Low-platinum hydrous metal oxides for PEMFC cathodes

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Objective and Approach

- Meet DOE goals to achieve 0.02 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.

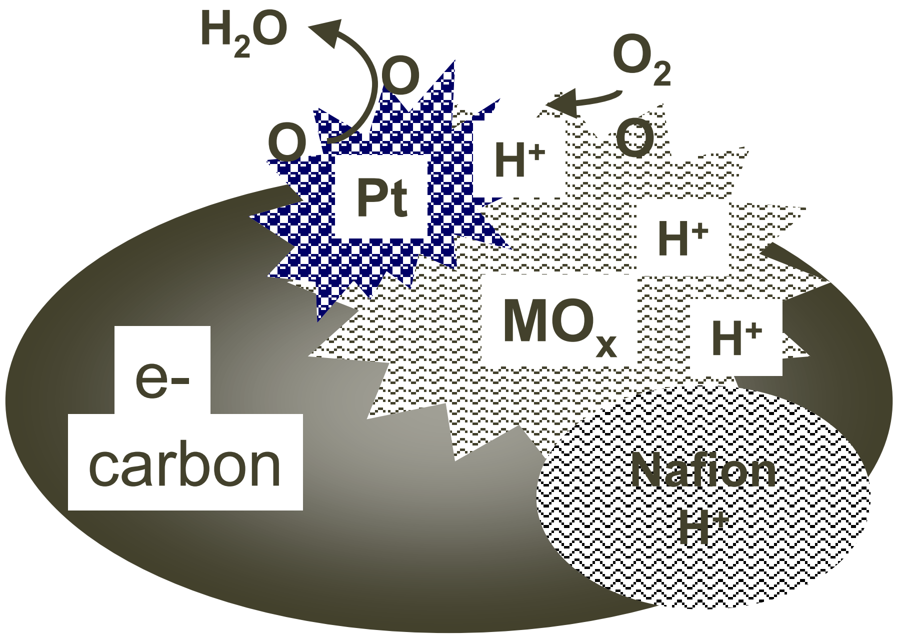
NRL approach is to support Pt on a metal oxide

improve opportunity for

* proton mobility to Pt sites

* chem/phys attraction of O_2

* metal-support interactions with Pt



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

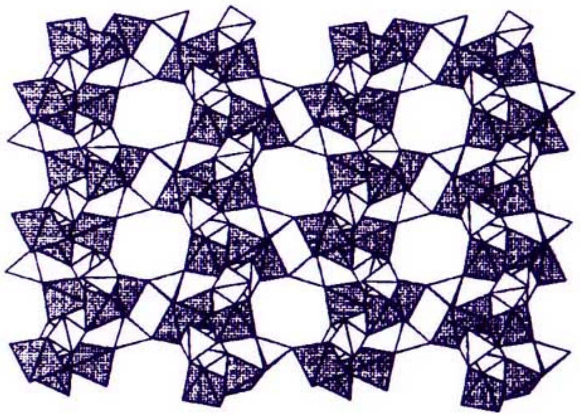
$O_2 + 4\ H^+ + 4e^- \rightarrow 2\ H_2O$

Catalyst development via electrochemical and structural analysis

Pt-MO_x systems

1. Pt-$FePO_x \cdot xH_2O$ - hydrous iron phosphate
   - Iron phosphate used as an anti-corrosion additive in paint
   - $FePO_x$ is a partial oxidation catalyst
2. Pt-$SnO_x \cdot xH_2O$ - hydrous tin oxide
   - Prior ORR literature shows promise for anhydrous Pt-SnO_x
   - Tin hydrates are corrosion resistant
3. Pt-$NbPO_x \cdot xH_2O$ - hydrous niobium phosphate
   - Niobium is ultra resistant to corrosion - used in electrolysis.
   - $NbPO_x$ is a partial oxidation catalyst

"Open Framework Inorganic Materials"
A. K. Cheetham G. Férey, T. Loiseau,
Angew. Chem. 1999, v. 38 p. 3286.



