

# ***Cathode Electrocatalysis: Platinum Stability and Non-Platinum Catalysts***

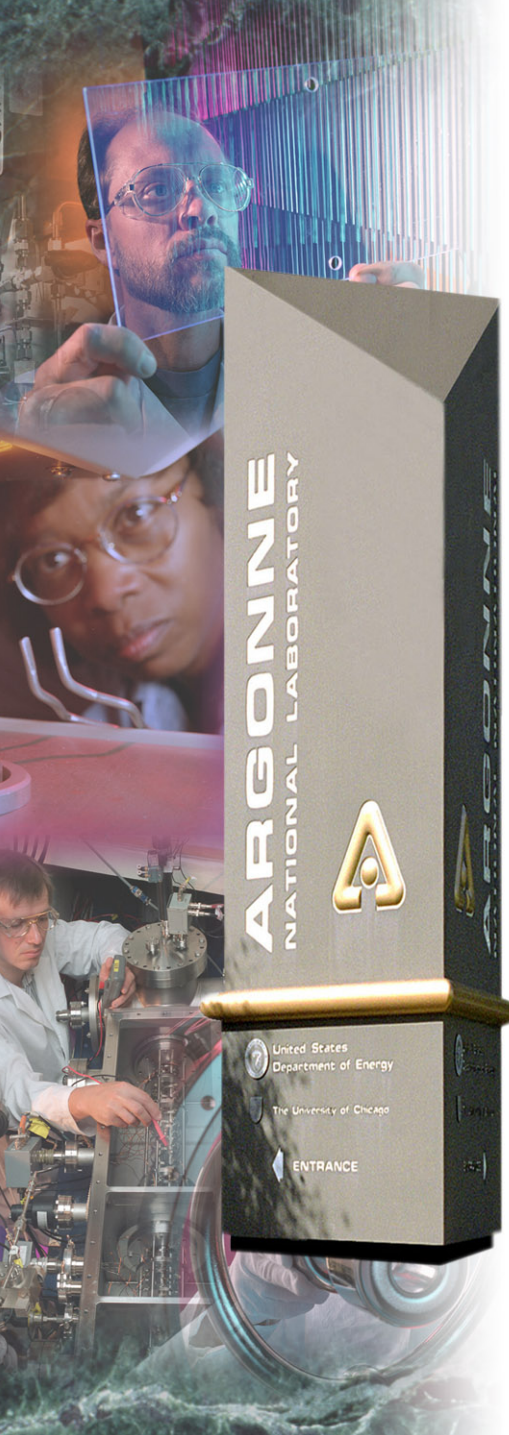
*Xiaoping Wang, Romesh Kumar, and Deborah Myers  
Chemical Engineering Division*

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**Argonne National Laboratory** Project ID: FCP8



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# Overview

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## Timeline

- **Start date: October 2003**
- **Project end date: Open**
- **Percent complete: 15%**

## Budget

- **FY '04: \$300 K**
- **FY '05: \$300 K**

## Barriers

- **This project addresses the following DOE Fuel Cell Component barriers:**
  - Stack Material and Manufacturing Cost
  - Component Durability
  - Electrode Performance

## Interactions

- **Regularly providing updates and soliciting feedback from the FreedomCAR Fuel Cell Technical Team**
- **Collaborations with BES-funded groups on characterization**

# ***Objectives and approach***

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- **Elucidate rates and mechanisms of the degradation of PEFC platinum electrode performance**
  - *Effect of electrolyte, potential (holding and cycling), time, and temperature*
- **Develop non-Pt cathode electrocatalysts for PEFCs**
  - *Transition metal carbides and nitrides*
  - *Bi-metallic systems*
  - *Metal centers attached to electron-conducting polymer backbones*

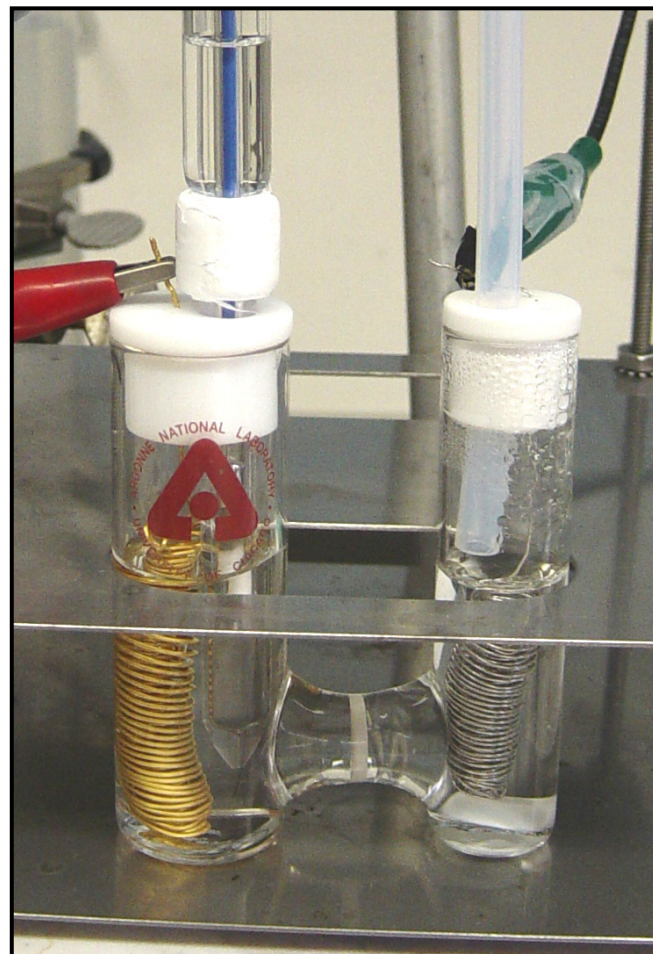
# ***Pt electrode stability test plan***

