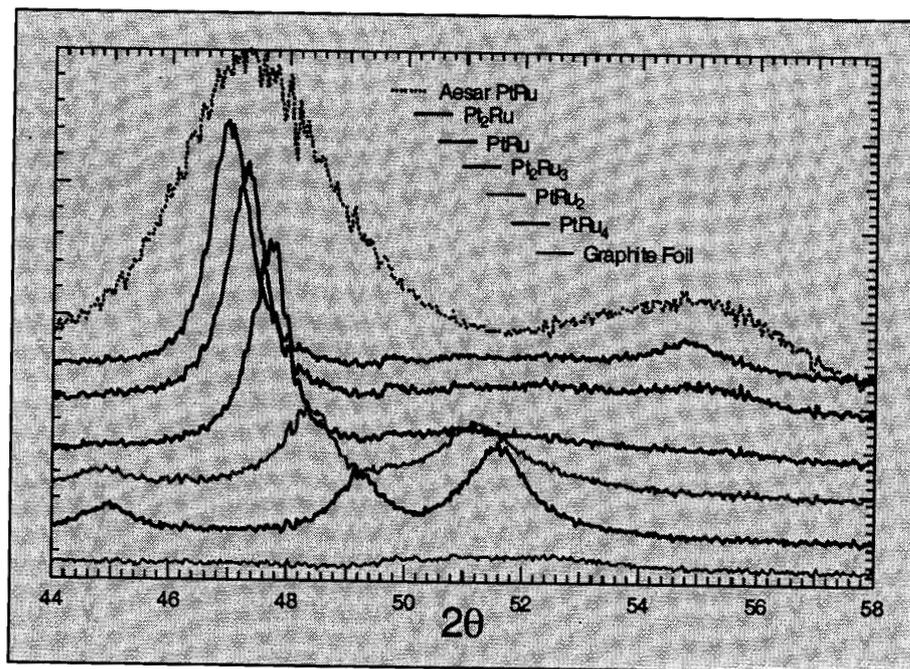
Sputtered thin film catalyst layers

SCHEMATIC OF SPUTTER-COATING PROCESS

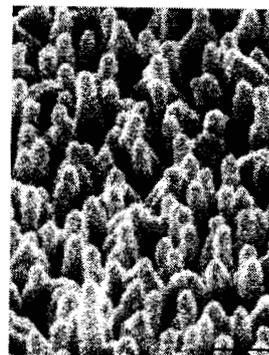
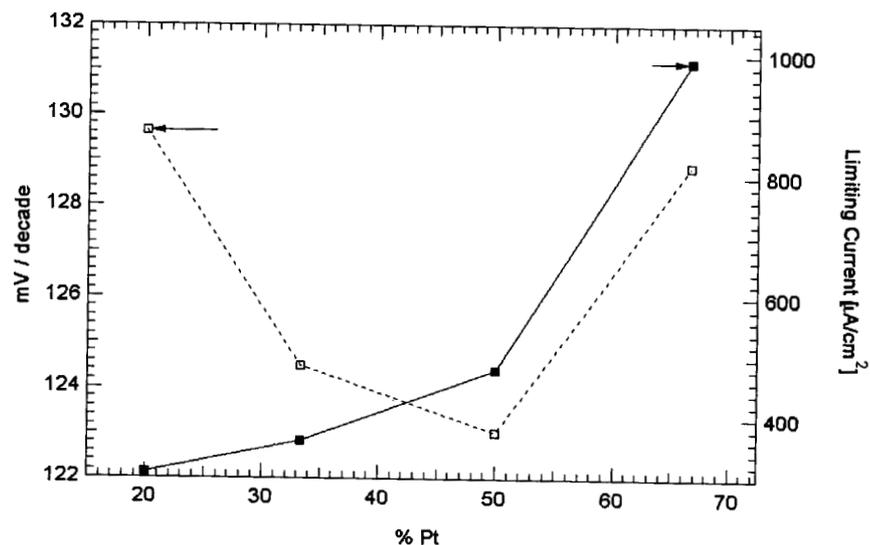