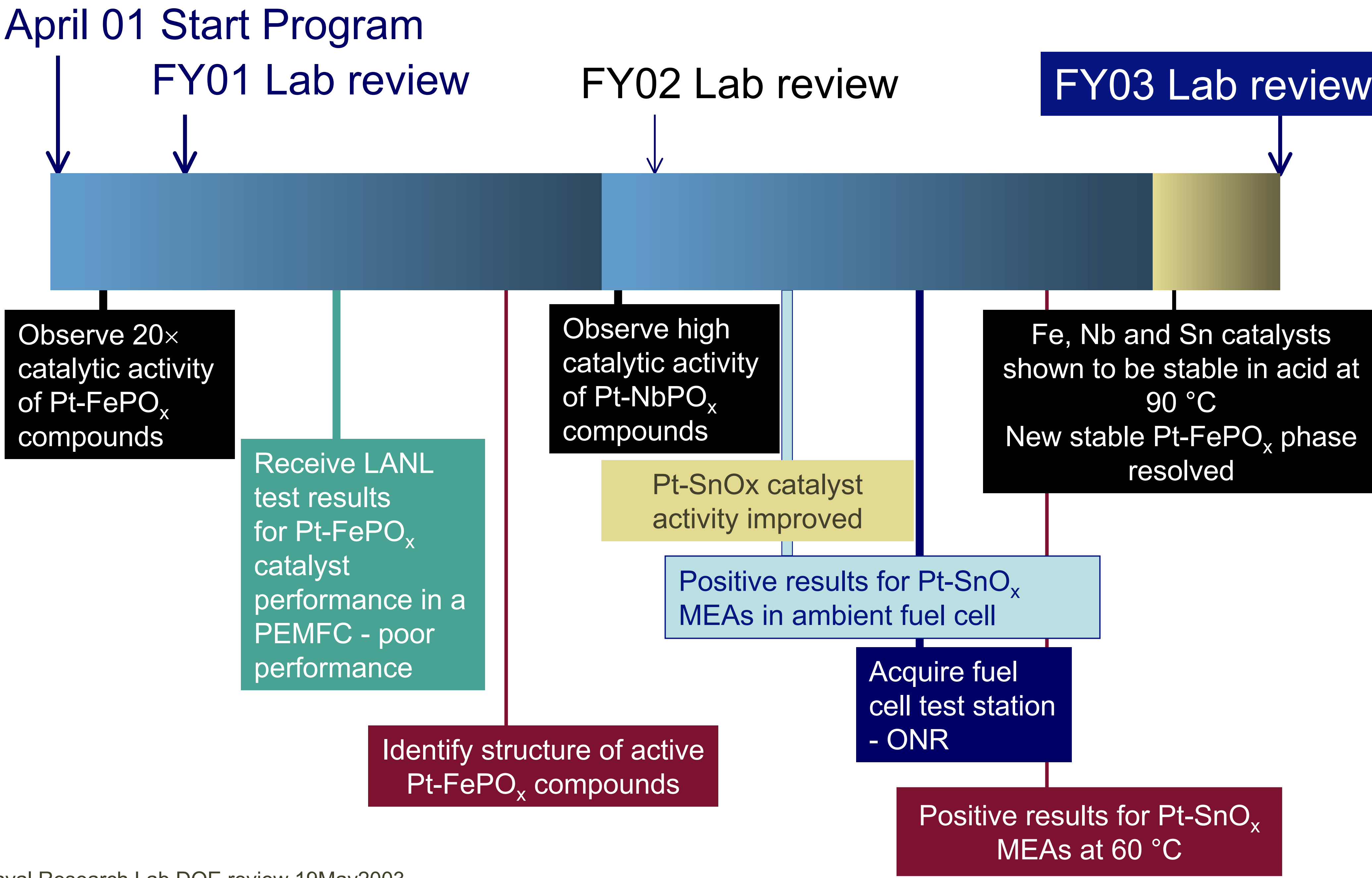
Example:
Microporous $AlPO_4$

✓Hydrous oxides are excellent for proton conduction

✓Selected oxides have other ideal catalytic properties (e.g. partial oxidation)

✓Materials have open framework structures

Progress to date (2 years)



April 01 Start Program

FY01 Lab review

FY02 Lab review

FY03 Lab review

Observe 20× catalytic activity of Pt-$FePO_x$ compounds

Receive LANL test results for Pt-$FePO_x$ catalyst performance in a PEMFC - poor performance

Identify structure of active Pt-$FePO_x$ compounds

Observe high catalytic activity of Pt-$NbPO_x$ compounds

Pt-SnOx catalyst activity improved

Positive results for Pt-SnO_x MEAs in ambient fuel cell

Acquire fuel cell test station - ONR

Fe, Nb and Sn catalysts shown to be stable in acid at 90 °C
New stable Pt-$FePO_x$ phase resolved

