



# Low Platinum Catalysts for Oxygen Reduction at PEMFC Cathodes FC-15

Karen Swider Lyons

Olga Baturina

Yannick Garsany

Naval Research Laboratory

Washington DC

2006 DOE Hydrogen Program Annual Review

17 May 2006

# Overview



## Timeline

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

## Budget

- \$200K/yr in FY05
- Cost share N/A

## 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

## Collaborators

- GM Fuel Cell Activities - RDE testing of NRL catalysts in 2005
- E-TEK - NRL catalysts sent in 2005
- University of Hawaii test facility - MEA with NRL catalysts shipped in 2005
- Ballard - NDA signed/discussions for collaborations in 2006

# Objectives



*Improve ORR to 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 - oxygen reduction reaction (ORR)
- Cathode has most Pt because
  - slow oxygen reduction kinetics
  - poor Pt stability and ripening over time.

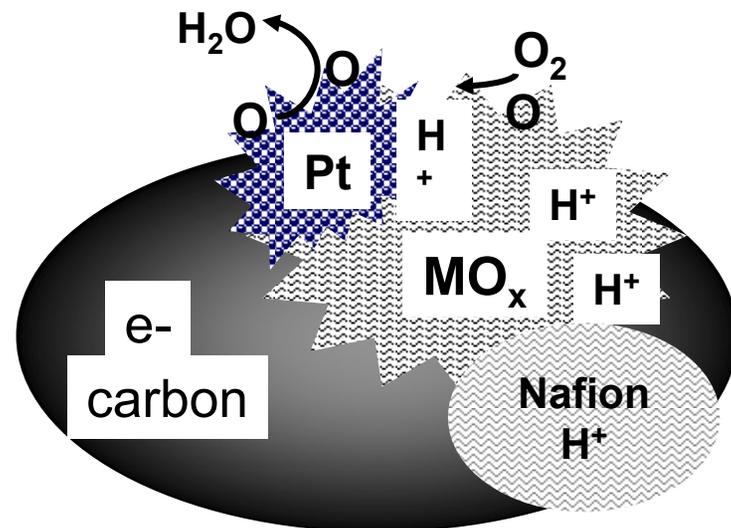
***90% of commercial heterogeneous catalysts are oxides or metals supported on oxides***

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

- Metal-support interactions (MSI)
  - electronic effects
- Proton mobility of oxide supports

**2005-2006 Objectives:**

- Devise mechanism(s) to explain catalyst activity.
- Improved synthesis & reproducible materials



*Pt supported on MO<sub>x</sub>·H<sub>2</sub>O supported on carbon*



# Approach: materials synthesis and characterization



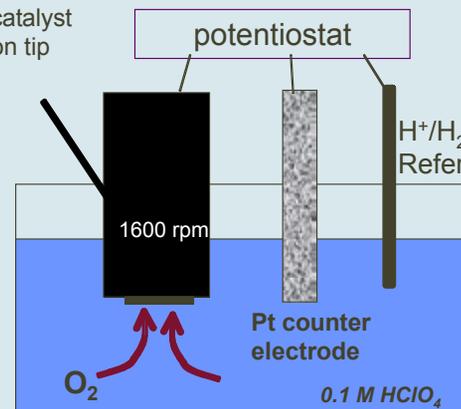
## SYNTHESIS

### Select catalyst supports with:

- Use acid or basic properties to affect electronic state of metal
- Acidic phosphates for Pt
- Basic oxides for Au
- **Stability in acid PEM environment**
  - 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 or impregnate phosphate directly onto VC**

- **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, TGA/DSC, EXAFS
- **Oxidation states**
  - XPS (ex-situ) & echem (HAD)

Glassy carbon rotating electrode w/ catalyst on tip



RDE method:

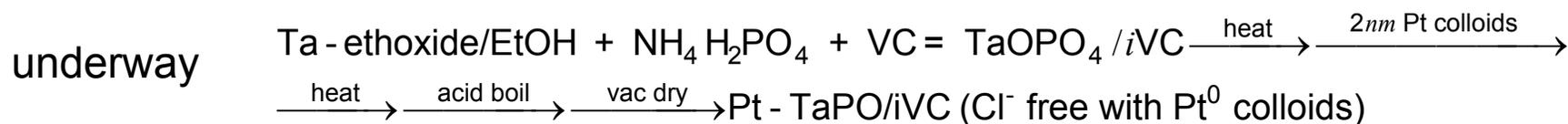
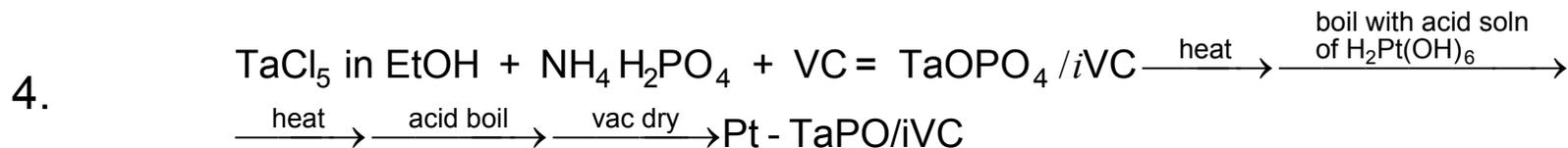
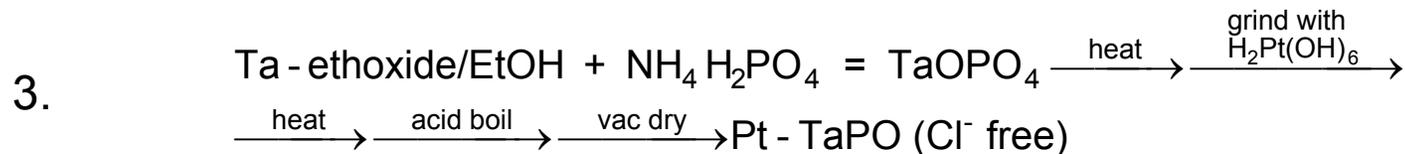
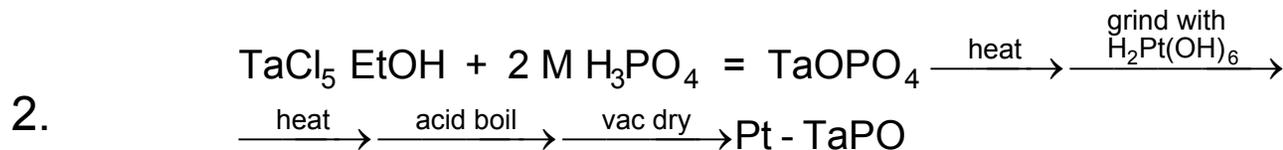
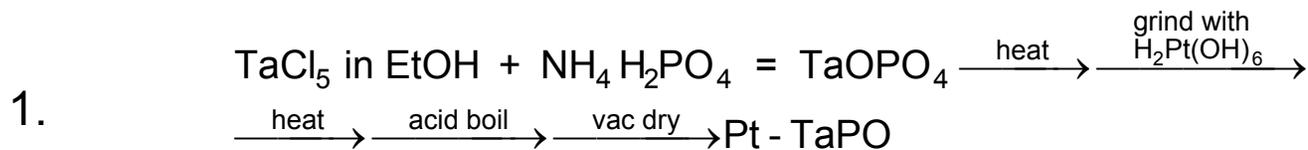
- Mix catalysts with Vulcan carbon & Nafion
- Disperse on RDE tip
- Evaluate in 0.1 M  $HClO_4$  at 25 & 60 °C