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- **Mechanisms and Rates of Pt Dissolution**
  - Potentiostatic dissolution rate measurements in adsorbing (phosphoric acid) and non-adsorbing (perchloric acid and Nafion®) electrolytes, effect of temperature and potential
  - Potential step dissolution rate measurements
  - Mechanism of platinum dissolution using RRDE
- **Particle Size, Oxidation State, and Distribution of Platinum**
  - Quantifying the extent of platinum loss in membrane-electrode assemblies using electrochemical and ex situ analyses
  - In situ X-ray fluorescence and wide-angle diffraction studies of membrane-electrode assemblies

# ***Dissolution experiments are performed using an H-cell to isolate the working electrode***

- Electrode surface area determination and electrochemical cleaning are performed in a pre-treatment cell
- Gold counter electrode is cleaned in aqua regia prior to each experiment
- Gold counter electrode and Hg/Hg<sub>2</sub>SO<sub>4</sub> reference are separated from Pt coil working electrode by a frit
- Amount of Pt dissolved in electrolyte is determined by ICP-MS (dl: 1 ppt)



## ***Dissolution of Pt in 85% H<sub>3</sub>PO<sub>4</sub> is more severe than in 0.6 M HClO<sub>4</sub>, slightly dependent on potential***

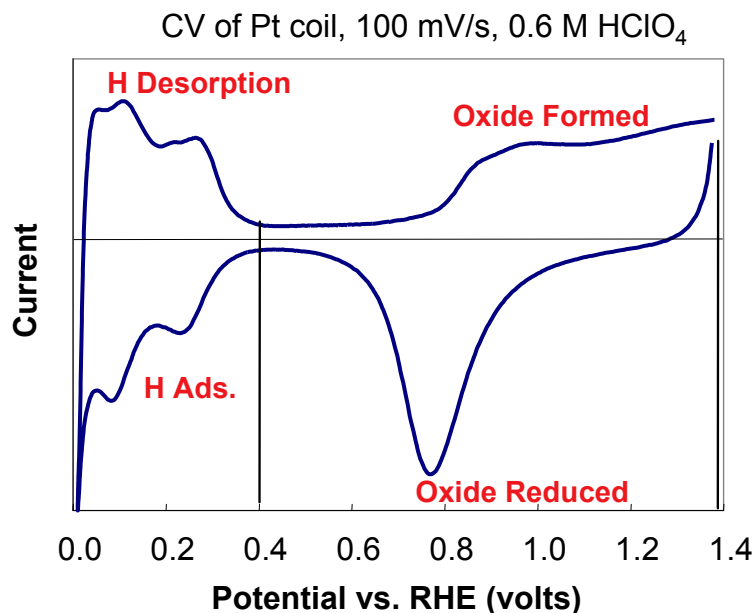
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- Pt concentration in electrolyte was determined at 2 h, then at 20-h intervals up to 120 h; concentration shown is steady-state value

<b>Electrolyte</b>	<b>Potential (V)</b>	<b>Pt concentration (ppb)</b>	<b>Electrochemically active surface area (cm<sup>2</sup>)</b>
<b>H<sub>3</sub>PO<sub>4</sub></b>	<b>0.85</b>	<b>44.4</b>	<b>55.6</b>
<b>H<sub>3</sub>PO<sub>4</sub></b>	<b>0.90</b>	<b>47.0</b>	<b>56.9</b>
<b>H<sub>3</sub>PO<sub>4</sub></b>	<b>0.95</b>	<b>47.8</b>	<b>57.0</b>
<b>HClO<sub>4</sub></b>	<b>0.90</b>	<b>12.5</b>	<b>50.0</b>

# The starting surface condition of Pt strongly affected the amount of Pt dissolved in $\text{HClO}_4$ at 0.9 V

Surface condition	Pt dissolved (ppb)	Time (h)	EASA ( $\text{cm}^2$ )
oxidized (exposed to 1.4 V)	9.39	8	39.4
oxidized (exposed to 1.4V)	10.0	24	36.4
reduced (exposed to 0.4 V)	5.00	24	38.7