Properties of sputtered Pt-Ru films

XRD of sputtered films of Pt_xRu_{1-x}

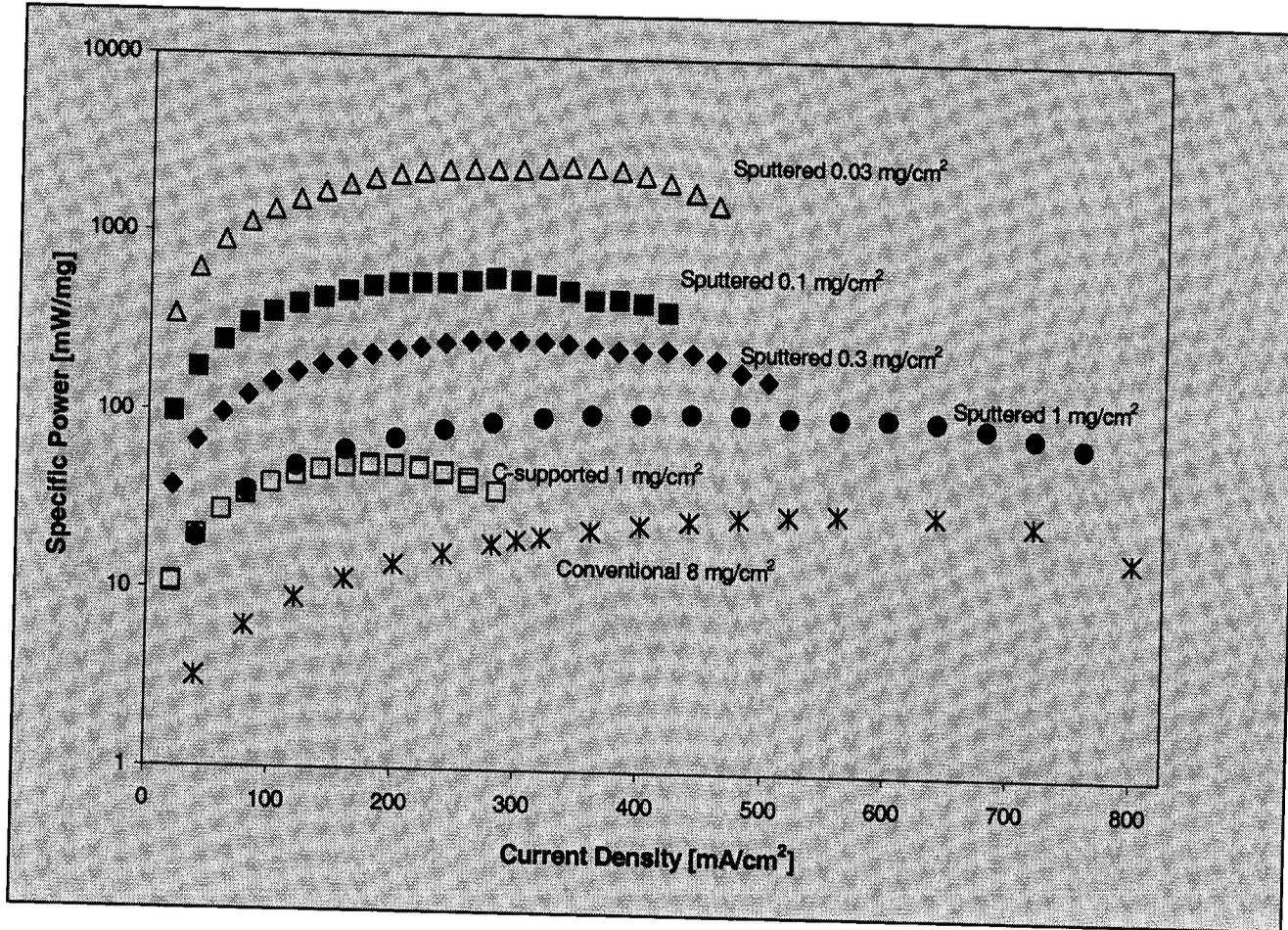


Electrochemical Activity



Unique microstructures

Utilization with thin film catalysts



800 mW/mg at 0.1 mg/cm², and 2000 mW/mg at 0.03 mg/cm²



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

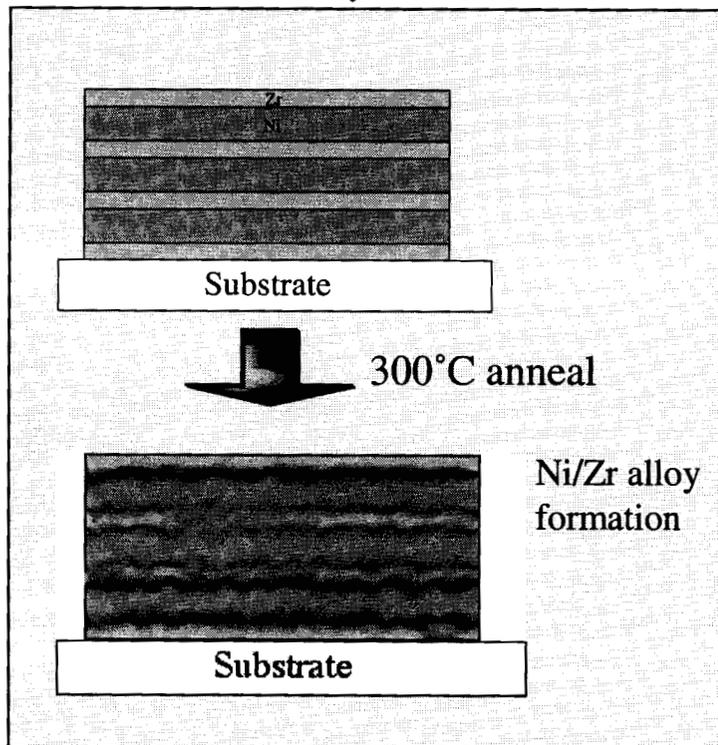
- Identifying alternates to precious metal catalysts
- Developing noble metal and non-noble metal combinations to reduce precious metal loading and enhance activity