# 2006 Accomplishments



- Reproducibility issues resolved
  - Long-term air stability of Pt- tantalum phosphates
  - RDE method
  - Inking/film method
  - Synthesis
    - All issues for working effectively with industry
- Better correlation between synthesis vs. electrochemical performance vs. materials characterization
- Continued work on mechanisms
  - Conductivity of Tantalum Phosphates
  - Additional work on supported gold catalysts for oxygen reduction

# Synthesis routes for TaPO

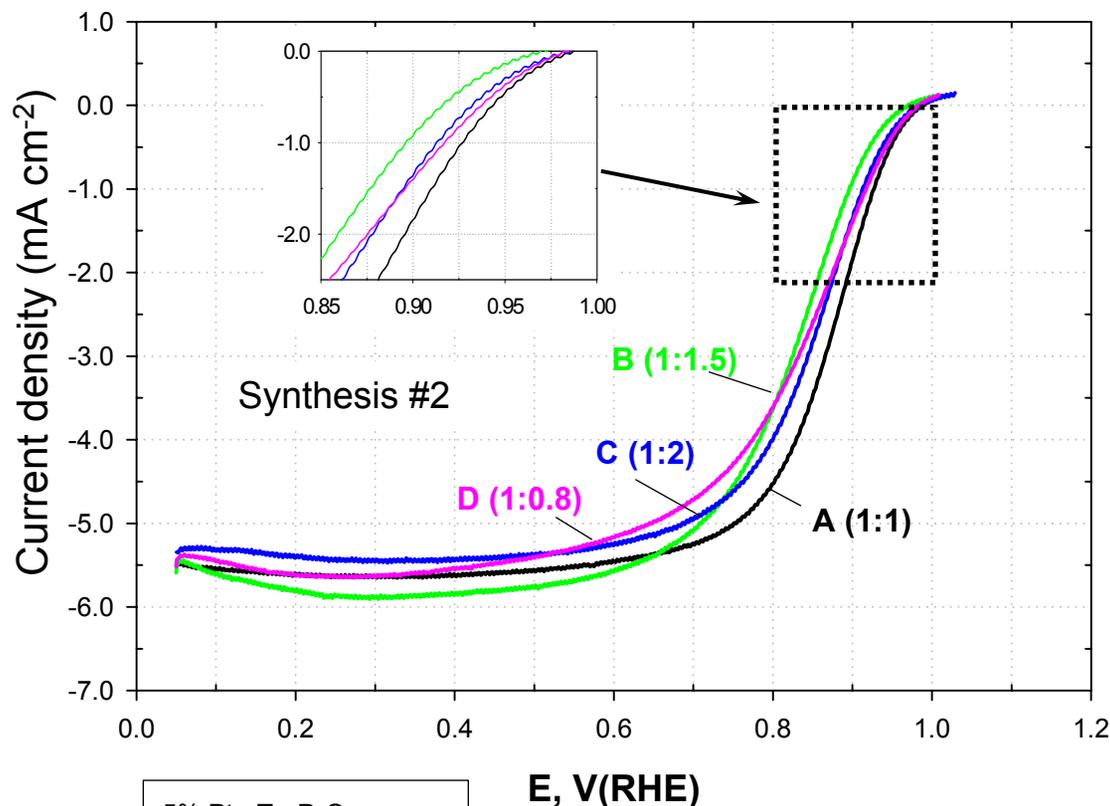


# Activity of catalysts varies with Ta:P ratio in Pt-Tantalum phosphates



ORR : 1600 rpm, 20 mV/s, 25°C; 11  $\mu\text{g}_{\text{Pt}} \cdot \text{cm}^{-2}$ .

Anodic scans.