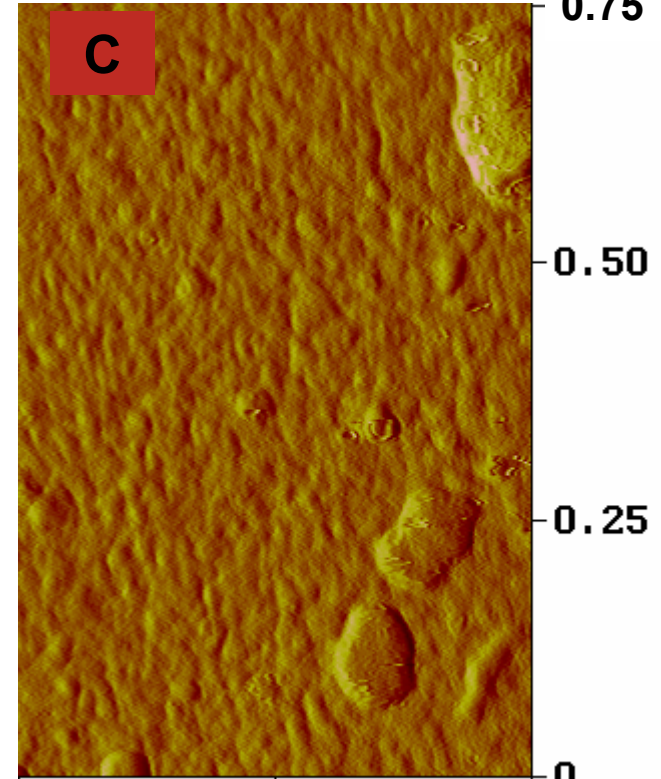
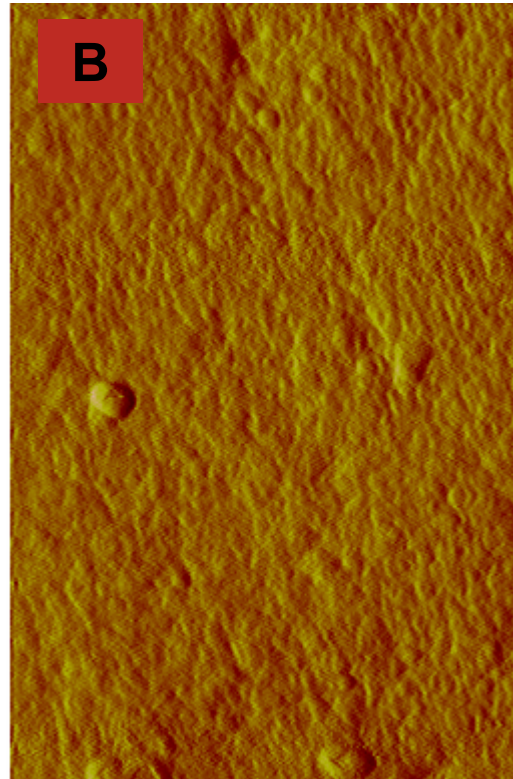
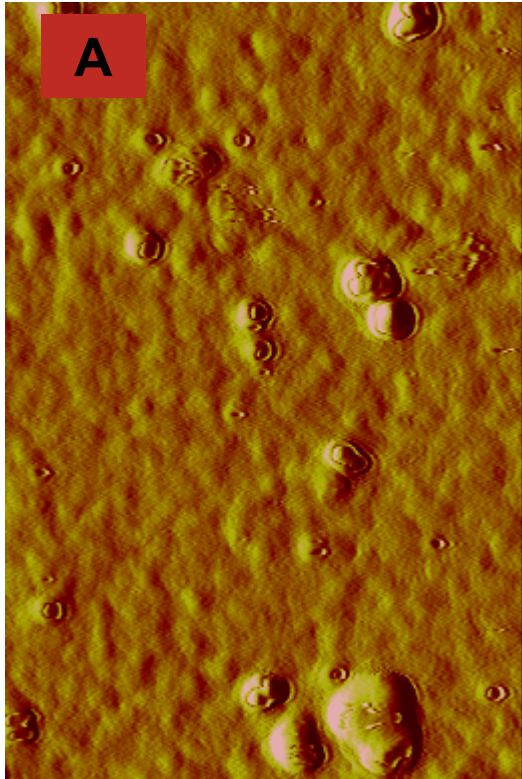


