Low-Platinum Catalysts for Oxygen Reduction at PEMFC Cathodes

Project ID # FC16

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start date:
  - April 1, 2001
- Percent complete: subjective

Budget

- $200K/yr in FY04 and in FY05
- Additional internal funds from NRL/ONR in FY05 to explore poison tolerance of catalysts

Barriers Addressed

O: Stack materials cost (Electrode goal = $5/kW)

- Use lower cost materials to replace Pt

Q: Electrode performance (reduce high overpotentials at cathode)

P: Durability (5000 h)

- Pt-TaPO Catalysts are stable in acid
- Pt distributed in oxides will be less prone to ripening than metallic particles, so there is opportunity for longer lifetime
- Higher tolerance to SO_2 poisoning

Partners

Materials test agreements signed:

- GM Fuel Cell Activities
- E-TEK

University of Hawaii test facility

Objectives

lower Pt content & cost of PEMFCs

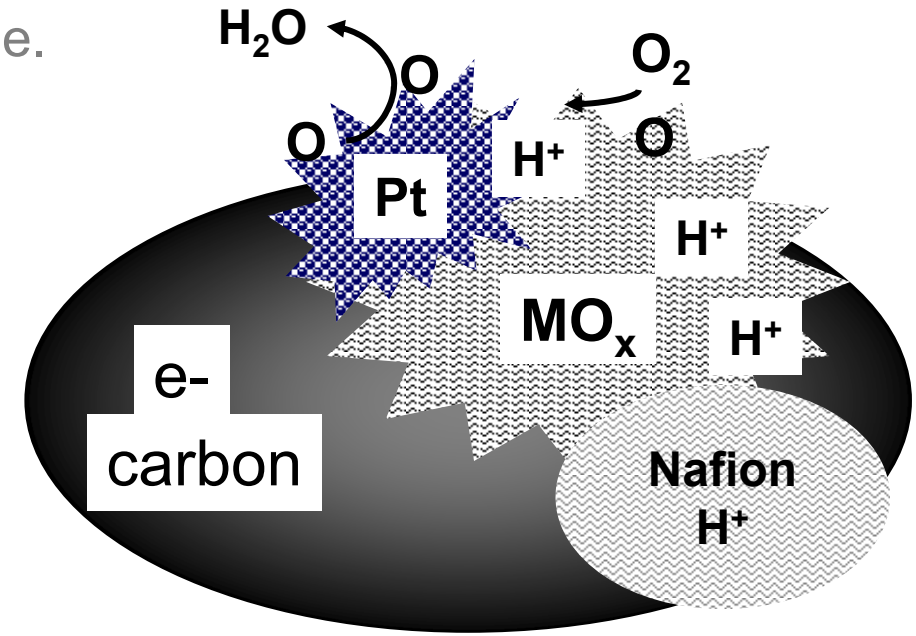
- Target DOE goals to achieve 0.2 g Pt/rated kW before 2010
- Focus on lowering Pt in fuel cell cathode
- Cathode has most Pt because
  - slow oxygen reduction kinetics
  - poor Pt stability and ripening over time.

Utilize oxide-based supports for Pt and other metals to *leverage:*

- Oxygen dissociation by oxides
- Metal-support interactions (MSI)
  - electronic effects
- Ionic mobility of oxide supports

2004-2005 Objectives:

- Rigorously characterize active and inactive catalysts
- Devise mechanism(s) to explain catalyst activity.



Pt supported on $MO_x \cdot H_2O$ supported on carbon

$$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O$$

90% of commercial heterogeneous catalysts are oxides or metals supported on oxides

Approach:
materials synthesis and characterization

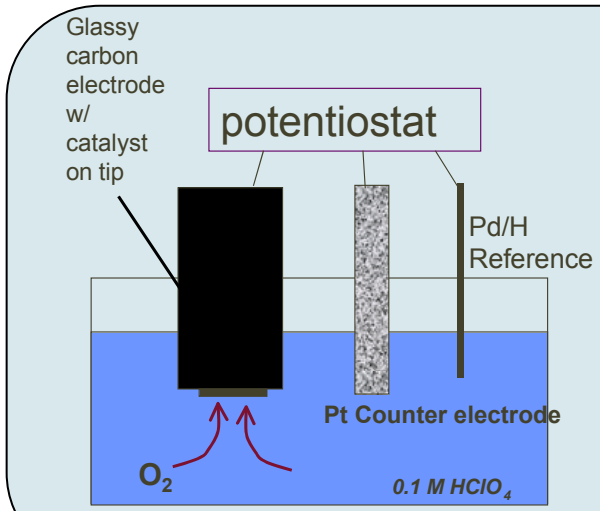
SYNTHESIS

Select catalyst supports with high:

- ***activity for oxygen***
  - ***Partial oxidation catalysts***
- ***acidity or basicity***
  - ***Use support to affect electronic state of Pt***
- ***stability in acid***
  - ***use Pourbaix diagrams as guide***