5% Pt -  $\text{Ta}_1\text{P}_1\text{O}_x$   
5% Pt -  $\text{Ta}_1\text{P}_{1.5}\text{O}_x$   
5% Pt -  $\text{Ta}_1\text{P}_2\text{O}_x$   
5% Pt -  $\text{Ta}_1\text{P}_{0.8}\text{O}_x$

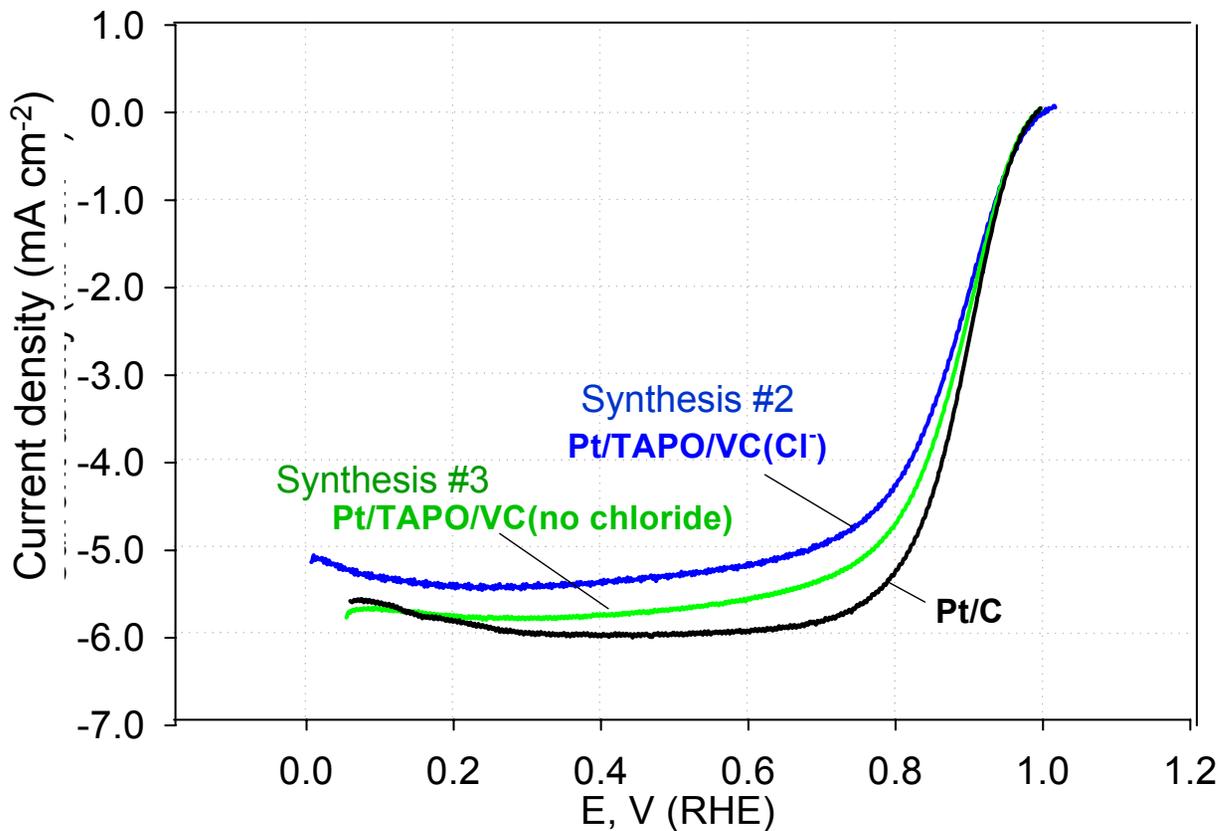
Activity of catalysts influenced by Ta:P ratio in TaPO (tantalum phosphate)

Highest activity for Ta:P 1:1

# Direct comparison of ORR of Pt-TaPO vs Pt/VC



ORR on Pt/TaPO/VC vs. 20% Pt/C (E-TEK): 1600 rpm, 20 mV/s, 25°C  
Pt/TaPO/VC - 11  $\mu\text{g}_{\text{Pt}}/\text{cm}^2$ , Pt/VC - 20  $\mu\text{g}_{\text{Pt}}/\text{cm}^2$



Latest catalysts  
Pt-TaPO comparable  
To Pt/VC standard  
with half the Pt

Difference in limiting  
current due to  
thickness  
of TaPO layers

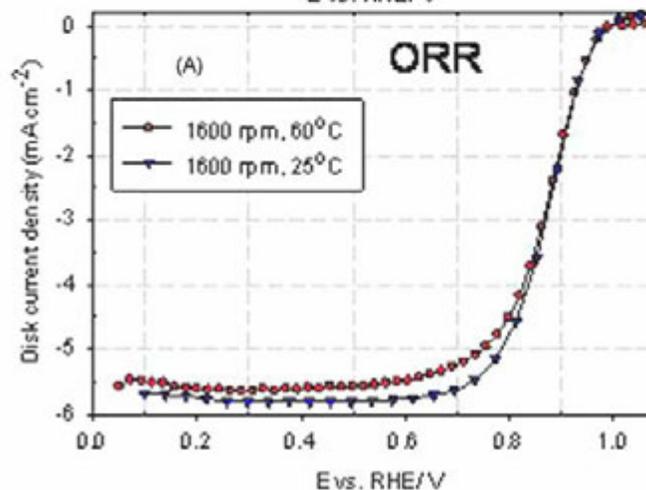
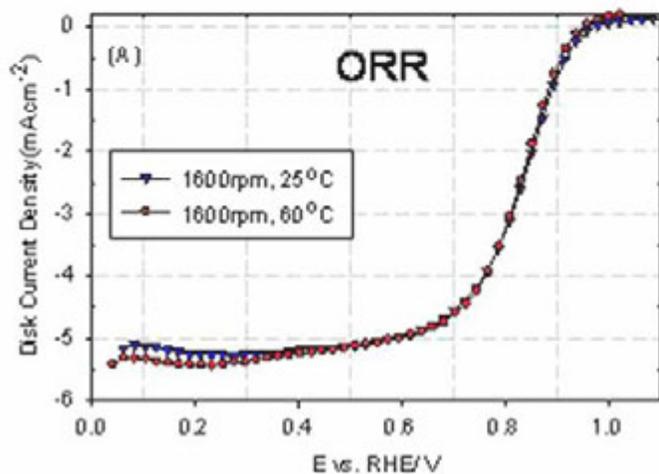
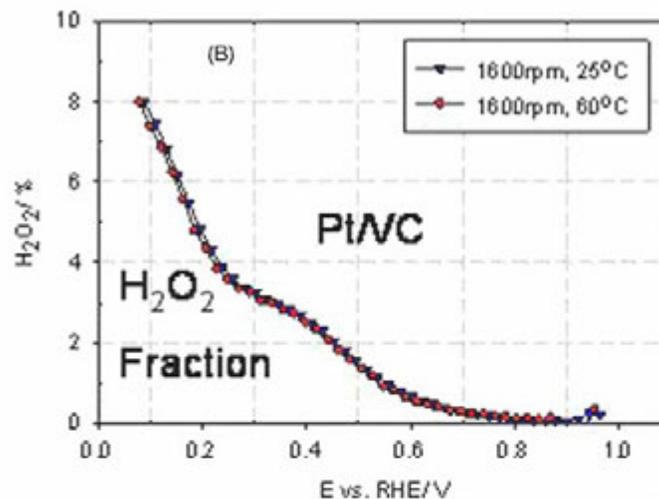
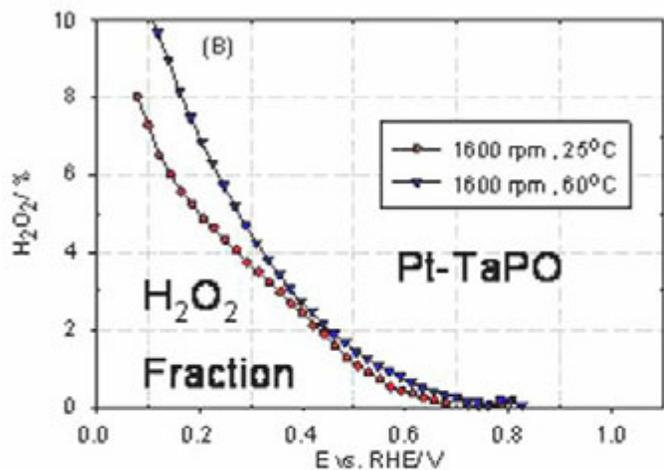
# Rotating ring disk shows that Pt-TaPO has negligible $\text{H}_2\text{O}_2$ production