Approach

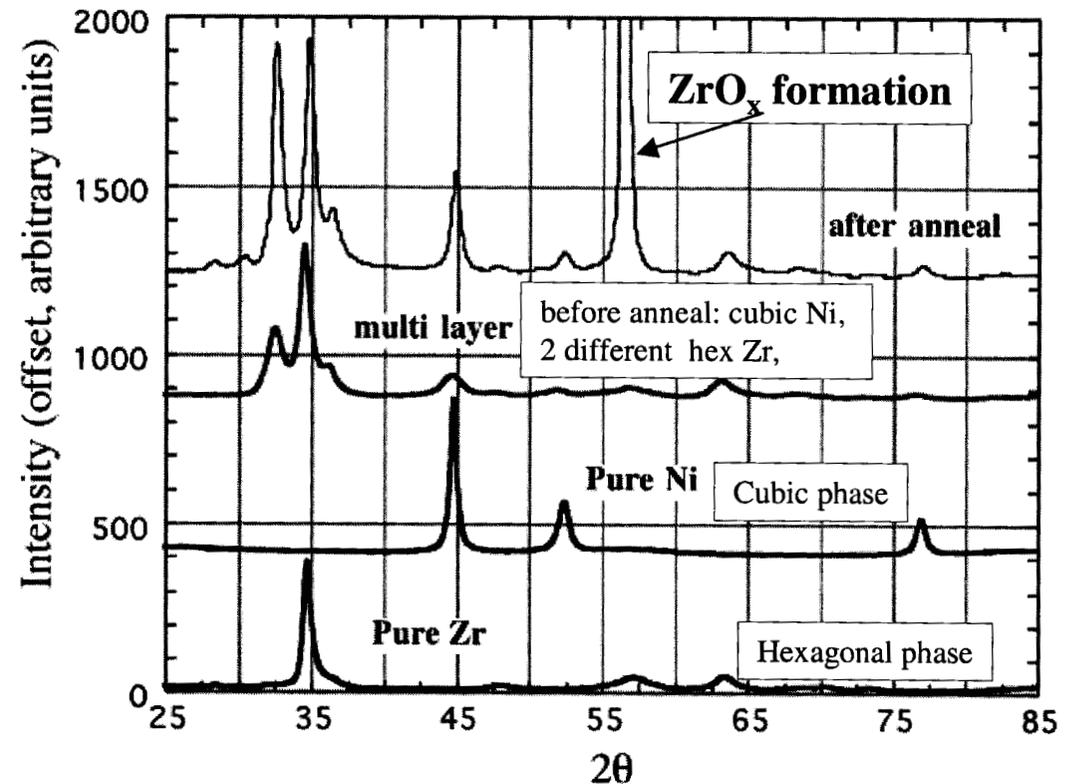
- Take advantage of sputter-deposition to identify a corrosion resistant non-noble metal system
 - non-equilibrium phases, unique nanophase structure, morphology and electronic properties.
- Ni/Zr system as proof-of-concept
- Characterization:
 - Corrosion studies in sulfuric acid, XRD, SEM
 - Fuel Cell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

Multilayer Ni/Zr films

Concept

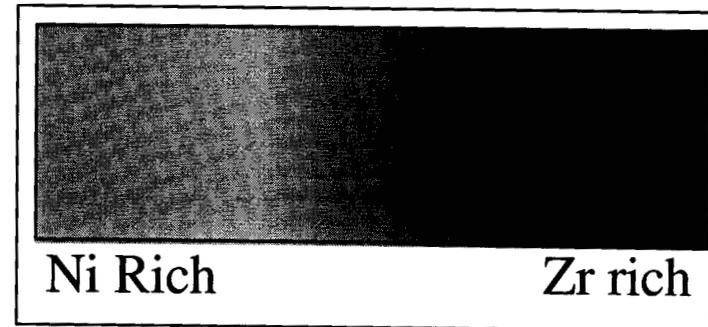
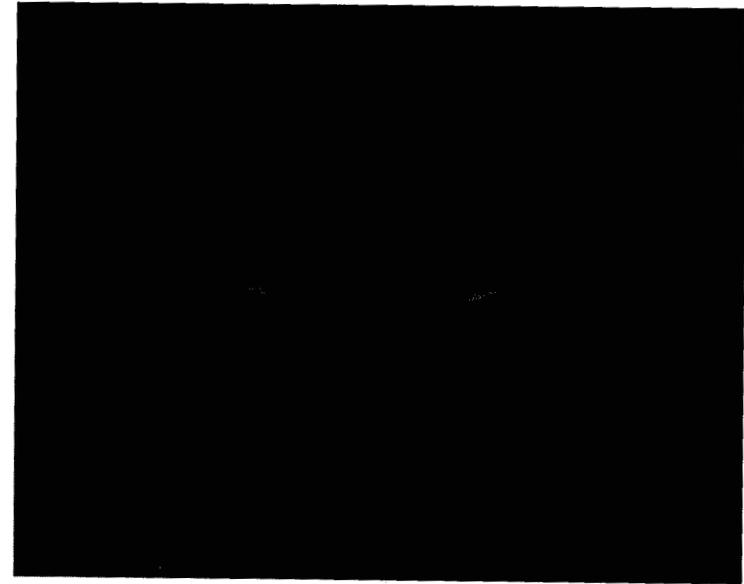
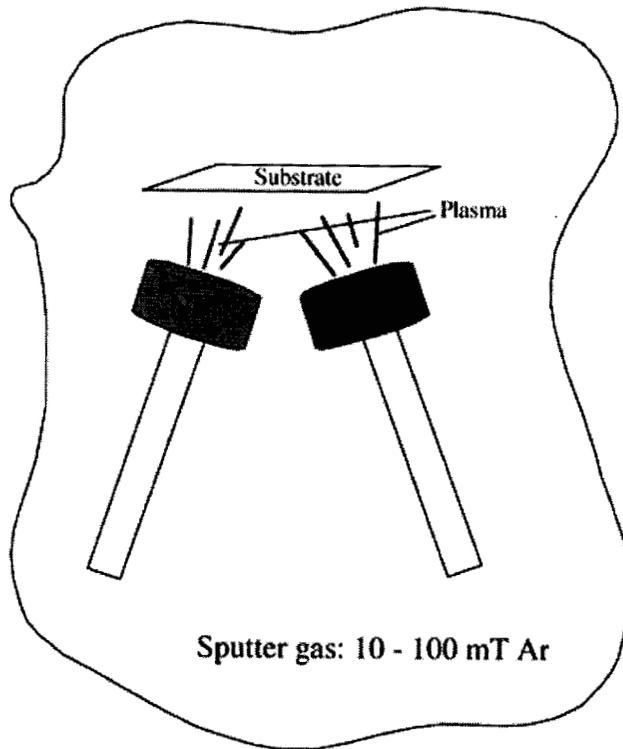