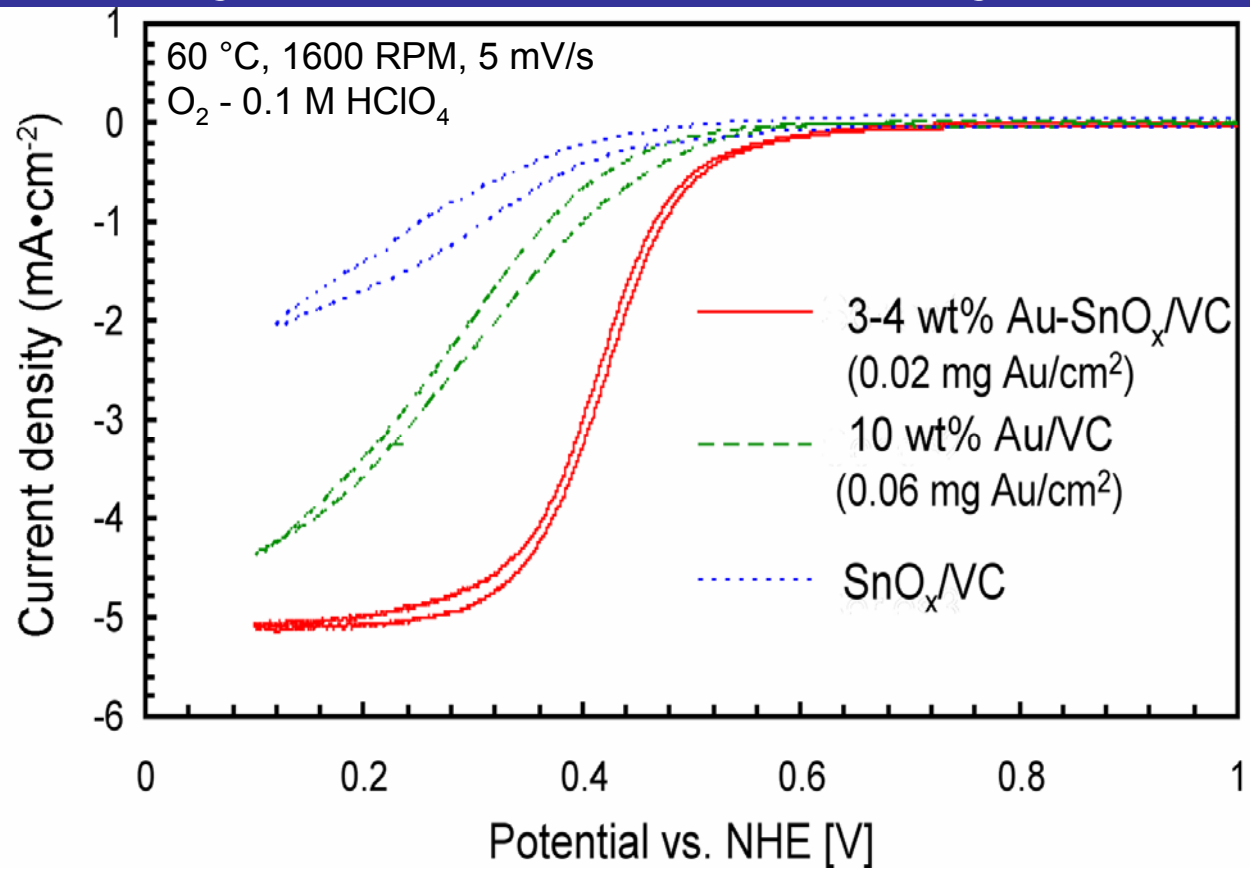
- ***Use solution synthetic techniques to make catalysts***
- ***Mix catalysts with Vulcan carbon (VC) to make inks and improve electronic conductivity***

- *Electrochemical evaluation*
  - *RDE - rotating disk electrodes*
  - *RRDE - rotating ring disk for completeness of ORR (conversion of O_2 to H_2O)*
- *Physical characterization*
  - *BET, SEM, FTIR, TGA/DSC*
- *Oxidation states*
  - *XPS and XANES (in-situ and ex-situ)*
- *Structural analysis*
  - *XRD with PDF analysis*
  - *EXAFS*



RDE method:
- Mix catalysts with Vulcan carbon & Nafion
- Disperse on RDE tip
- Evaluate in 0.1 M $HClO_4$ at 60 °C at 10 mV/s

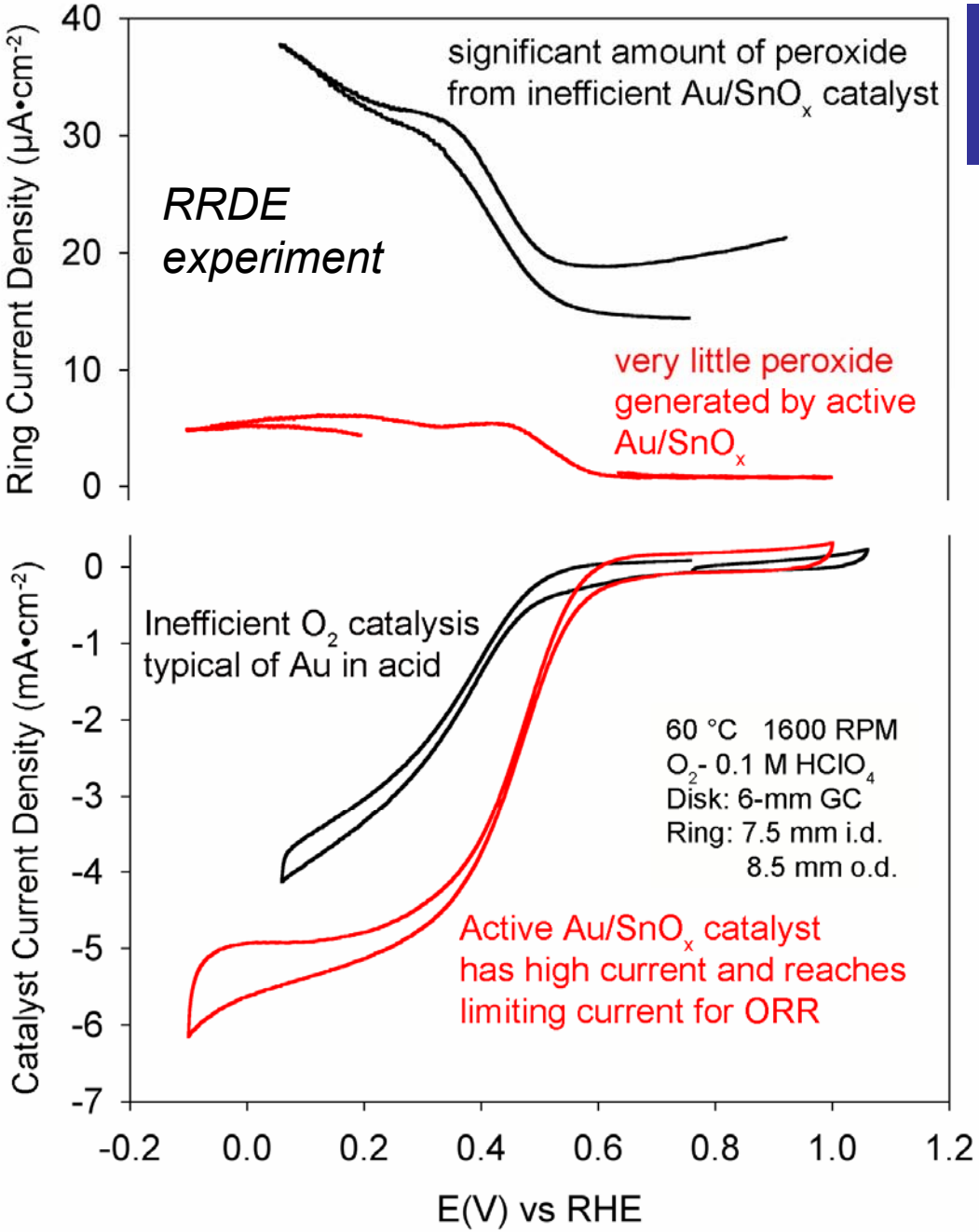
Result:
Au catalysis improved by SnO_x support