## Compare Pt-TaPO/VC to Pt/VC

(A) Potentiodynamic ( $20 \text{ mV s}^{-1}$ , positive sweep)  $\text{O}_2$  reduction current densities on a thin film RRDE with Pt-TaPO/Mulcon catalyst ( $11 \mu\text{g cm}^{-2}$ ) at  $25^\circ\text{C}$  and  $60^\circ\text{C}$  in  $0.1 \text{ M HClO}_4$  saturated with  $1 \text{ bar O}_2$ . (B) Fraction of  $\text{H}_2\text{O}_2$  formation during ORR at  $1600 \text{ rpm}$  for a ring potential of  $E_r = 1.2 \text{ V vs. RHE}$

(A) Potentiodynamic ( $20 \text{ mV s}^{-1}$ , positive sweep)  $\text{O}_2$  reduction current density on a thin film RRDE with Pt/Mulcon catalyst ( $14 \mu\text{g cm}^{-2}$ ) at  $25^\circ\text{C}$  and  $60^\circ\text{C}$  in  $0.1 \text{ M HClO}_4$  saturated with  $1 \text{ bar O}_2$ . (B) Fraction of  $\text{H}_2\text{O}_2$  formation during ORR at  $1600 \text{ rpm}$  for a ring potential of  $E_r = 1.2 \text{ V vs. RHE}$ .



# Analysis of Pt-TaPO catalysts by NRL and GM

## Compare synthesis methods



NRL RDE results: 20 mV/s; 25°C; 0.1 M HClO<sub>4</sub>; 1600 rpm

catalyst	Pt impregnation/ heating	HAD [m <sup>2</sup> /g <sub>Pt</sub> ]	Pt loading, μg <sub>Pt</sub> /cm <sup>2</sup>	A/mg <sub>Pt</sub> at 0.9V	A/mg <sub>Pt</sub> at 0.85V	μA/cm <sup>2</sup> <sub>Pt</sub> at 0.9V	μA/cm <sup>2</sup> <sub>Pt</sub> at 0.85V
20% Pt/C Standard	As received	50	20	0.24	0.66	480	1330
Pt-TaPO/VC TaPO with Cl <sup>-</sup>	Synthesis #1	8.8	11	0.25	0.72	2800	8140
Pt-TaPO/VC TaPO with Cl <sup>-</sup>	Synthesis #2	14	11	0.25	0.90	4370	6320
Pt-TaPO/VC TaPO Cl <sup>-</sup> free	Synthesis #3	No credible HAD	11	0.27	0.86	-	-
Pt-TaPO/VC High surface area TaPO on VC; w/ Cl <sup>-</sup>	Synthesis #4 200 °C/H <sub>2</sub> red	7.5	10	0.044	0.15	585	2040

GM RDE results: 5 mV/s; 60°C; 0.1 M HClO<sub>4</sub>; 1600 rpm

catalyst	Pt impregnation/ heating	HAD [m <sup>2</sup> /g <sub>Pt</sub> ]	Pt loading, μg <sub>Pt</sub> /cm <sup>2</sup>	A/mg <sub>Pt</sub> at 0.9V	A/mg <sub>Pt</sub> at 0.85V	μA/cm <sup>2</sup> <sub>Pt</sub> at 0.9V	μA/cm <sup>2</sup> <sub>Pt</sub> at 0.85V
PtTaPO/VC TaPO with Cl <sup>-</sup>	Synthesis #2	19	19.5*	0.129	0.47	667	2419
PtTaPO/VC TaPO with Cl <sup>-</sup>	Synthesis #2 H <sub>2</sub> O wash	25	6.5*	0.182	0.57	726	2263
Pt/VC <sup>1</sup>	--	65 72	14.3 14.3	0.13 0.16	- -	200 230	- -

<sup>1</sup> H.A. Gasteiger et al. Applied Catalysis B: Environmental 56 (2005) 9-35

