

Non-Precious Metal Electrocatalysts

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

*This presentation does not contain any proprietary or
confidential information*

Argonne National Laboratory



A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago



Project objective

- **Develop a non-precious metal cathode electrocatalyst for polymer electrolyte fuel cells**
 - Promotes the direct four-electron transfer with high electrocatalytic activity (comparable to that of Pt)
 - *O₂ reduction reaction (ORR) in acidic media (e.g, in PEFC)*
 - *Two-electron transfer*
$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$$
 - *Four-electron transfer*
$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2 \text{H}_2\text{O}$$
 - *Four-electron process is desirable due to its higher efficiency and non-corrosive product*
 - Chemically compatible with the acidic polymer electrolyte
 - Low cost



Budget – New FY'04 Project

- FY'04 Funding: \$300 K

Technical Barriers and Targets

- **This project addresses DOE's Technical Barriers for Fuel Cell Components**
 - O: Stack Material and Manufacturing Cost
 - P: Component Durability
 - Q: Electrode Performance

- **DOE's Technical Targets:**
 - Low cost, <\$5/kW
 - Durability, >5,000 operating hours

Approaches

- **Complex oxides containing transition metals with multiple oxidation states (e.g., spinels and perovskites)**
 - Oxides of metals with multiple oxidation states (e.g., Co, Ni, Fe, Mn) contain oxygen vacancies or defects that may facilitate oxygen binding and dissociation
 - Host oxide is chosen to be stable in the acidic environment (e.g., titanium and chromium oxide)
- **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
- **Metal centers attached to an electron-conducting polymer backbone**
 - Allows easy control of spacing between metal centers
 - Electron conductor in close proximity to reaction site can promote high catalyst utilization



Safety

- **Internal safety reviews have been performed for all aspects of this project to address ESH issues**
 - Electrocatalyst and electrocatalyst/electrolyte ink synthesis
 - *All synthesis is performed in a hood to exhaust vapors of organic solvents and to prevent dust inhalation*
 - *Used electrocatalysts and inks are collected and disposed of through the laboratory's Waste Management Operations*
 - Electrocatalyst testing
 - *Purge gas is either inert Argon or Oxygen*
- **Safety reviews are updated and renewed annually**

Project timeline

FY'04				FY'05	
1	2	3	4	5	6

- 1: Establish and verify test procedure ✓
- 2: Identify one or more potential cathode electrocatalysts ✓
- 3: Determine kinetics and stability of potential electrocatalysts ✓
- 4: Begin first principles calculations, quantum chemical modeling to guide selection of potential electrocatalysts
- 5: Refine choice of electrocatalysts based on modeling and experimental work and evaluate these catalysts
- 6: Fabricate and evaluate a membrane-electrode assembly using newly-developed cathode electrocatalyst



A rotating ring-disk electrode apparatus is being used to evaluate ORR kinetics

- **Electrocatalyst preparation**

- Mix powdered electrocatalyst with 5 wt% solution of polymer electrolyte (Nafion[®]) to form an ink
- Vulcan XC72 carbon is added to ink if material is not an electron conductor
- Ink supported on a glassy carbon rotating disk electrode (RDE)

- **Electrochemical measurements (23°C)**

- RDE/thin film technique allows one to eliminate the effects of mass transfer
- Platinum ring electrode will be used to detect intermediates (e.g., H₂O₂)
- Background voltammograms in deaerated 0.5 M H₂SO₄ to determine material stability
- Steady-state voltammograms in O₂-saturated 0.5 M H₂SO₄ at various rotation rates to determine kinetics of ORR



The kinetics of the oxygen reduction reaction (ORR) were determined on Pt/C to verify the RDE technique

- **Electrocatalyst**

- 20 wt% Pt on Vulcan XC-72 (E-TEK)
- Mixed with 5 wt% of polymer electrolyte (Nafion[®]) to form an ink with Pt/C : Nafion = 60:40
- Ink supported on a glassy carbon rotating disk electrode (RDE)