XRD of 50/50 NiZr films



- 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

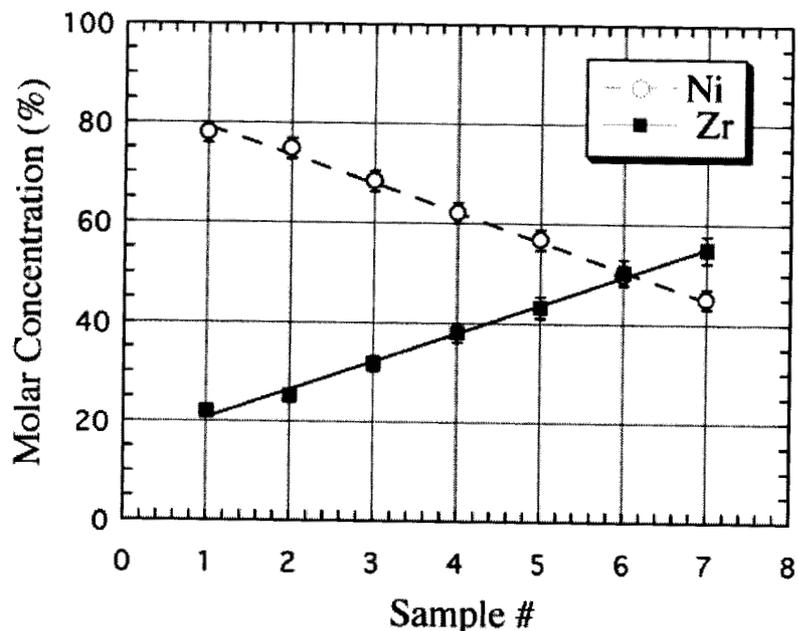
Co-sputtering of Ni/Zr



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

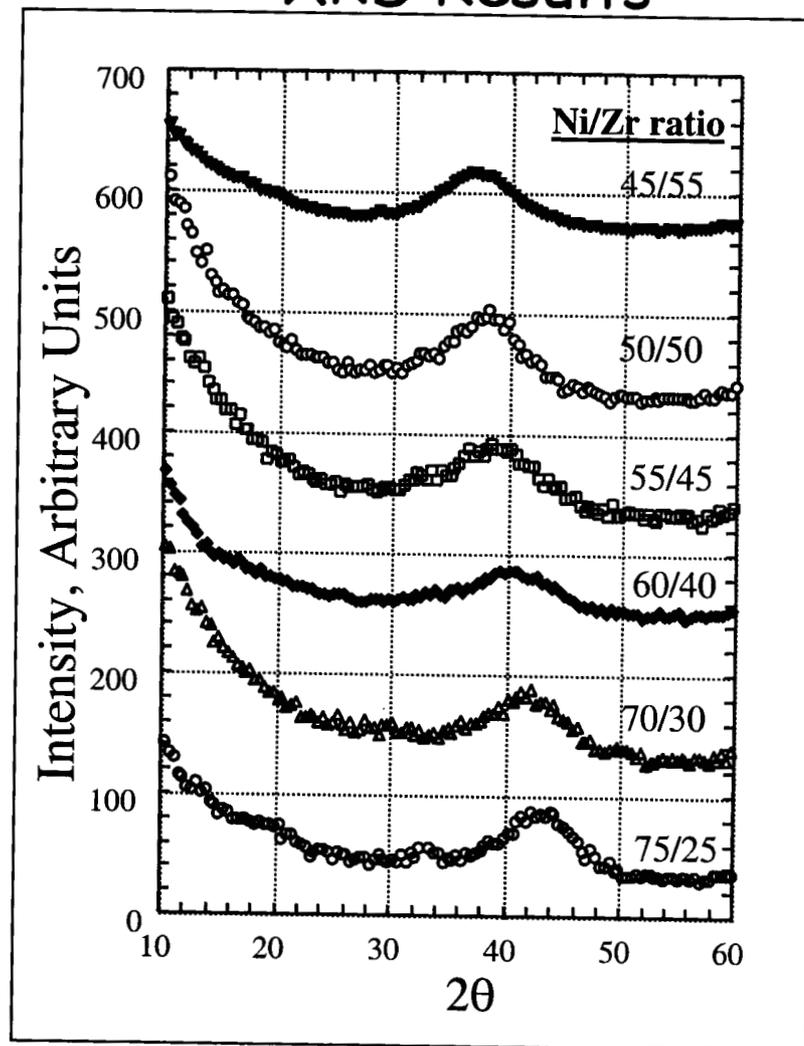
Composition and Structure of co-sputtered Ni/Zr films