Metallic Au
on hydrous SnO_x

- Au is a poor ORR catalyst in acid
- OH^- critical to ORR on Au, so catalyst works better in base
  - Blizanac, Lucas, Gallagher, Arenz, Ross, Markovic, J. Phys. Chem. B, 108, 625 (2004)
- SnO_x is a well known catalyst support - poor activity for ORR alone
- Au/SnO_x together have higher activity than expected from individual components

Accomplishment:
Demonstrate 4-electron ORR on Au/SnO_x



ORR: $O_2 + 4e^- + 4H^+ = H_2O$
Peroxide: $O_2 + 2e^- + 2H^+ = H_2O_2$

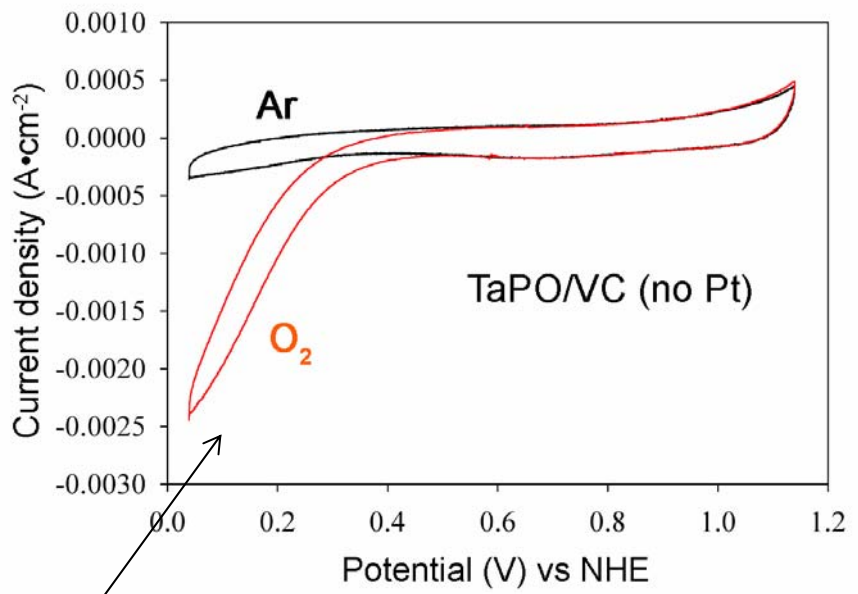
Together, Au and SnO_x produce little H_2O_2, so $4e^-$ reaction enabled

Mechanism:

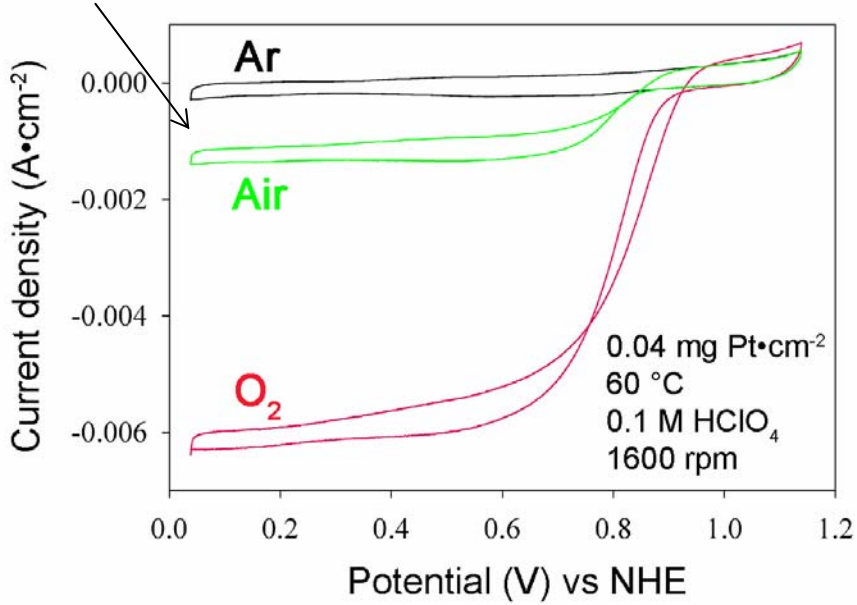
1. SnO_x polarizes electrons to Au (MSI or electronic effects)

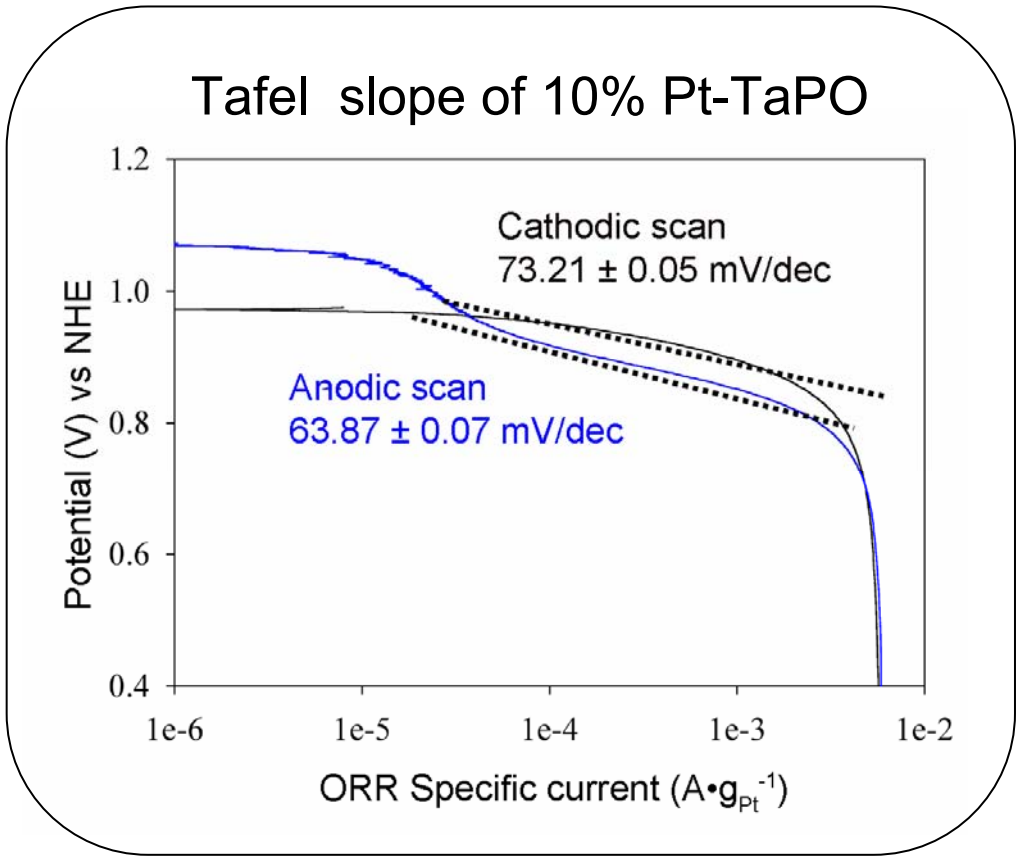
or 2. SnO_x converts O_2 to OH^- and OH^- is converted to H_2O by Au (bifunctional)