# ***AFM images shows Pt surface morphology changes with electrochemical treatment***

**Blank –  
as received**

**Potential cycling (1.4  
~ 0.1V) and potential  
holding (0.4V/10min)**

**In addition to B,  
potential held at  
0.95 V for 24 h**



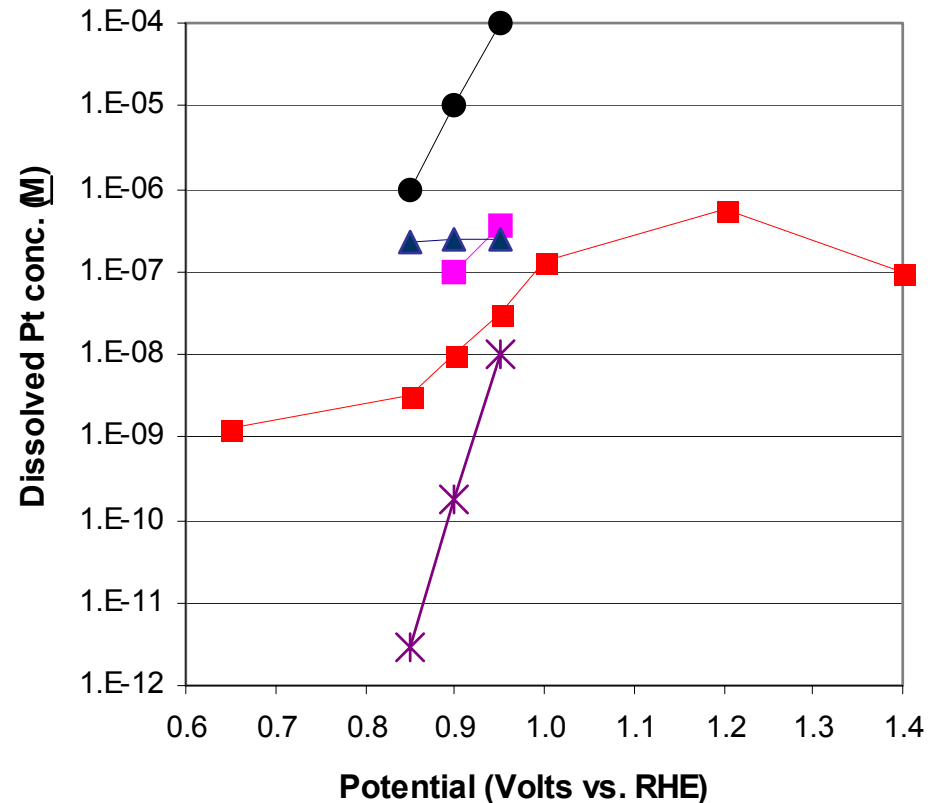
Images taken by H. You, ANL-MSD

0.50 0.75 1.00  $\mu\text{m}$



# Platinum stability studies - Conclusions

- Pt dissolution is more severe in phosphoric acid than in perchloric acid (cf. Nafion)
- Dissolved Pt equilibrium concentration is less dependent on potential than predicted by Pourbaix diagram (in agreement with GM Pt/C data)
- Pt concentration at 25°C is higher than predicted by Pourbaix diagram
- Preliminary results indicate that Pt concentration at 1.4 V is lower than at 1.2 V



- Bindra et al., phosphoric acid, 196°C, Bindra et al., JES, 126 (1979) 1631.
- GM, Pt/C, sulfuric acid, 80°C, Fall 2004 ACS Meeting
- ▲ ANL, phosphoric acid, 25°C
- ANL, perchloric acid, 25°C