EDAX Results of composition

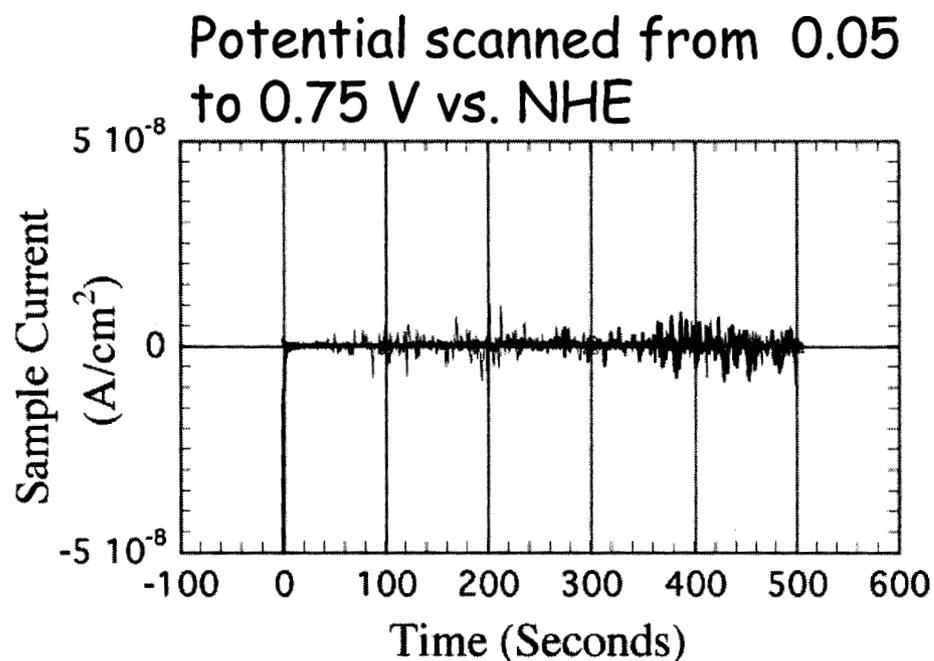
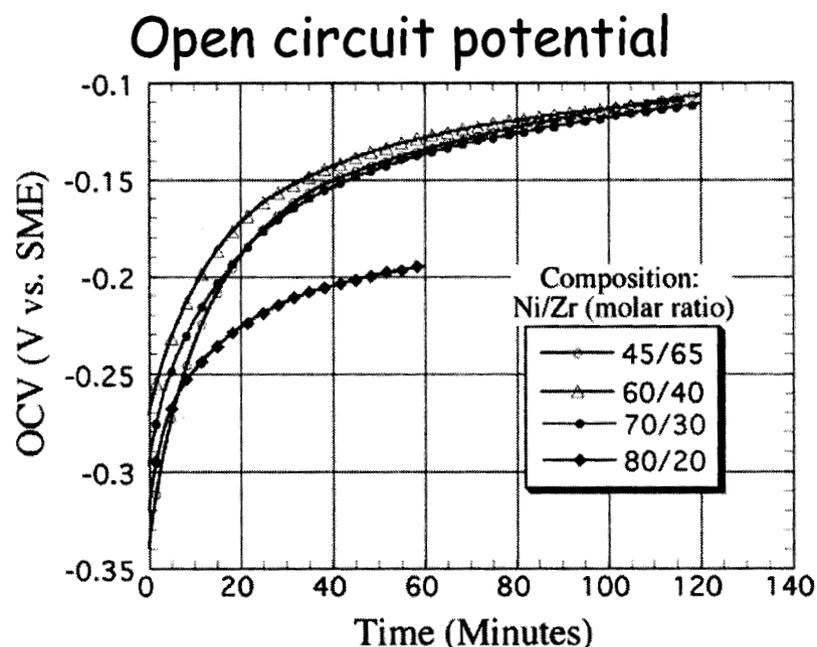


- Ni/Zr 45/55 to 75/25
- Amorphous to nanocrystalline
- Grain diameter 1.5 nm

XRD Results



Polarization Studies in sulfuric acid solution

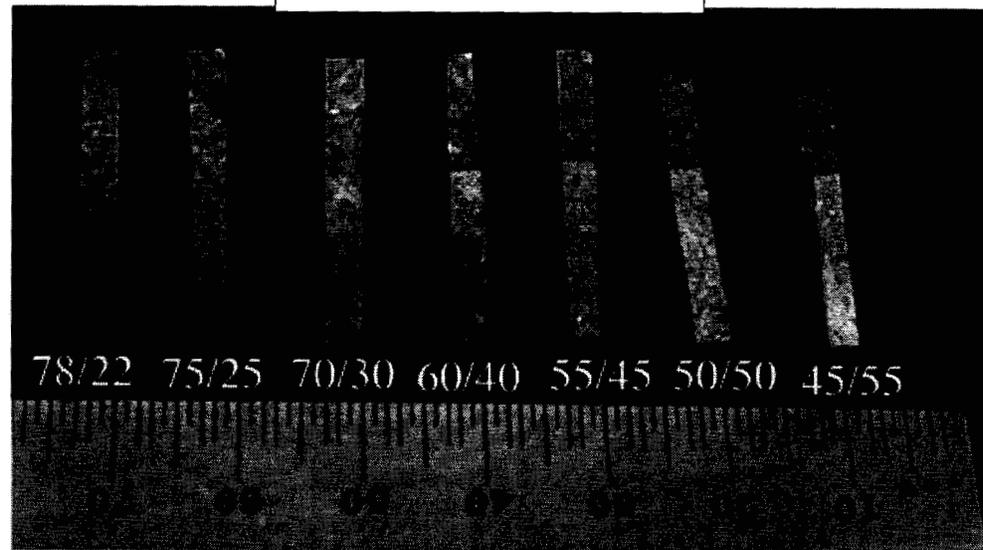


- Films with < 70% Ni had similar high open circuit potential of about +0.55V vs. NHE, indicative of passivation.
- Faradaic current of the order of 1 nanoampere/cm² over wide potential window: Good corrosion resistance