Result:
High ORR activity for Pt-TaPO



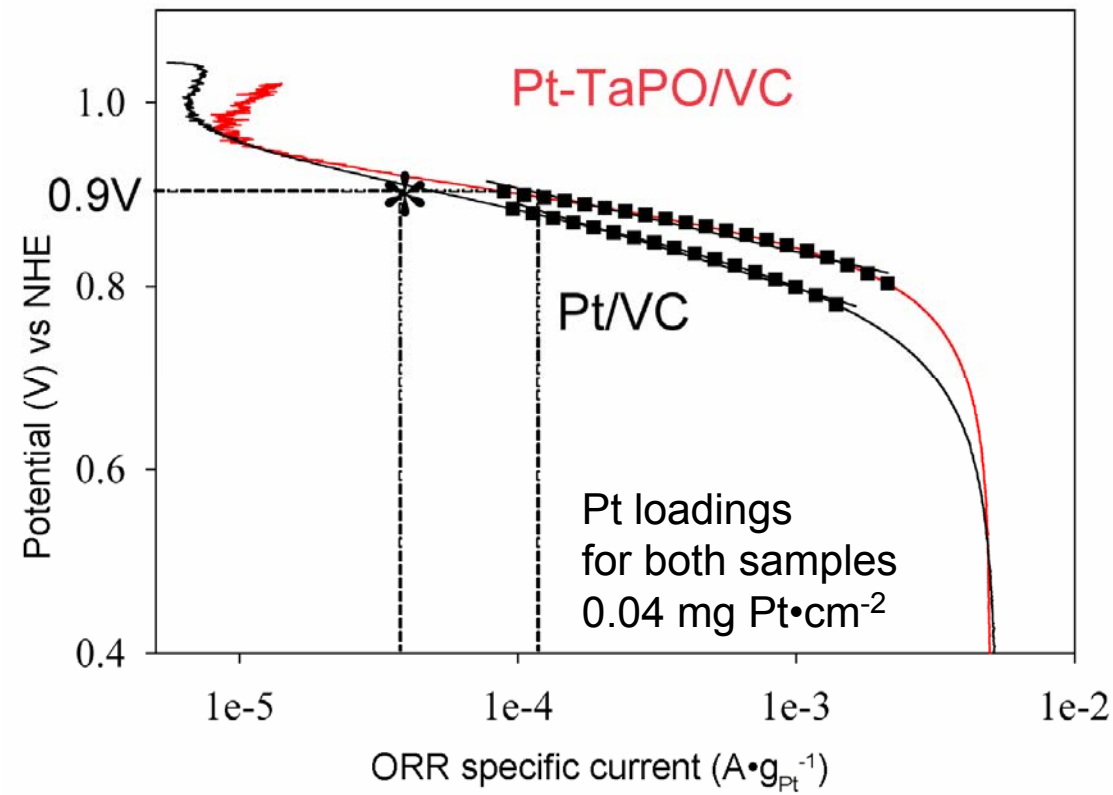
- *TaPO has little ORR activity*
- *Pt-TaPO high ORR activity*





Best recipe: TaPO synthesized in solution, washed, filtered & heated to 150 °C
TaPO then Pt impregnated, heated to 150 °C
Boiled in 0.1 M $HClO_4$
Mixed with VC for electronic conductivity

Accomplishment:
Pt activity of Pt-TaPO 6x higher than that of Pt/VC



Comparison of ORR activity at 0.9V

	Pt ($A \cdot mg_{Pt}^{-1}$)	Pt-TaPO ($A \cdot mg_{Pt}^{-1}$)
GM*	0.16	--
NRL	0.17	1.04

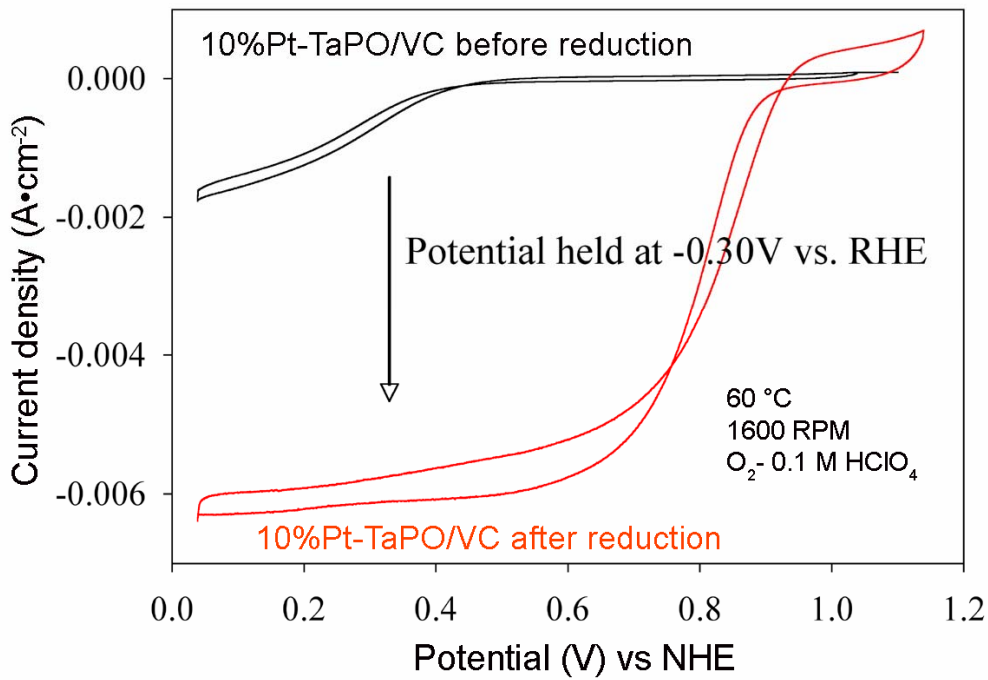
*Gasteiger, et al., Appl. Catal. B 56, 9 (2005)