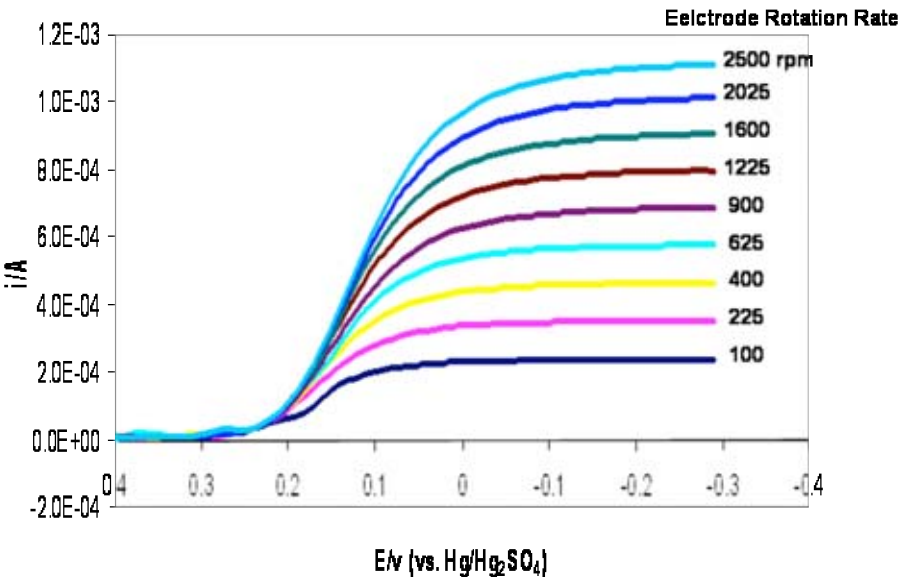
- **Electrochemical measurements (23°C)**

- In Ar-deaerated 0.5 M H₂SO₄
 - *Used to determine the electrochemically active surface area of Pt from hydrogen adsorption/desorption peaks in the cyclic voltammogram*
 - *Background voltammograms at various rotation rates*
- In O₂-saturated 0.5 M H₂SO₄
 - *Steady-state voltammograms of the ORR at various rotation rates*



Levich-Koutecky equation used to extract kinetic current from steady-state voltammograms

- Steady-state voltammograms of the ORR on Pt/C/Nafion® on a glassy carbon RDE



Equation	Electrode Type
Levich-Koutecky equation $\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{K\omega^{1/2}}$	Smooth electrode
Kinetic current derived from Levich-Koutecky equation $i_k = \frac{i_d \cdot i}{i_d - i}$	Smooth electrode
Extended Levich-Koutecky equation $\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_f} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{i_f} + \frac{1}{K\omega^{1/2}}$	Thin film electrode

- Three methods were used to determine the ORR kinetic current from the RDE experiments on Pt/C

Tafel plots were used to extract kinetic parameters for the ORR on Pt/C/Nafion®

- Tafel plot $\eta = \frac{RT}{\alpha nF} \ln i_o - \frac{RT}{\alpha nF} \ln i, \quad \eta = E - E_{eq}$

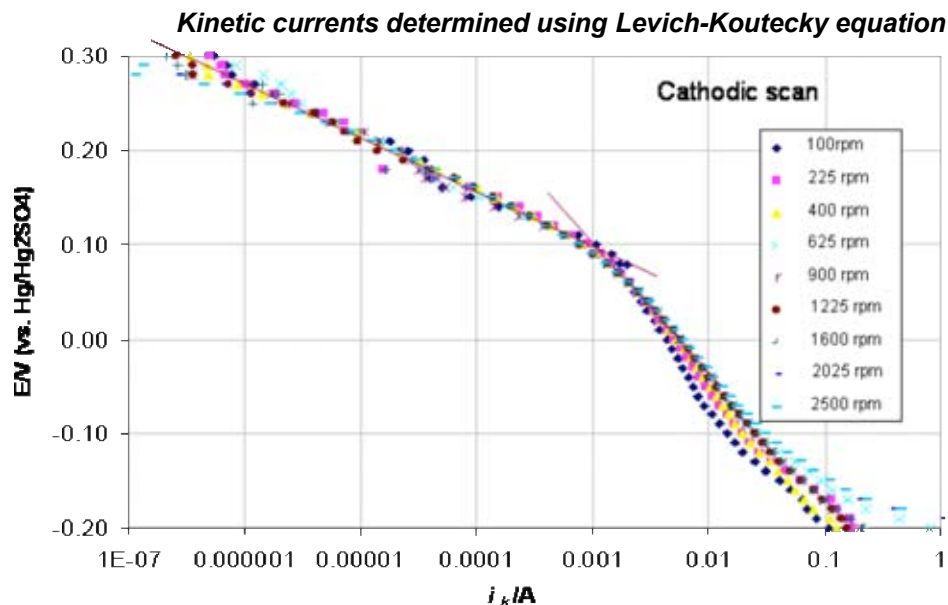
- Tafel-like plot $E = E_{eq} + \frac{RT}{\alpha nF} \ln i_o - \frac{RT}{\alpha nF} \ln i$