Corrosion Resistance of Ni/Zr samples in sulfuric acid

Samples with different Ni/Zr ratio



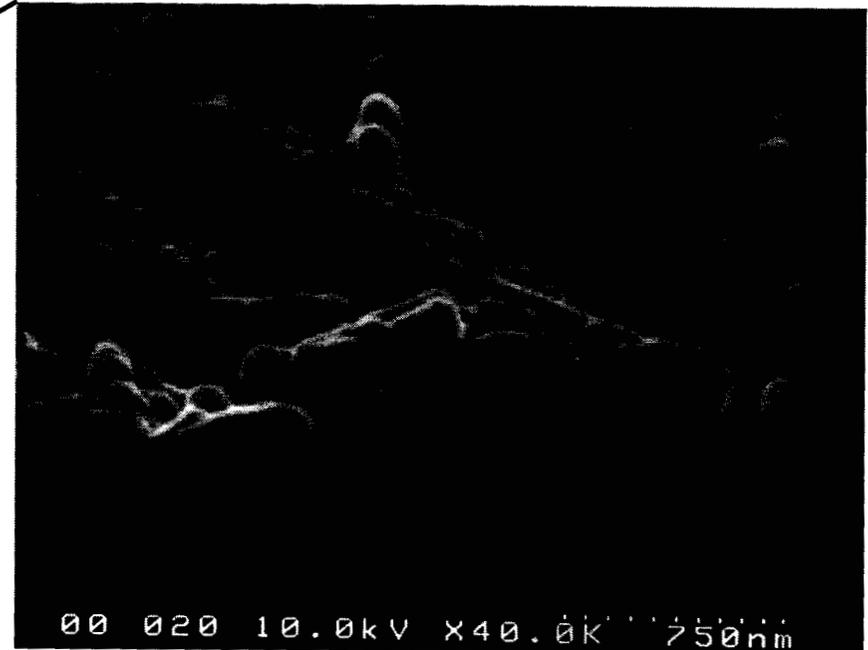
- Samples with nickel content $<70\%$ show no visible evidence of corrosion
- Samples with nickel content $>70\%$ tend to dissolve in sulfuric acid over extended period of time
- Consistent with positive open circuit potential values.

Nanoscale Morphology of Ni/Zr films

Ni-Zr films on Toray paper



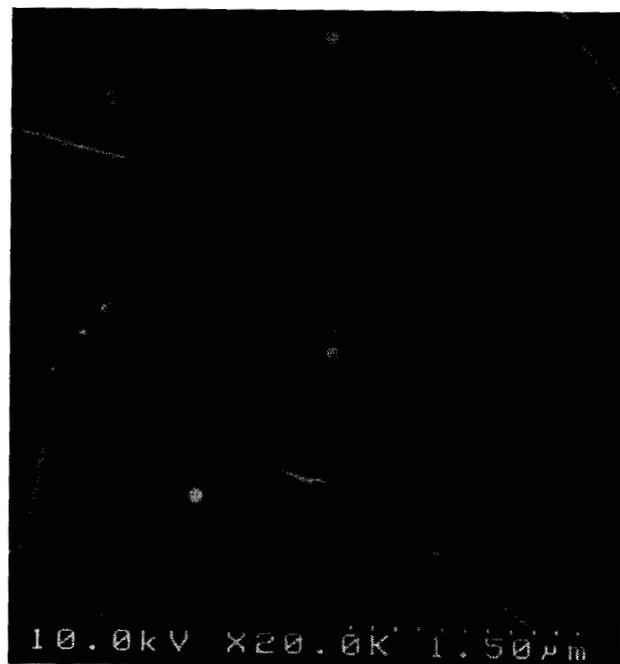
Magnified view of film



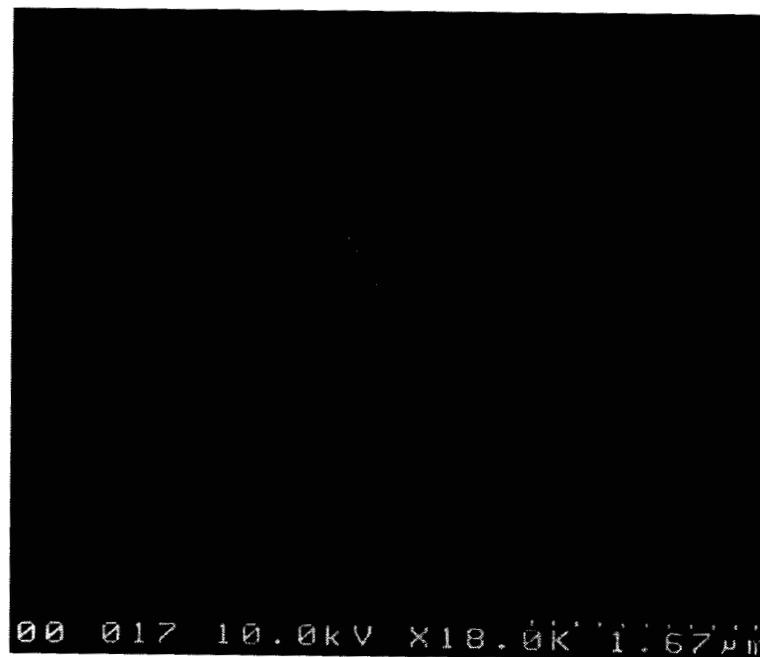
Rough nano-scale morphology can result in high surface area and active sites for catalysis