# ***Platinum stability studies - Next steps***

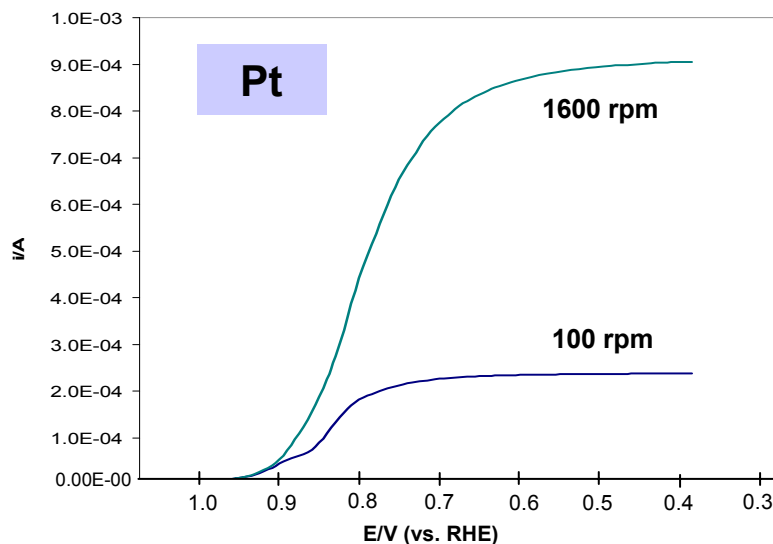
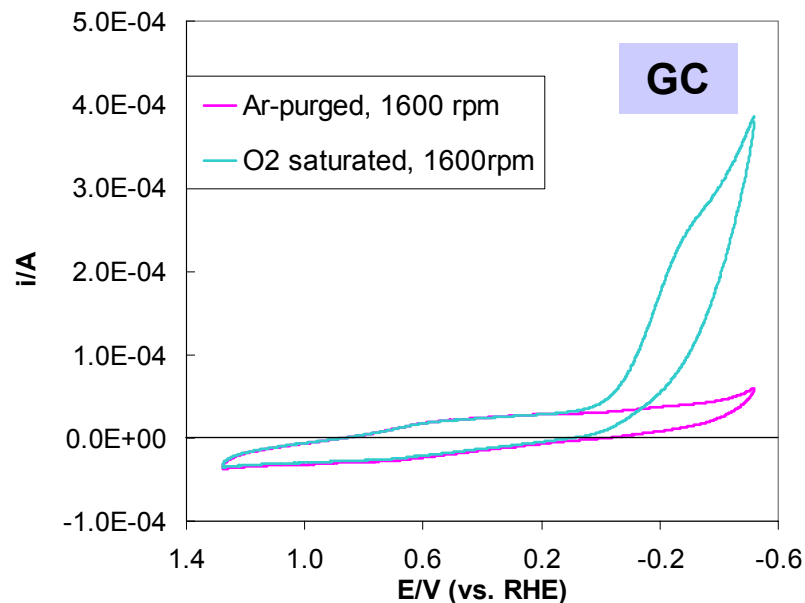
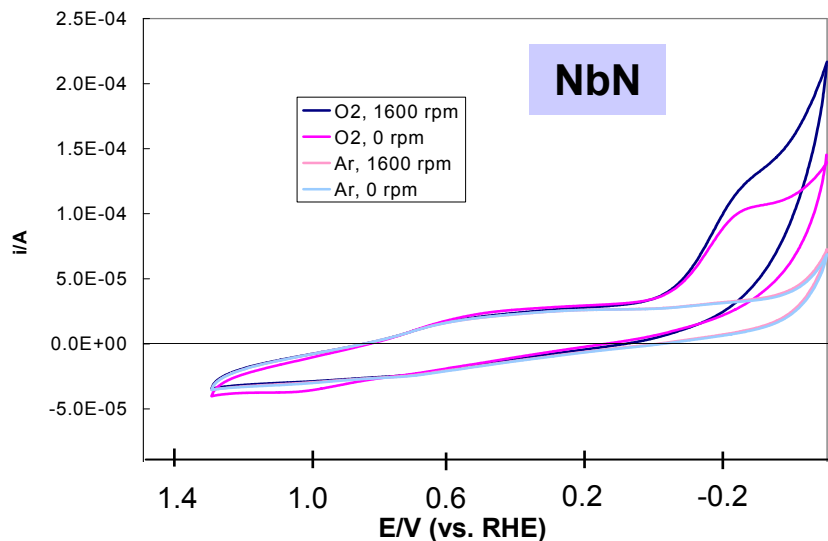
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- Repeat dissolution experiments at  $>1.0$  V
- Determine effect of temperature using perchloric acid electrolyte
- Determine effect of the following parameters using a Pt/C high surface area electrode (E-Tek):
  - Potential
  - Temperature (up to  $80^{\circ}\text{C}$ )
  - Atmosphere
  - Potential cycling (cf. drive cycles)

# ***Non-Pt ORR electrocatalyst materials and rationale***

- **Transition metal carbides and nitrides**
  - Contain surface vacancies and defects
  - Isoelectronic with platinum (e.g., WC), catalytically active in hydro-treating and dehydration reactions
  - Resistant to acidic corrosion and electronically conducting
- **Bi-metallic systems (e.g., base metal, noble metal)**
  - Surface segregation of minor noble metal component to form protective layer
  - Base metal component chosen to modify d-band center of precious metal making it more “Pt-like”
  - Alternative supports to modify electronic properties of small metal particles
- **Metal centers attached to electron-conducting polymer backbones**
  - Allows easy control of spacing between metal centers
  - Electron conductor in close proximity to reaction site can promote high catalyst utilization

# Carbides/nitrides have activity towards ORR that is far below that of Pt catalysts



## ORR activity:

Pt (0.93 V) >> TiN ~ WC (~ 0.28 V)

> GC ~ ZrC ~ TaC ~ NbN ~ TaN (~ 0.18 V)

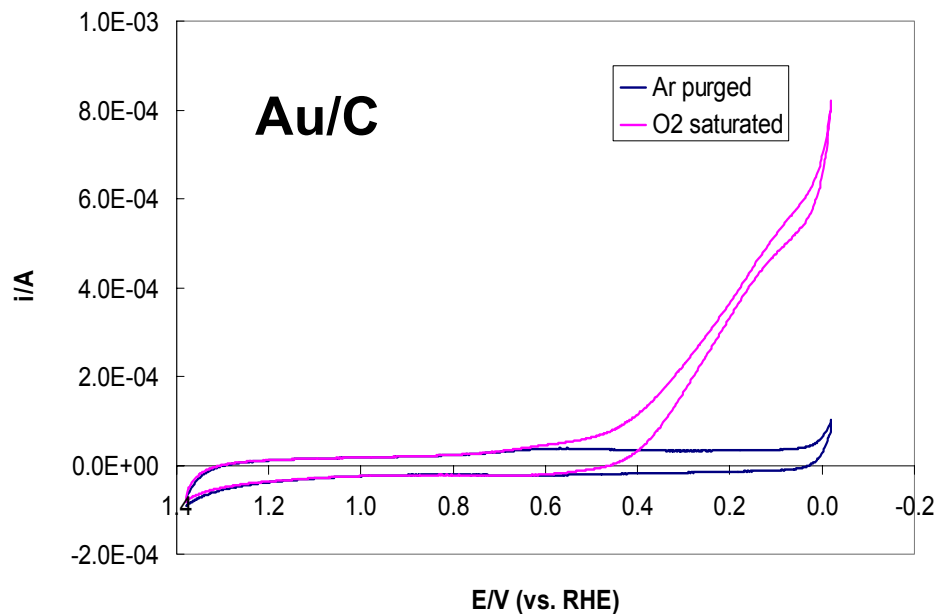
> CrN<sub>x</sub> ~ ZrN ~ NbC (~ 0.08 V) > TiC