- A plot of E vs. $\ln i$ should give a straight line with

$$\text{Slope} = -\frac{RT}{\alpha nF}, \quad \text{Intercept} = E_{eq} + \frac{RT}{\alpha nF} \ln i_o$$

i_o : exchange current density, α : transfer coefficient

Tafel slopes for the ORR on Pt/C/Nafion[®] agree well with literature values



Tafel plot of ORR on Pt/C electrode has high and low slope regions

Method to obtain i_k		Negative scan direction		Positive scan direction	
		Tafel slope (mV/dec)		Tafel slope (mV/dec)	
$(i_d \cdot i)/(i_d - i)$	Average of all rotation rates	low i	high i	low i	high i
			-58	-127	-82
Levich-Koutecky		-77	-134	-86	-134
Extended Levich-Koutecky		-73	-130	-86	-136
Martin (1992) Microelectrode Pt	30°C, 5 atm	-65	-123		
	50°C, 1.1 atm	-71	-130		
Gojkovic (1998) Pt/C/Nafion mixture, 25°C		-60		-80	
Paulus (2001) Pt/C/Nafion film, 20°C				-63	-120



Exchange current density for the ORR on Pt/C/Nafion[®] agrees with literature values

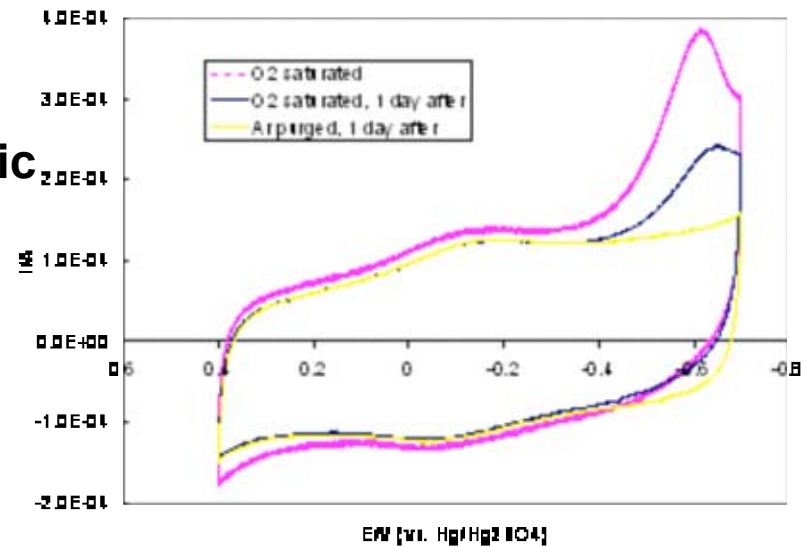
Temperature (°C)	i_o (A/cm ²)				Remarks
	Negative scan		Positive scan		
	low i	high i	low i	high i	
23	4.6×10^{-11}	9.3×10^{-8}	1.0×10^{-9}	9.4×10^{-8}	This work Averaged for 100 ~ 2500 rpm
30	1.7×10^{-10}	2.8×10^{-7}			Martin (1992) Pt microelectrode Po ₂ = 5 atm
40	7.3×10^{-10}	3.2×10^{-7}			
40	2.0×10^{-9}				Appleby (1993) 20 wt% Pt/C in a full cell
95	3.1×10^{-9}				



Progress on testing candidate materials

Oxides	Milling	Oxide to Carbon Ratio (wt%)			Composite to Nafion Ratio (vol%)
Co-Cr-O	Wet, 16h	20:80	50:50	80:20	50:50
Ni-Cr-O	"	20:80	50:50	80:20	62:38
Fe(III)-Ti-O	Dry, 16h		20:80		64:36
Fe(II)-Ti-O	Wet, 9h	50:50		80:20	40:60
Fe(III)-Ti-O	No milling		75:25		40:60
Ce-W-O	"	65:35		85:15	40:60
Ce-V-O	No milling		80:20		40:60

- **Voltammetry of Ni-Cr-O/Carbon/Nafion showed ORR activity, but instability in acidic environment**
- **Other complex oxides showed either no ORR activity or instability in acid**
- **Beginning testing of carbides and nitrides**



Future work – FY'04 and beyond

- Investigate methods for stabilizing complex transition metal oxides
- Test the ORR activity of select transition metal carbides and nitrides
- Begin synthesis of metal centers attached to polymer backbones
- Incorporate higher temperature ORR kinetic measurements when a high-temperature RDE becomes available
- Begin theoretical work (e.g., DFT calculations) to guide choice of candidate materials
- Fabricate and test a membrane-electrode assembly using newly-developed cathode electrocatalyst

Acknowledgments

- **Funding from the U.S. Department of Energy, Energy Efficiency, Renewable Energy: Hydrogen, Fuel Cells & Infrastructure Technologies Program is gratefully acknowledged**
- **Nancy Garland, DOE Technology Development Manager**