Morphology of films after exposure to 2 M sulfuric acid

Ni/Zr 50/50



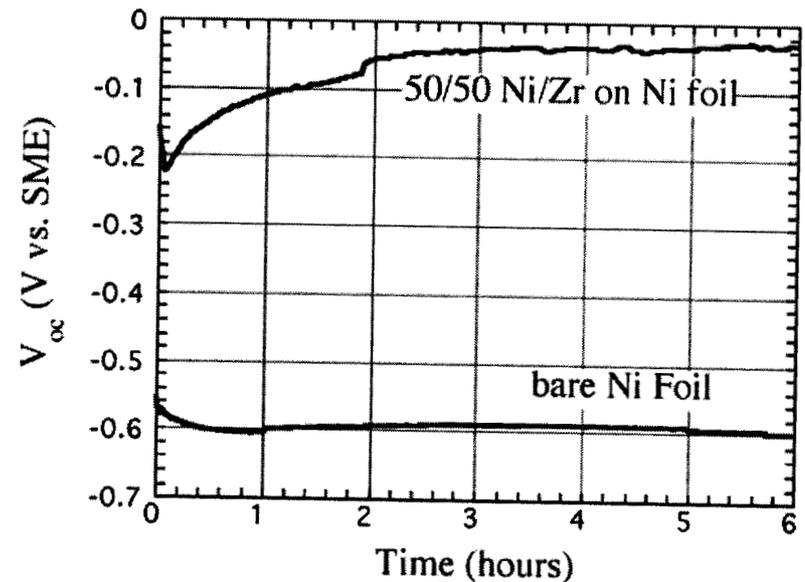
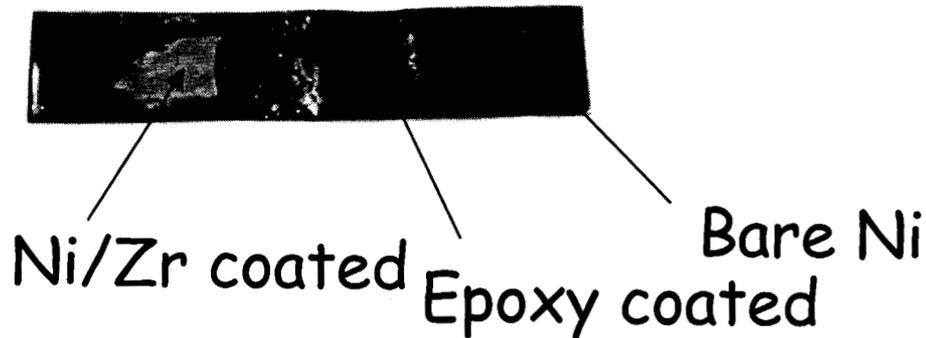
• Smooth films that conform to graphite foil substrate before acid exposure



After 48 hours of exposure
Pristine surface, no visible change

Coated Ni Foil exposed to sulfuric acid

Open circuit potential measurements

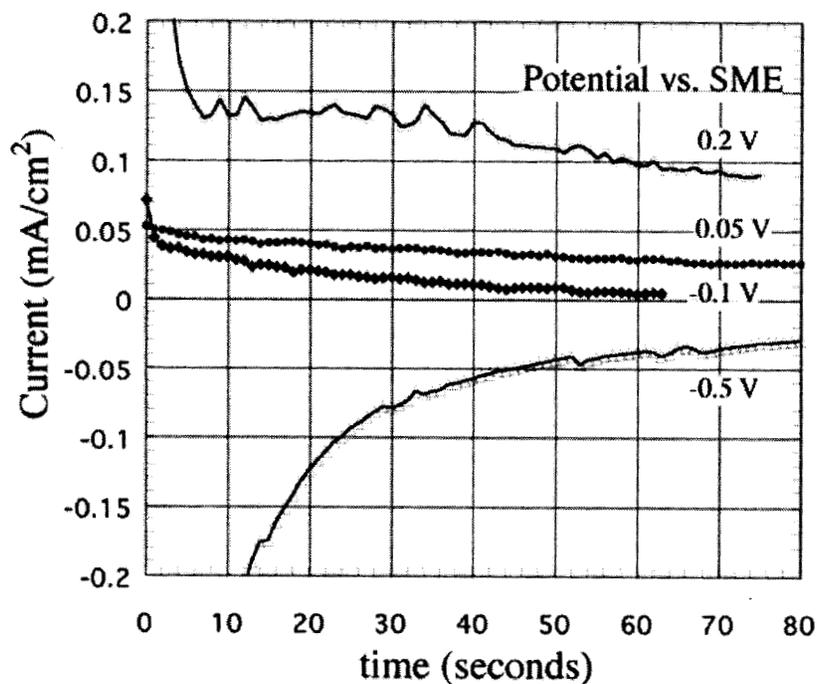


- Ni/Zr is a corrosion resistant coating for base metals.
- Protective coating for metal biplates and fuel cell hardware

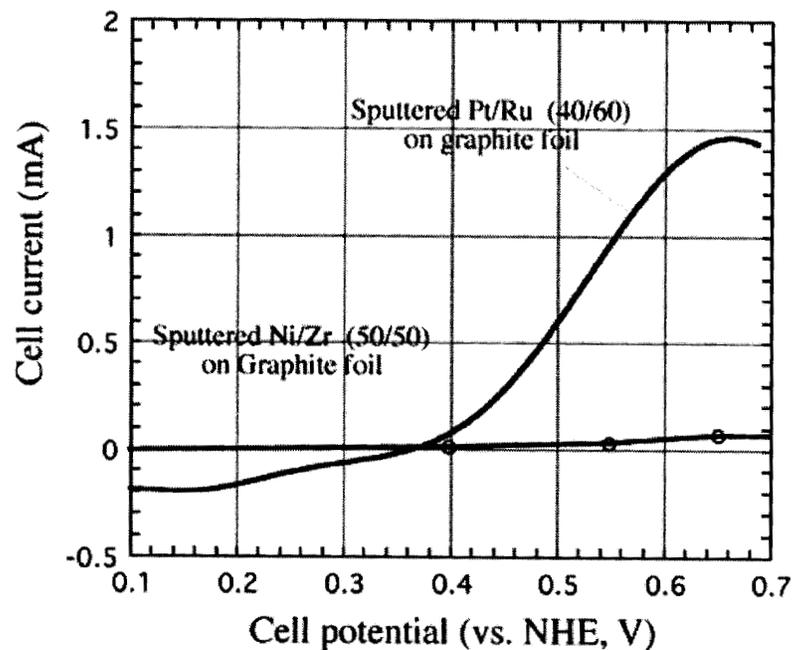


Methanol oxidation activity of Ni/Zr (Preliminary Studies)