# Au-based systems and preparation methods

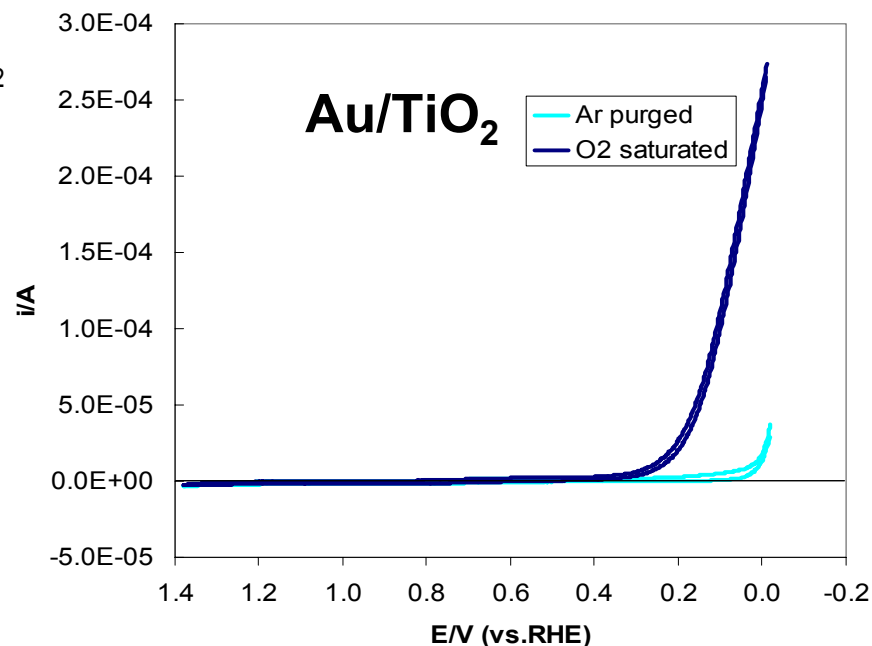
System	Metal content (wt%)	Preparation method	Heat treatment	Comments
Au/TiO <sub>2</sub>	5% Au	Precipitation deposition (PD) using Na <sub>2</sub> CO <sub>3</sub>	300°C/2h /air	tested
Au-Ni/TiO <sub>2</sub>	5% Au, 1.4% Ni	Co-PD using Na <sub>2</sub> CO <sub>3</sub>	500°C/5-10h/4% H <sub>2</sub> /He	tested
Au/C	5% Au	PD using Na <sub>2</sub> CO <sub>3</sub>	300°C/ 2h /air	tested
		PD using NH <sub>4</sub> OH and in situ reduction using NaBH <sub>4</sub>	120°C / 4h/ air	tested
	10 % Au	PD using Na <sub>2</sub> CO <sub>3</sub>	200, 250, 300, 350°C 2h/ air	tested
	15 % Au			
20 % Au				
Au-Ir/C	5% Au, 1% Ir	Co- PD using NaOH and in situ reduction using NaBH <sub>4</sub>	120°C / 4h/ air	tested
	5% Au, 5% Ir		400°C/2h / 3.8% H <sub>2</sub> /He	
	5% Au, 1% Ir	PD using NaOH and in situ reduction using NaBH <sub>4</sub> for Au, then PD for Ir	120°C / 4h/ air	tested
	5% Au, 5% Ir		400°C/2h / 3.8% H <sub>2</sub> /He	
Au-Ni/C	5% Au, 0.4% Ni	Sequential-PD using NaOH Ni first, then Au	600°C/2h / 3.8% H <sub>2</sub> /He	
	5% Au, 1.5% Ni			
	5% Au, 6% Ni			
Au-Co/C	5% Au, 0.4% Co	Sequential-PD using NaOH Co first, then Au	600°C/2h / 3.8% H <sub>2</sub> /He	
	5% Au, 1.5% Co			
	5% Au, 6% Co			
Au-Fe/C	5% Au, 0.4% Fe	Sequential-PD using NaOH Fe first, then Au	600°C/2h / 3.8% H <sub>2</sub> /He	
	5% Au, 1.5% Fe			
	5% Au, 6% Fe			