\* Pt Loading is likely lower

# Characterization & Improvement to High Surface Area TaPO

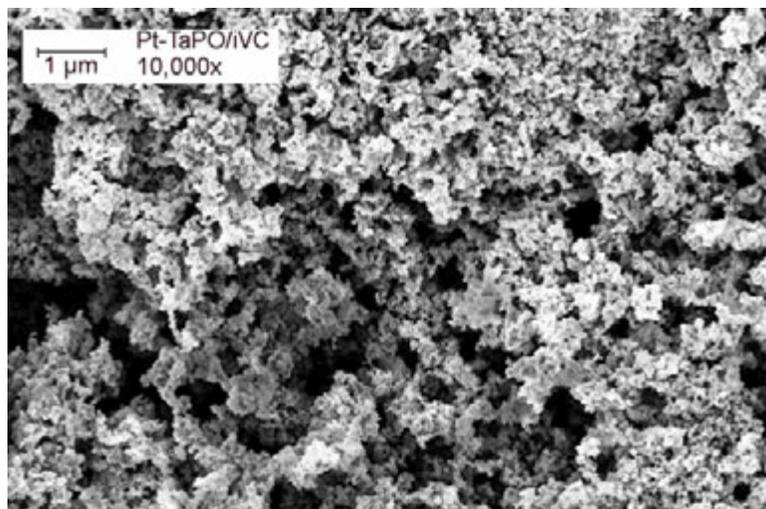
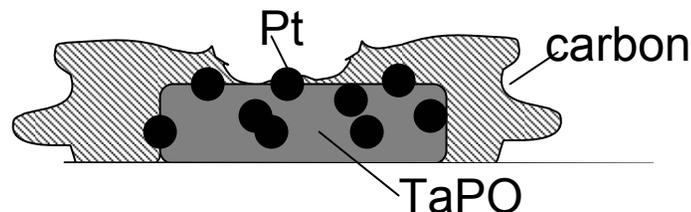


*SEM micrographs*



Synthesis #1, #2, #3: Micron-scale TaPO impregnated with Pt and then mixed with Vulcan carbon

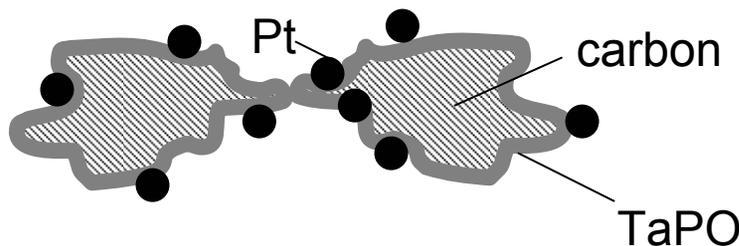
EXAFS of Pt shows 2 nm metal particles - highly oxidized



Synthesis #4:

Coat high surface area Vulcan carbon with TaPO and then add Pt

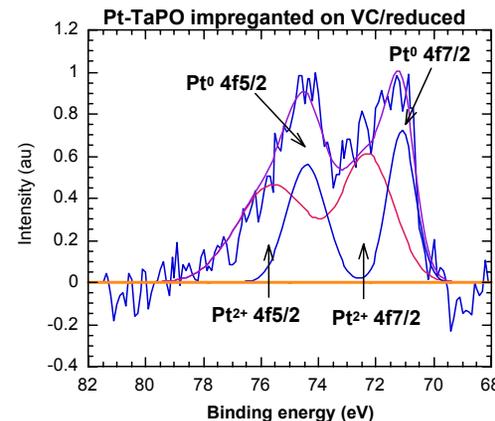
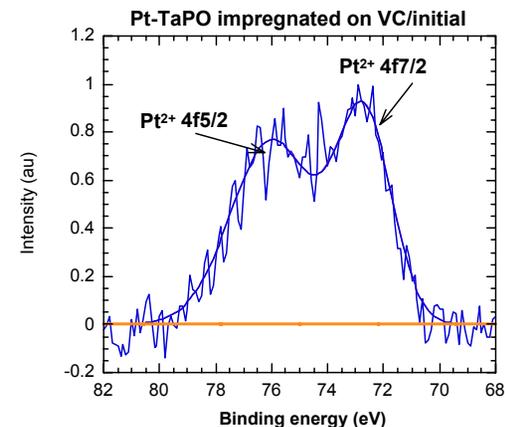
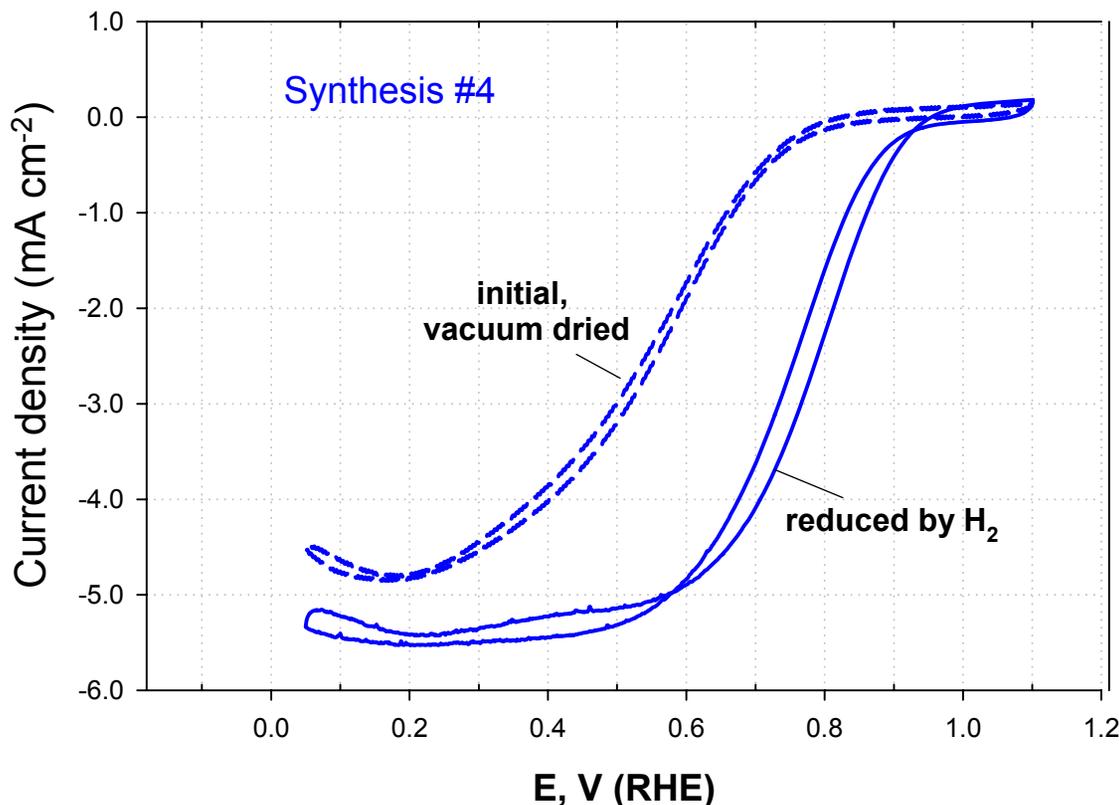
- ✓ High surface area catalyst
- ✓ Pt and carbon are not in contact