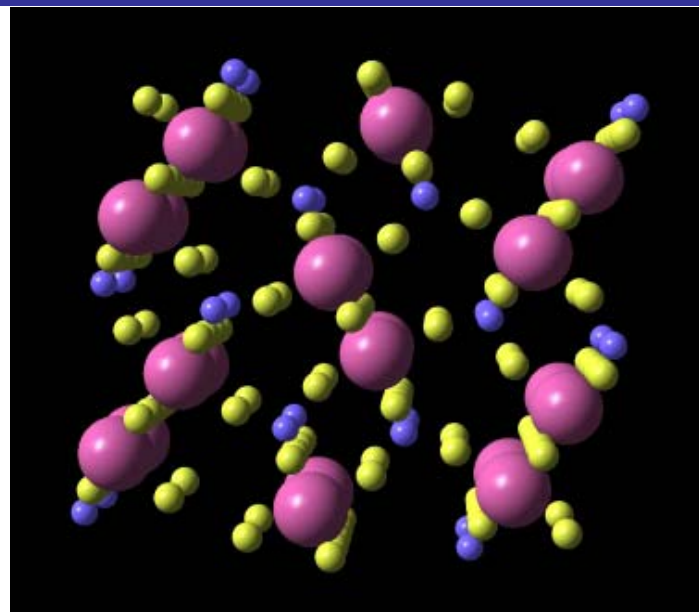
- NRL Pt-TaPO catalysts have ~6x higher activity per wt Pt than Pt/VC standards at 0.9 V
  - **6x less Pt = 6x less expensive**
- Improvement in activity increases with decreasing potential, but converges at high potentials

--Actual activities must be proven in a fuel cell

Attributes of Pt-TaPO catalysts

- Pt is metallic in active TaPO catalysts
  - shown with XPS
  - electrochemistry (Pt features under hydrogen)
- Pt-TaPO catalysts and inks becomes less active when stored in air due to formation of Pt^{4+}
  - Shown with XPS
  - Activity regained by holding catalysts momentarily in hydrogen and/or low potentials





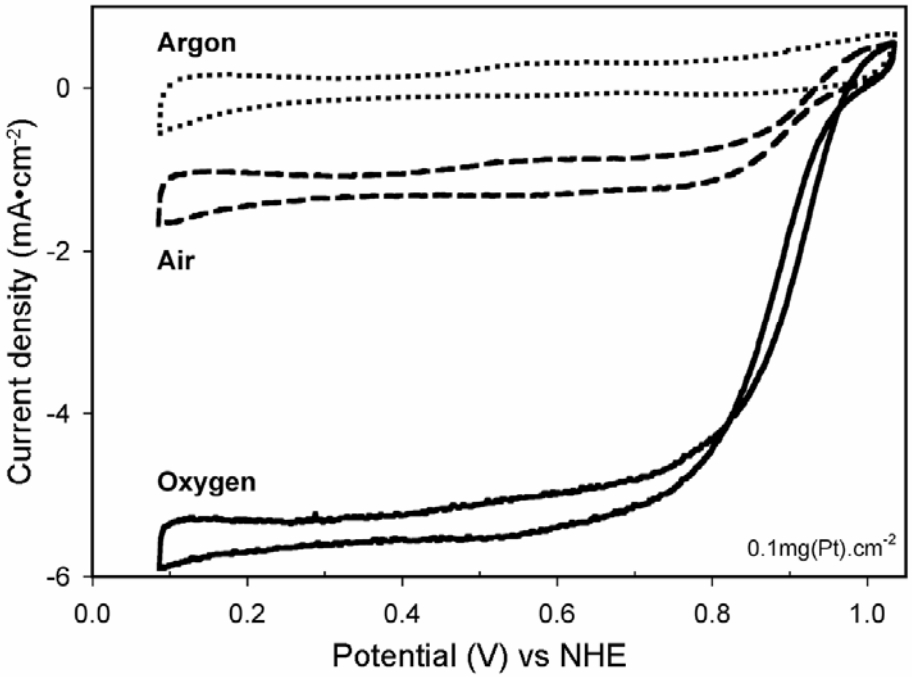
Most active TaPO substrates appear to be densely packed, disordered hydrous TaPO, with Ta-deficient structure and 0.2 nm pores (Pair density function analysis of XRD and confirmed with EXAFS)

•NOT KNOWN whether catalysts become more stable after being "activated" in MEAs

•Electrochemical formation of hydroperoxide groups possible & may improve stability

Prior Result: high ORR on Pt-FePO

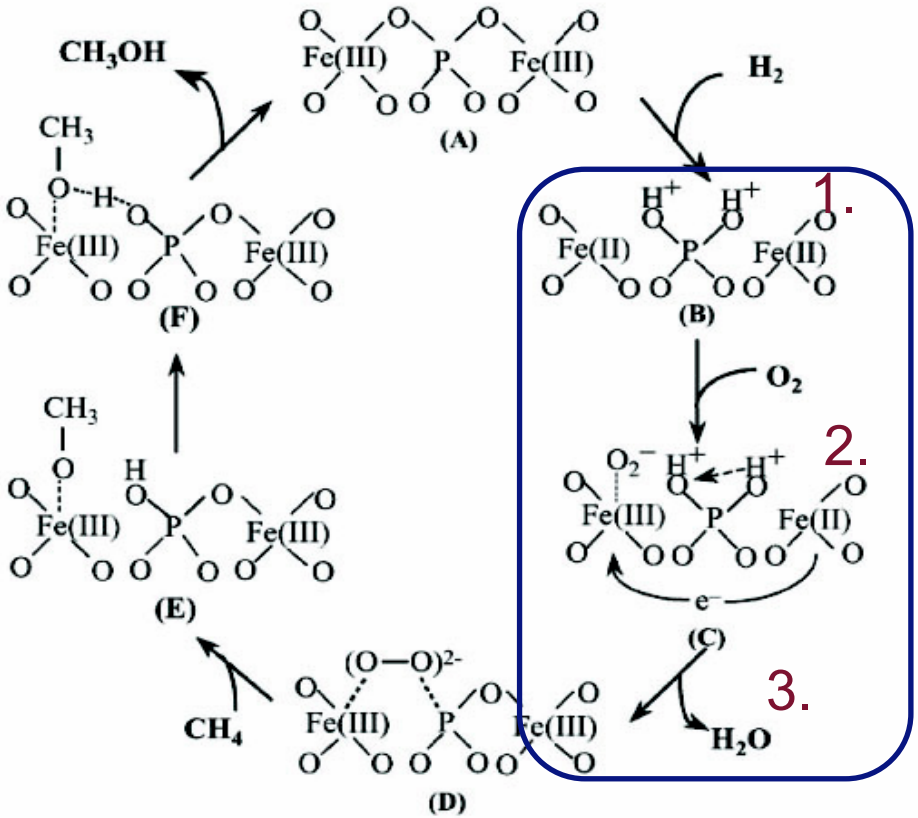
9% Pt-FePO



- No Pt metal - only Pt^{2+} and Pt^{4+}
- High ORR activity of Pt-FePO attributed to bifunctional mechanism of Pt ions with FePO support