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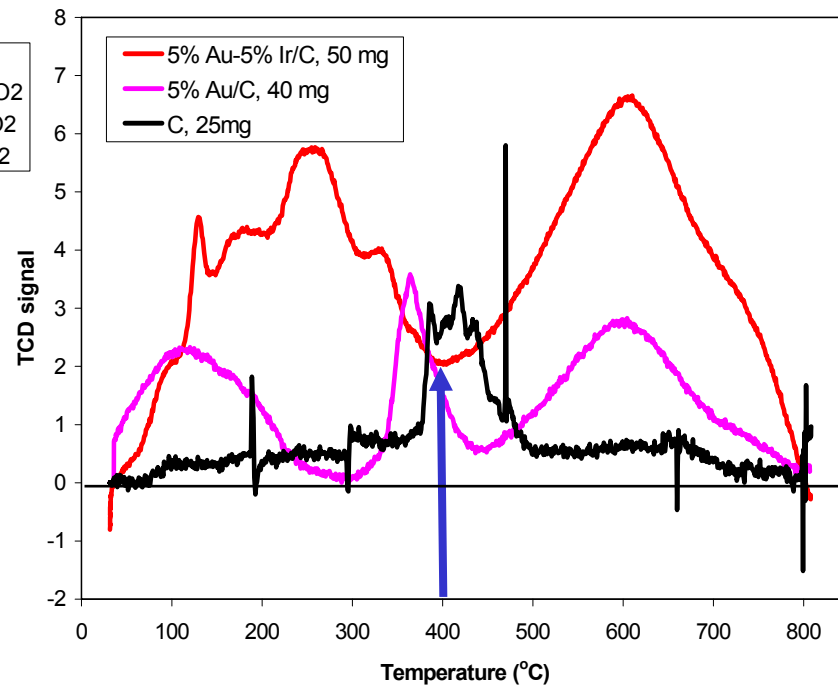
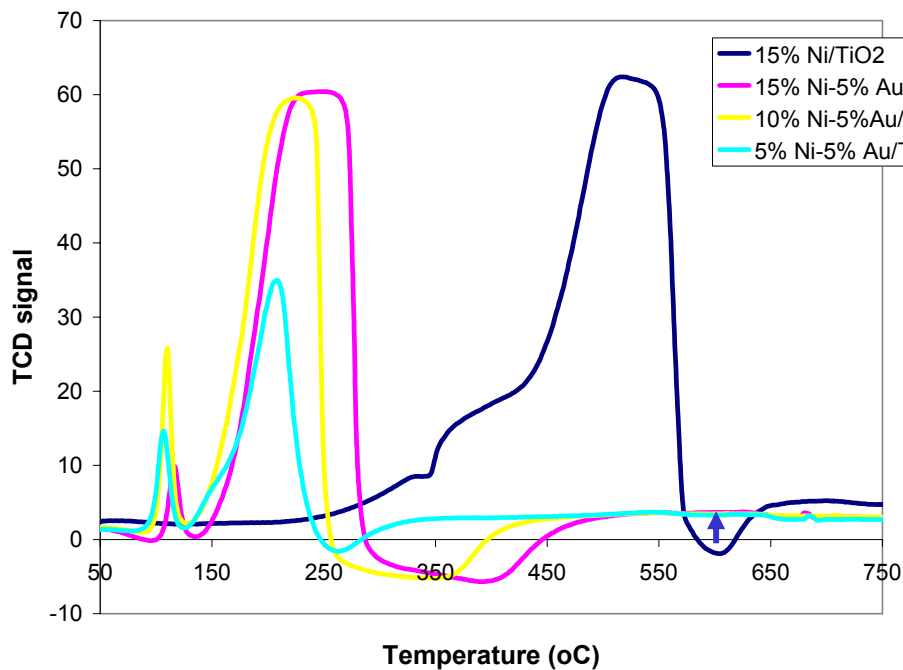
# 5 wt% Au/C showed higher ORR activity than 5 wt% Au/TiO<sub>2</sub>