# Analysis of high surface area Pt-TaPO impregnated on Vulcan carbon (Synthesis #4)



ORR on PtTaPO-iVC: 1600 rpm, 20 mV/s, 25°C, 10  $\mu\text{g}_{\text{Pt}}/\text{cm}^2$



Solution impregnation of  $\text{H}_2\text{Pt}(\text{OH})_6$

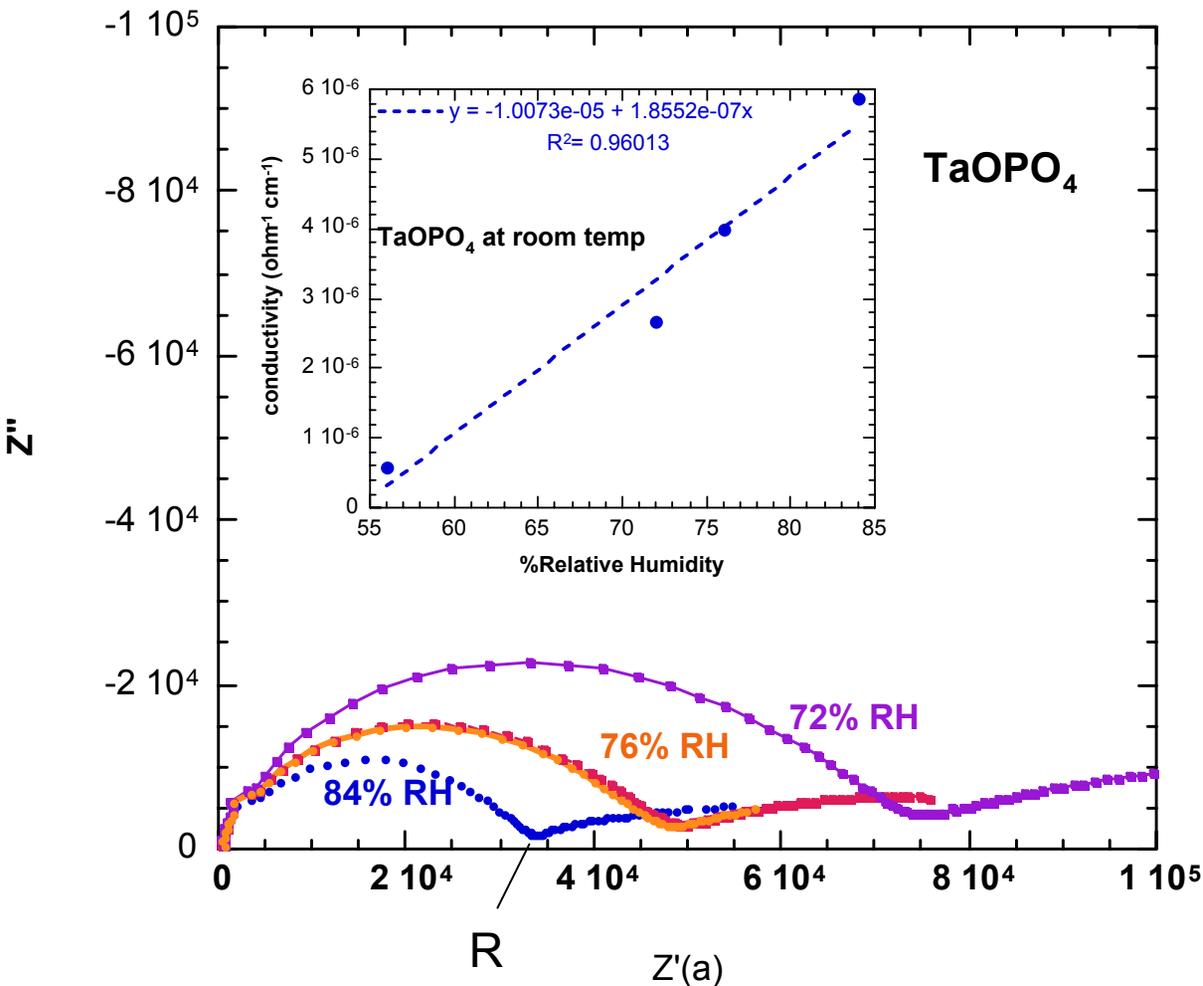
Initial sample only has  $\text{Pt}^{2+}$