Ni/Zr 50/50

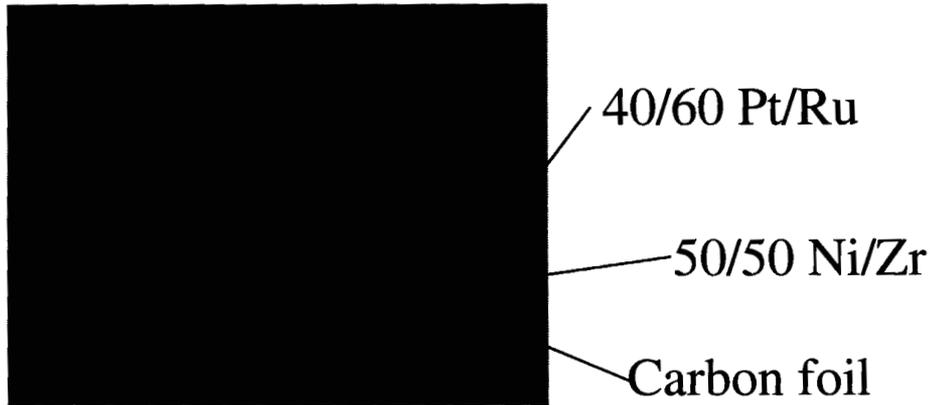


Polarization in 1M methanol/
1M sulfuric acid, 25°C.



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

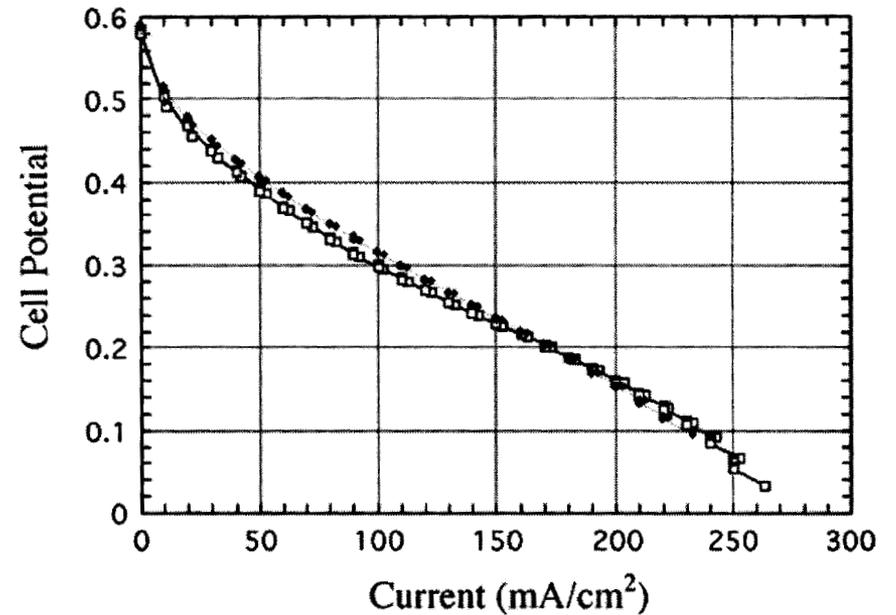
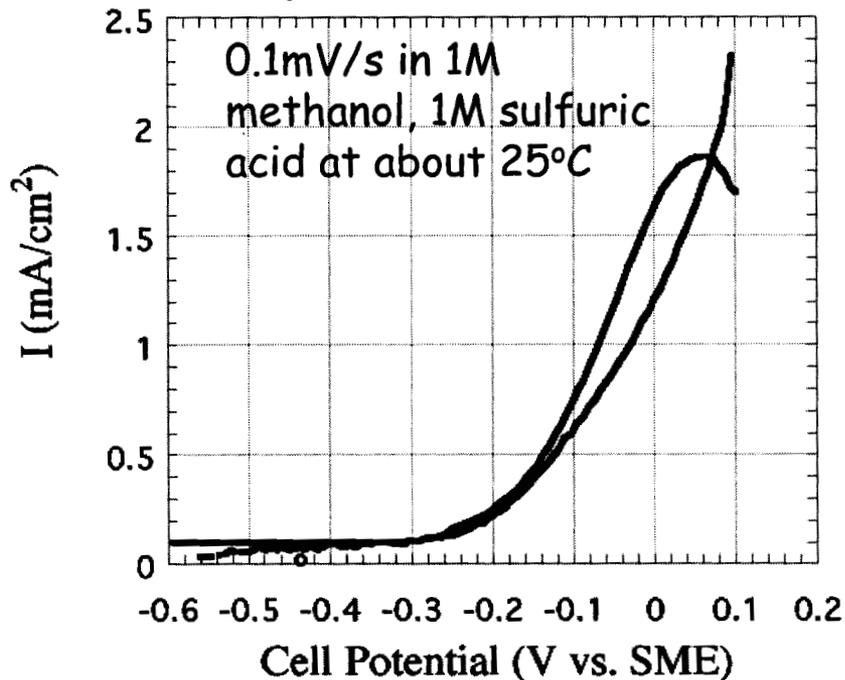
Pt-Ru coatings on Ni/Zr



Fuel Cell Studies:

0.1 mg/cm² PtRu/NiZr
Nafion 117, Standard Pt cathode, 1 M methanol, 90°C

Half cell studies



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



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.

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.