Bouwman, et al, *J. Electrochem. Soc.*, 151 (2004) A1989-A1998.

1. Protons from electrolyte
2. Oxygen dissociation from atm
3. Release of water

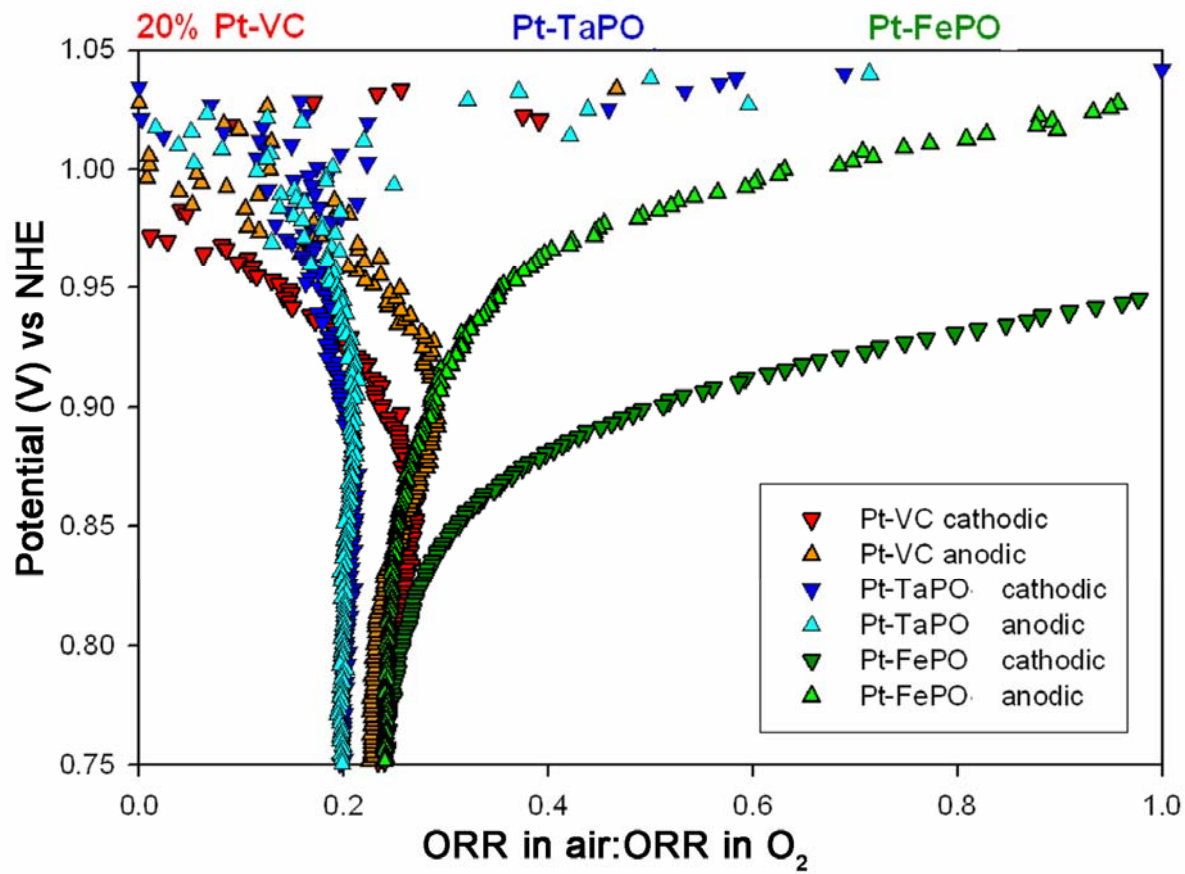


Methane partial oxidation to methanol K. Otsuka. Y. Wang Applied Catalysis A: General 222, 145-161 (2001).

Proposed mechanism at 350 °C

Result:
Oxygen activity of catalysts gives clues about mechanism

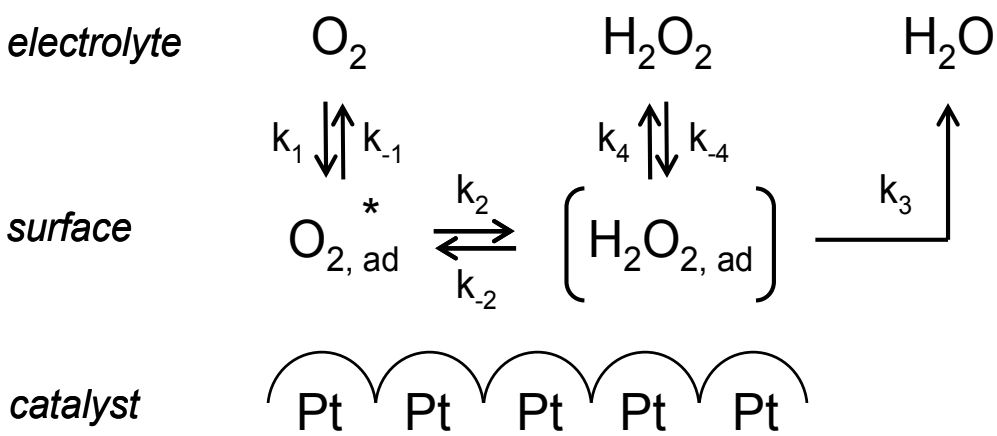
- Catalyst activities converge at 0.21 at lower potentials/higher currents
- At high potentials, Pt-FePO activity identical in air and oxygen
  - ratio of activity in air to O_2 goes to 1 at high V
- Pt/VC standard and Pt-TaPO proportional to amounts of O_2
  - Pt/VC activity disproportionately low in air at high V