After reduction in  $\text{H}_2$ , about half of Pt is reduced to metal

*Sample needs to be further reduced to make all  $\text{Pt}^0$*

*OR impregnate with  $\text{Pt}^0$  colloids*

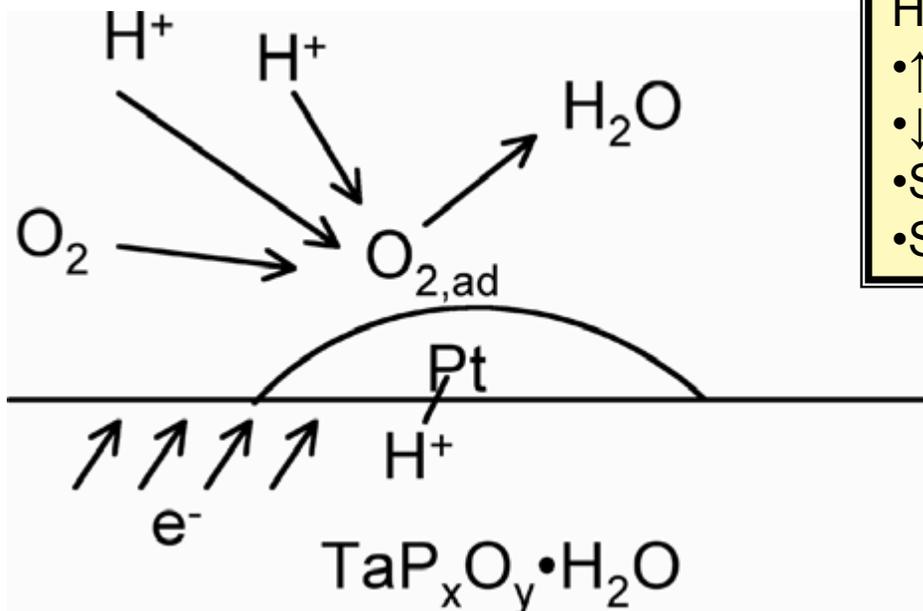
# Proton conductivity of TaPO



- Room temp  
 $\sigma_{H^+} \sim 1e^{-6} \text{ S cm}^{-1}$
- Linear with RH indicative of vehicle mechanism
- $\sigma_{H^+}$  changes little with Ta:P ratio

2-probe impedance spectroscopy in air at room T vs RH  
Intercept of first arc with  $Z'(a) =$  bulk resistance,  $R$

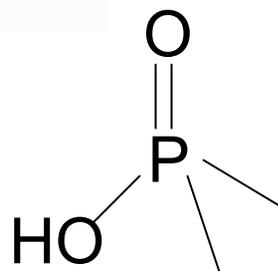
# Metal-support interactions Pt-TaPO



## **MSI/Electronic effects Pt-TaPO -**

H<sup>+</sup> from 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



Phosphorous oxoacids have one P-OH group that is ionizable as proton donors

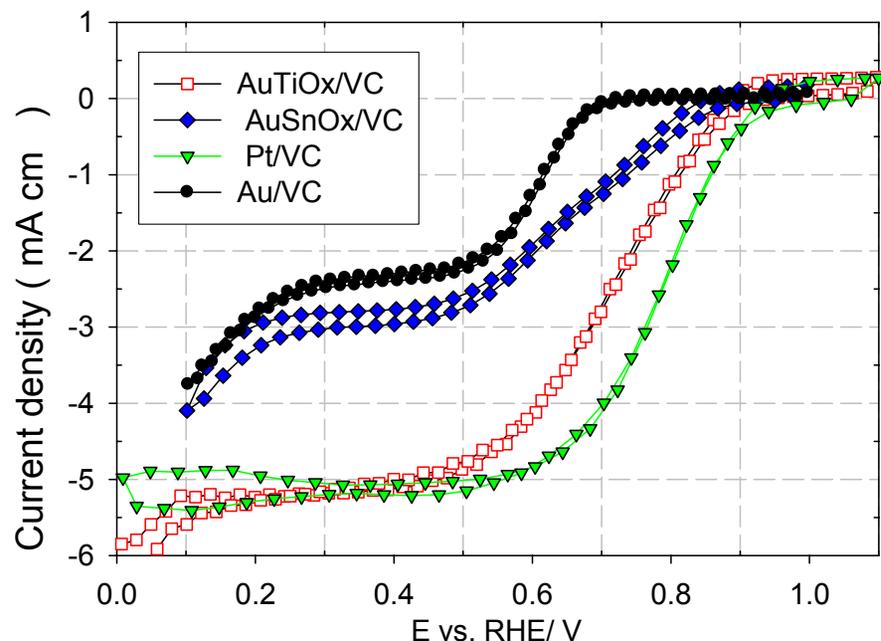
Greenway, Chemistry of the Elements

Donation of H<sup>+</sup> by hydrous phosphate is key

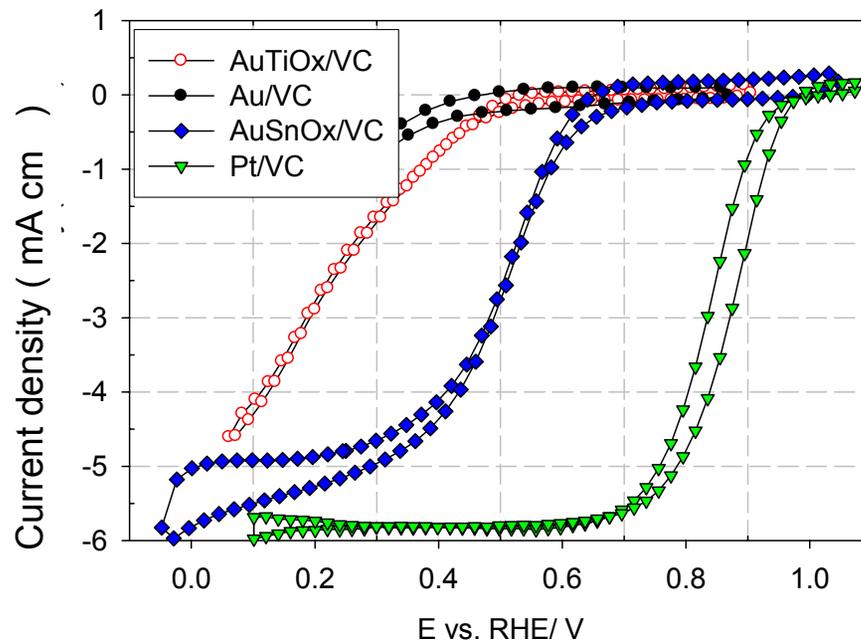


# Modification of ORR on Au in acid and base with oxide supports

in 0.1 M NaOH at 25°C (1600 rpm)



in 0.1 M HClO<sub>4</sub> at 25°C (1600 rpm)