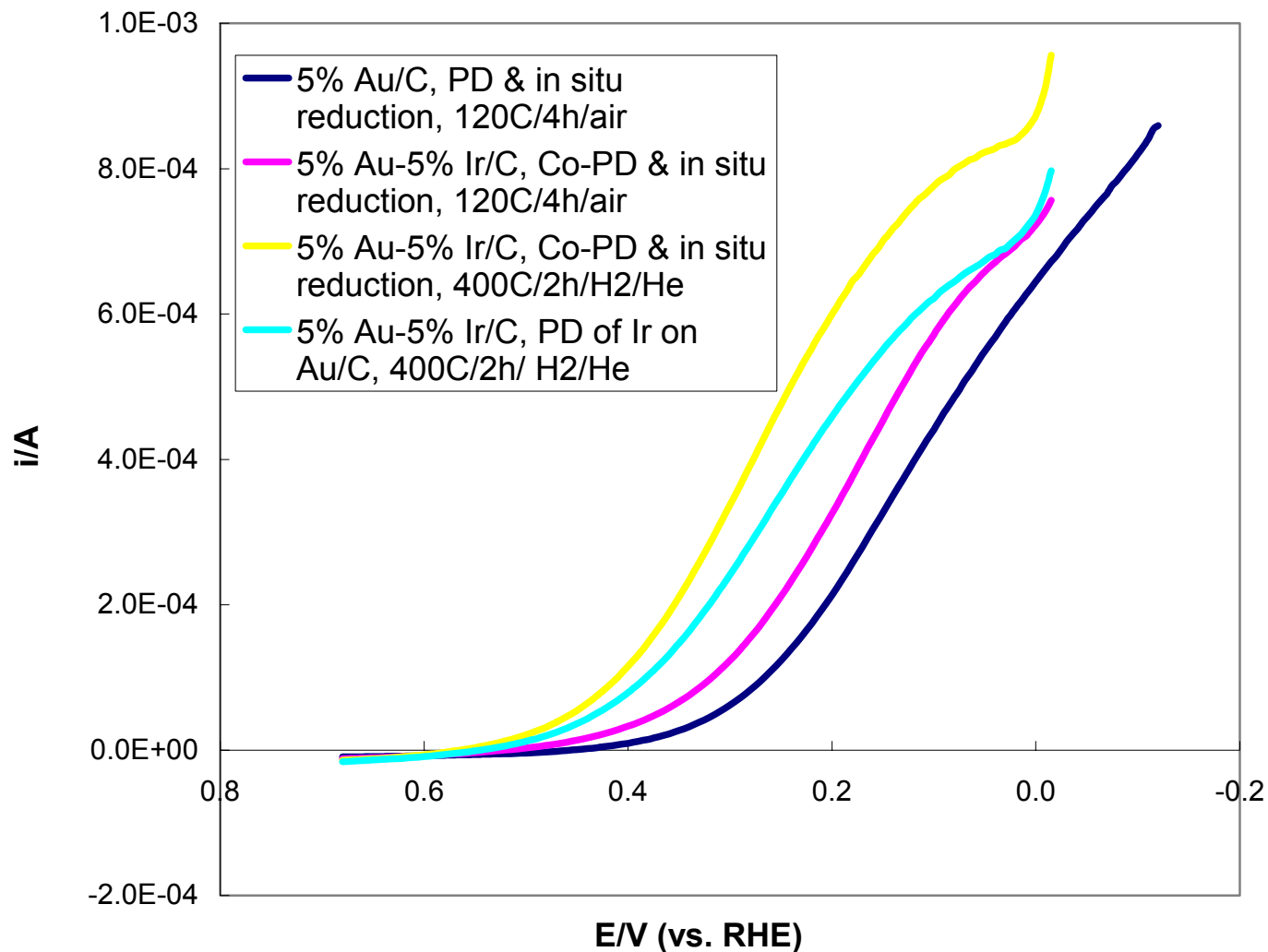
**1600 rpm**  
**10 mV/s**



# Temperature programmed reduction (TPR) used to determine heat-treatment conditions in reducing atmosphere for bimetallic systems



# Addition of 5% Ir to 5% Au/C enhanced ORR activity





# ***Progress vs. FY '05 Milestones***

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- **Synthesize and test two or more combinations of metal center-polymer electrocatalysts for stability and ORR activity (02/05)**
  - Synthesis of material is underway, testing of ORR to be completed shortly
- **Synthesize and test two or more bimetallic alloys identified by the modeling effort (06/05)**
  - Established reference performance of Au-based bimetallic systems, Au/C and Au/TiO<sub>2</sub>
    - *Tested Au-Ni/TiO<sub>2</sub>, Au-Ir/C*
    - *Preparation and testing of more supported Au-M is underway*
- **Fabricate and test an MEA using the new electrocatalyst (09/05)**

# ***Response to FY '04 Reviewers' Comments***

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- **“RDE measurements could be confounded by use of H<sub>2</sub>SO<sub>4</sub>.”**
  - Perchloric acid electrolyte is now used for the electrochemical evaluations.
- **“Too diverse approach. Focus limited resources on approach with highest probability of success.”**
  - This is a challenging field of research and the highest probability of success comes with a diverse approach. We are focusing on one approach at a time and continue on to the next approach after researching one area.
- **“Fabrication of MEAs – better to collaborate with someone with more experience”**
  - Will collaborate with LANL for MEA fabrication.

# ***Non-Pt Catalyst - Future work***

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- Prepare and test the ORR activity of select bi- or tri-metallic systems
  - Surface and bulk characterization to verify the desired catalyst composition/structure, particle size, and electronic properties (e.g., HRXRD, XPS, XANES, HRTEM)
  - Explore different synthesis methods and temperature treatments
- Continue synthesis and characterization of metal centers attached to polymer backbones
- Incorporate higher temperature ORR kinetic measurements when a high-temperature RDE becomes available
- Fabricate and test a membrane-electrode assembly using newly-developed cathode electrocatalyst

# ***Acknowledgments***

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- **Funding from the U.S. Department of Energy, Energy Efficiency, Renewable Energy: Hydrogen, Fuel Cells, and Infrastructure Technologies Program is gratefully acknowledged**
- **Nancy Garland, DOE Technology Development Manager**
- **H. You for AFM images, M. Ferrandon and J. Krebs for TPR analyses**
- **Y. Tsai and ANL's Analytical Chemistry Laboratory for ICP-MS analyses**

# *Hydrogen safety*

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- **When a reducing atmosphere is needed during catalyst preparation , “safe” hydrogen (<4% H<sub>2</sub> in He) is used. This hydrogen concentration is below the flammability limit of hydrogen in air**

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