Ratio of ORR activity in air to that in O_2

–cathodic and anodic sweeps with RDE

Mechanisms for Pt-MPO activity

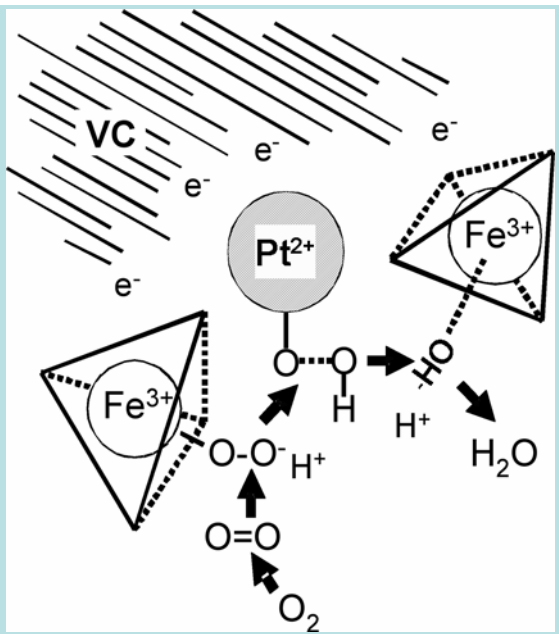


MSI/Electronic effects Pt-TaPO -
TaPO electron withdrawing
- ↑ binding energy of Pt d orbitals
- ↓Pt DOS and Fermi level
- Shift 6s,p orbitals above Fermi Level
- Shift 5d orbitals below Fermi Level

Additional edge effects between Pt particles and oxide?

Pt METAL

- Oxygen dissociates on Pt - slow step
- Progresses to H_2O_2 and water



Bifunctional mechanism with FePO and Pt ions

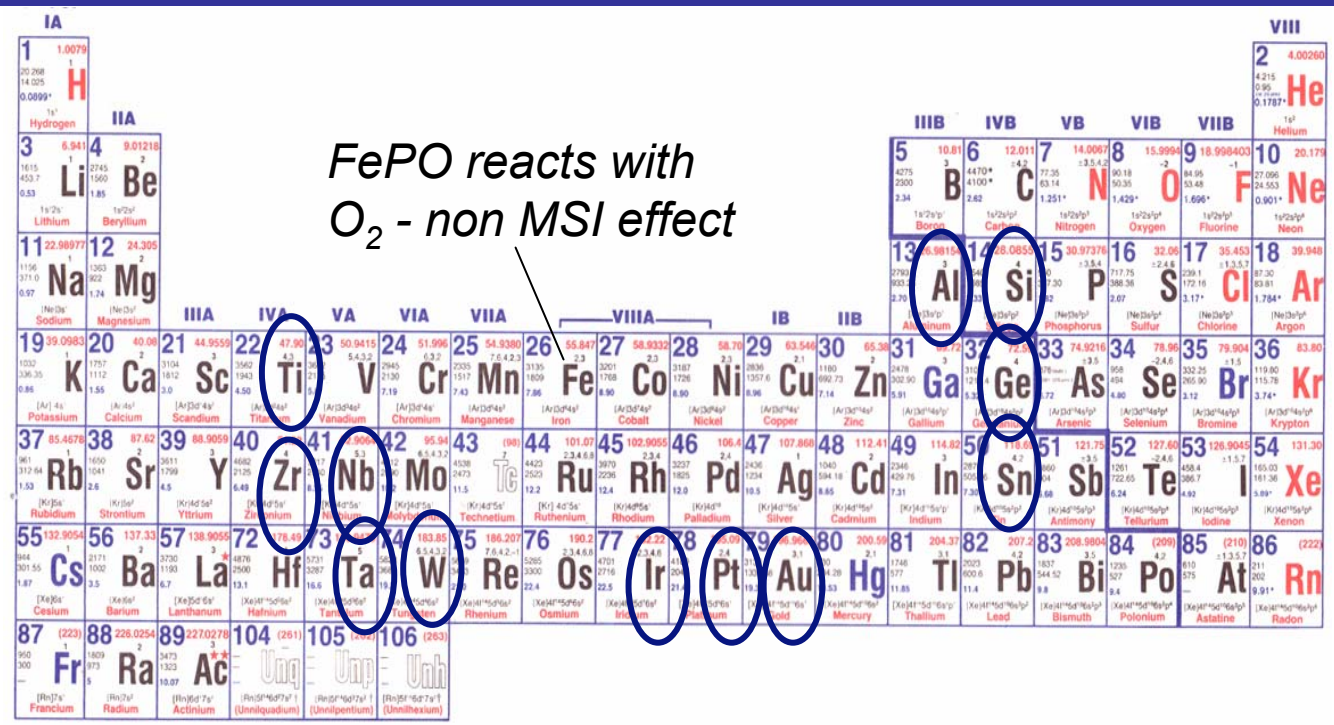
- Oxygen reacts with surface M-O and protons to form M-O-OH
- $^{-}$OH dissociates to water on Pt^{2+}
- M-O regenerated

"slow step" by oxide

Properties of active catalysts

	Pt-FePO	Pt-TaPO	Au-SnO_x
Electrochemical attributes	High ORR (3x std) despite no Pt metal No CO adsorption Tolerant to SO_2 poison Electrochemically activated	High ORR (6x std) Oxide may eliminate Pt particle ripening No CO adsorption Tolerant to SO_2 poison Electrochemically activated	Rare example of 4 e^- ORR on Au in acid Electrochemically activated
State of Pt/Au	Pt ions in micropores	~20 nm metal particles on surface/partially oxidized	~15 nm metal particles on surface/partially oxidized
Support properties	0.7 nm micropores Hydrous Fe^{2+}/Fe^{3+} Tetrahedral Fe Tetrahedral P	0.2 nm micropores Hydrous Ta^{5+} Octahedral Ta Tetrahedral P Ta-deficient structure	0.4 nm micropores Hydrous Sn^{2+}/Sn^{4+} Octahedral Sn Disordered $Sn_6O_4(OH)_4$
Likely mechanism	Bifunctional with O_2 dissociation on FePO (FePOOH)	MSI/electronic	Bifunctional with SnOOH or MSI
Issues	Long-term acid stability; unviable with Nafion	"Deactivates" in air over time; not clear if catalyst will remain stable in MEA	Potential too low to be viable for fuel cell Long-term acid stability

Leveraging MSI for Catalysis



Materials selection limited to those stable in low pH at high potentials (circled)
No rare earths are acid stable

Electron withdrawing/acidic ← → **Electron donating/basic**

Pt activity improved when alloying with or supported on an electron withdrawing compound

Phosphates may improve "acidity"

Au activity improved by making electron donating compounds

Few choices of electron donating d-electron compounds

Sn has borderline acid stability

Responses to Previous Year Reviewers' Comments

- Too little mechanistic data
  - We directed a significant amount of FY04 effort to determining mechanisms.
    - bi-functional mechanism for Pt- FePO
    - MSI/electronic effects in Pt-TaPO
- Role of MO_X not clear
  - Au/SnO_x example clearly shows catalysis benefit of MO_X support. Role of FePO and TaPO discussed.
- Demonstrations with companies and in MEAs
  - We solved the practical obstacles that we face working with companies, i.e., we now can supply several grams of well formulated inks having stable compounds. Now ready to work openly with partners, with recognition that NRL formulations may need modification to work with proprietary MEA processes.