Last year showed 4-electron ORR on Au in acid when supported on tin oxide

This year, tried Au on TiO<sub>2</sub>

Au-TiO<sub>2</sub> active in base, but inactive in acid

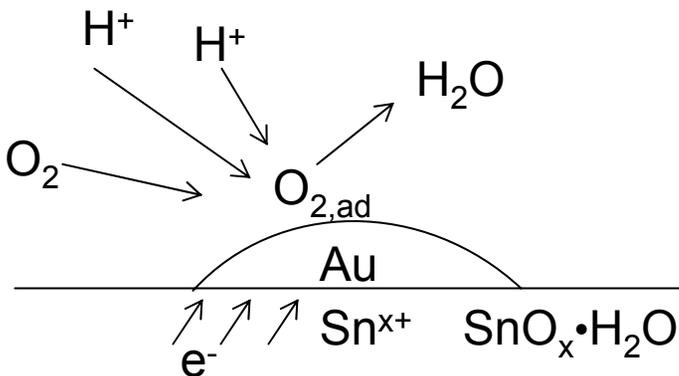
Au-SnO<sub>2</sub> inactive in base, active in acid

TiO<sub>2</sub> acidic while SnO<sub>2</sub> is amphoteric

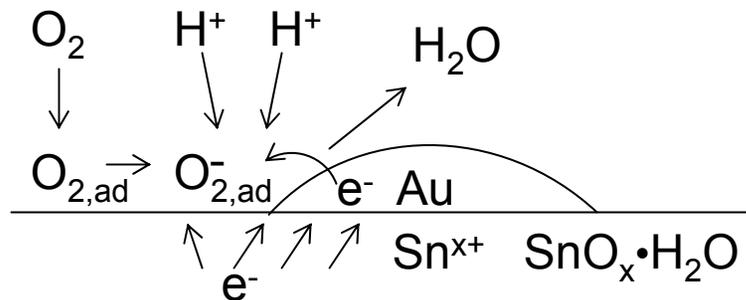
# Proposed mechanisms for 4-electron ORR on Au in acid



a)



b)



- *Au is chemisorbed on “basic” Sn<sup>x+</sup>*
- *Sn donated electron density to the Au, enabling O<sub>2</sub> adsorption, and then ORR*
- *(O<sub>2</sub> does not adsorb on unsupported Au in acid)*

- *O<sub>2</sub> is chemisorbed as O<sub>2</sub><sup>-</sup> on the SnO<sub>x</sub> surface*
- *The O<sub>2</sub><sup>-</sup> (or OH<sup>-</sup>) reacts directly with the Au*

# 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

*Proton donation by phosphates improves “acidity”*

Au activity improved by making electron donating compounds

*Few choices of electron donating d-electron compounds*

*Sn has borderline acid stability*

# Future plans Pt-TaPO



- Improved synthesis
  - Chloride-free
  - Impregnated TaPO on Vulcan carbon (high SA)
    - Minimize Pt and C contact
  - Metallic colloids
- Continued characterization
  - TEM (collaborate with CWRU for HRTEM)
  - In situ EXAFS to look at metal support interactions
- Continued collaboration with industry
  - GM FCA; Ballard; E-TEK
- Fuel cell/MEA testing
  - In house and with industry

# Gold-based cathode catalysts



- Explore Au electrocatalysts
  - More plentiful than Pt
  - Higher stability in acid (less prone to corrosion)
- Study mechanisms
  - Synthesis of related compounds
  - In situ IR of Au-SnO compounds (Adzic, BNL)
  - Chianelli/UTEP - CERES modeling of metal-support interactions (ONR funded)
  - Leverage newly developed modeling capability of Army MURI team (CWRU lead)

# Backup:

## Response to reviewer's comments



- Collaborate more with industry
  - 2005 problem with air stability of catalyst solved and materials sent to GM and ETEK
  - Testing by GM was very productive
- More work on mechanisms
  - Mechanistic studies are contingent on reproducibility
    - We understand mechanisms better now that we can compare sample performance reproducibly

# Backup: Publications and Presentations



“Enhanced Oxygen Reduction Activity in Acid by Tin-Oxide Supported Au Nanoparticle Catalysts,” W. S. Baker, J. J. Pietron, M. E. Teliska, P. J. Bouwman, D. E. Ramaker, and K. E. Swider-Lyons\*, *J. Electrochem. Soc.*, in press.

“Leveraging Metal-support Interactions to Improve the Activity of PEMFC Cathode Catalysts,” K. E. Swider-Lyons, M. E. Teliska, W. S. Baker, P. J. Bouwman, J. J. Pietron, ECS Transactions, LA-P1.

“Leveraging Metal-Support Interactions to Improve The Activity of PEMFC Cathode Catalysts,” K. E. Swider-Lyons, M. E. Teliska, W. S. Baker, J. J. Pietron, *Fifth International Symposium On Proton Exchange Membrane Fuel Cells*, 208<sup>th</sup> Meeting of the Electrochemical Society, Los Angeles, CA, 16-21 October 2005.

“Using Metal Oxide and Phosphate Supports to Improve Oxygen Electrocatalysts in PEM Fuel Cells,” Electrochemistry Gordon conference, Buellton, CA, 12-17 February 2005.

# Backup: Critical Assumptions and Issues



Pt metal electrocatalysts supported on carbon have high cost and are prone to corrosion, particularly after 1000 hrs of use.

The oxygen reduction reaction on Pt and Au has been studied extensively for decades and some feel that there is much unknown about the process.

There are few approaches to developing new catalysts; most researchers focus on alloying.

Our goal is to develop new sorts of materials, beyond simply Pt alloys. New materials are difficult to develop because they must have the dual attribute of exceeding Pt metal activity plus be acid stable. We have found a class of phosphates that offer these attributes for Pt and have shown that oxide supports can improve the activity of Au. Supporting metals on oxides to improve activity is the standard approach used in the development of conventional heterogeneous catalysts.

Catalyst development requires very “high end” materials science and electrochemistry, drawing from expertise in synthesis, materials characterization, colloids, catalysis, and electroanalytical chemistry.

This DOE program is a tremendous asset because it provides no-nonsense metrics for performance plus constructive feedback from reviewers and industry teams.