Future Work

- Catalyst improvements to 10x less Pt (DOE goal)
  - Increase catalysts surface area/decrease Pt size
  - New oxide catalysts (non Pt catalysts??)
  - Improve inks
- Continued work on mechanisms
  - Electrochemistry
  - In situ XAS (oxidation states, d-band structure)
  - Other in situ experiments: FTIR, NMR, PDF of XRD
- Evaluate catalysts in MEAs at NRL
  - Get truer evaluation of durability
  - Pt-TaPO long-term activity under O_2
- ***Work with industry***
  - Actively pursue partners for larger-scale demonstration of Pt-TaPO catalysts
    - Amount of effort depends on compatibility of inks with MEA methods

Publications and Presentations

Articles in Refereed Journals

1. P. J. Bouwman, W. Dmowski, J. Stanley, G. B. Cotten, K. E. Swider-Lyons, "Platinum iron phosphates for oxygen reduction in PEMFCs" *J. Electrochem. Soc.*, 151 (2004) A1989-A1998.

Conference Proceedings Articles (contact karen.lyons@nrl.navy.mi for copies of work in press):

1. N.P. Ugarte, K.E. Swider-Lyons, "Low-Platinum Tin-Oxide Electrocatalysts for PEM Fuel Cell Cathodes," in *Proton Conducting Fuel Cells III*, Electrochemical Society Proceedings Series, ed. M. Murthy, PV 2002-31.
2. P. J. Bouwman, W. Dmowski, K.E. Swider-Lyons, "Platinum Iron Phosphate Catalyst for Oxygen Reduction" in *Advanced Materials for Fuel Cells and Batteries*, The Electrochemical Society, Pennington, NJ, submitted 2003.
3. W. Dmowski, T. Egami, P. J. Bouwman, K.E. Swider-Lyons, "Atomic Structure of Disordered Pt-Ru Black and Platinum Iron Phosphate Electrocatalysts" in *Advanced Materials for Fuel Cells and Batteries*, The Electrochemical Society, Pennington, NJ, submitted 2003.
4. W. S. Baker, P. J. Bouwman, M. E. Teliska, W. Dmowski, K. E. Swider-Lyons, "Platinum and non-platinum-metal tin oxide supported catalysts for PEMFC cathodes," *Proton Conducting Membrane Fuel Cells IV*, 2004, Editors: J.W. Van Zee, et al, Electrochemical Society Proceedings, submitted 2004.
5. P. J. Bouwman, M. E. Teliska, K. Swider Lyons, "Increased poisoning tolerance of Pt-FePO oxygen reduction catalysts," in *Proton Conducting Membrane Fuel Cells IV*, 2004, Editors: J.W. Van Zee, et al., Electrochemical Society Proceedings, submitted 2004.

Patent disclosures:

1. K. S. Lyons, P. J. Bouwman, "Hydrous phosphate catalysts with low platinum," Navy Case No. 84,631, 26 March 2003. Filed Sept 03.
2. K. S. Lyons, N. P. Ugarte, "Platinum-impregnated hydrous tin oxide catalysts," Navy Case No. 84,632, 26 March 2003. Filed Oct 03.

Recent Papers presented at Professional Society Meetings

1. P. J. Bouwman, W. Dmowski, K. E. Swider-Lyons, "Hydrous Pt-FePOx catalysts for oxygen reduction in proton exchange membrane fuel cells," Symposium on Advanced Materials for Fuel Cells and Batteries, 204th Meeting of The Electrochemical Society, 12-17 Oct 2003, Orlando, FL.
2. K. Swider-Lyons, P. J. Bouwman, W. Dmowski, "The use of nanocomposite materials to lower the platinum content of fuel cells and potential environmental payoffs," Symposium on Nanotechnology and the Environment: Nanotech-enabled Green Energy, 227th ACS National Meeting, 28 Mar - 1 Apr 2004, Anaheim CA.
3. W. S. Baker, P. J. Bouwman, W. Dmowski, K. E. Swider-Lyons, "Platinum and Non-Platinum-Metal Tin Oxide Supported Catalysts for PEMFC Cathodes," 206th Meeting of the Electrochemical Society, 3-8 October 2004, Honolulu, HI.
4. P. J. Bouwman, M. Teliska, W. Dmowski, K. E. Swider Lyons, "Increased Poisoning Tolerance of Pt-MO_x Oxygen-Reduction Catalysts," 206th Meeting of the Electrochemical Society, 3-8 October 2004, Honolulu, HI
5. K. E. Swider Lyons, P. J. Bouwman, Wendy S. Baker, Margaret E. Teliska, Wojtek Dmowski "Oxide- and Phosphate-Based Catalysts for Oxygen Reduction at PEMFC Cathodes," Symposium on Materials Aspects of Fuel Cells, Materials Research Society Meeting, 29 Nov – 3 Dec 2004, Boston, MA.
6. W. Dmowski, P. J. Bouwman, K. E. Swider Lyons, "Atomic structure of platinum-iron phosphate electrocatalysts," Symposium on Materials Aspects of Fuel Cells, Materials Research Society Meeting, 29 Nov – 3 Dec 2004, Boston, MA.

Hydrogen Safety

- **Hydrogen safety is not a critical issue for this program because most catalyst testing done under oxygen.**
- Hydrogen is only used occasionally in half cell measurements, when we test MEAs, and operate fuel cells for synchrotron research.
- The amount of hydrogen used in the MEA single-cell tests are low and we comply with Navy Laboratory safety regulations.
- For synchrotron tests at Brookhaven National Laboratory, we employ an approved electrolyzer to make hydrogen on demand, so that no hydrogen is stored.