Positive results for Pt-SnO_x MEAs at 60 °C

Catalyst stability evaluation

Method: *recommended by H. Gasteiger and S. Kocha of GM*

- ✓ Stir catalyst in sulfuric acid and/or phosphoric acid for 12 h at 90 °C
- ✓ Test catalyst performance in RDEs before and after acid wash
- ✓ Test acid solution for evidence of metal leaching with ICP

RESULTS

Pt-$FePO_x$

- Portion of catalyst dissolve in acid, leaving an acid-stable, phosphate-rich compound with 9.5 % Pt
- RDE of acid stable Pt-$FePO_x$ phase is better than that of the original material

Pt-SnO_x

- Compound is insoluble in sulfuric acid
- RDE evaluation underway

Pt-$NbPO_x$

- Compound is insoluble in sulfuric acid and phosphoric acid
- RDEs are unaffected by acid treatment

Evaluation of catalyst leaching with ICP still underway

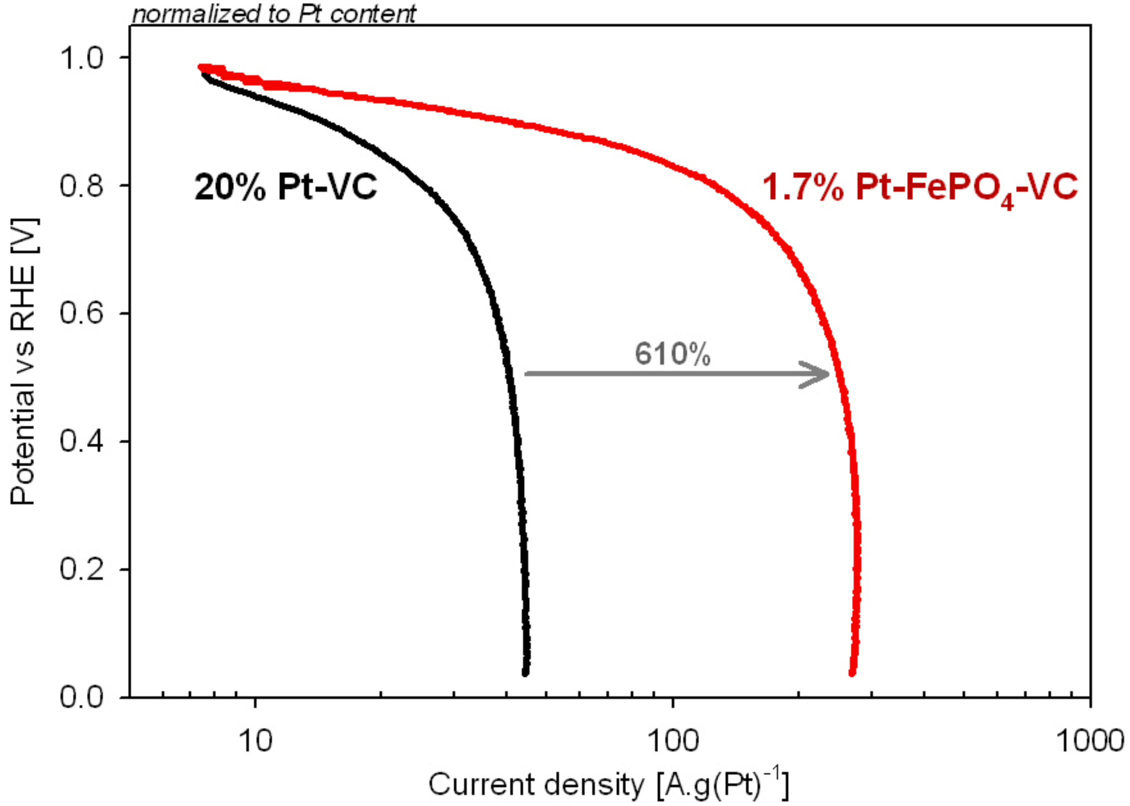
All materials dissolve in aqua regia (like Pt metal)

RDE results for acid-stable Pt-FePO$_x$

Tafel plot:
1.7% Pt-FePO$_x$- 80% Vulcan carbon
vs. 20% Pt-VC standard

Rotating disk electrode of catalyst ink in Nafion ionomer:

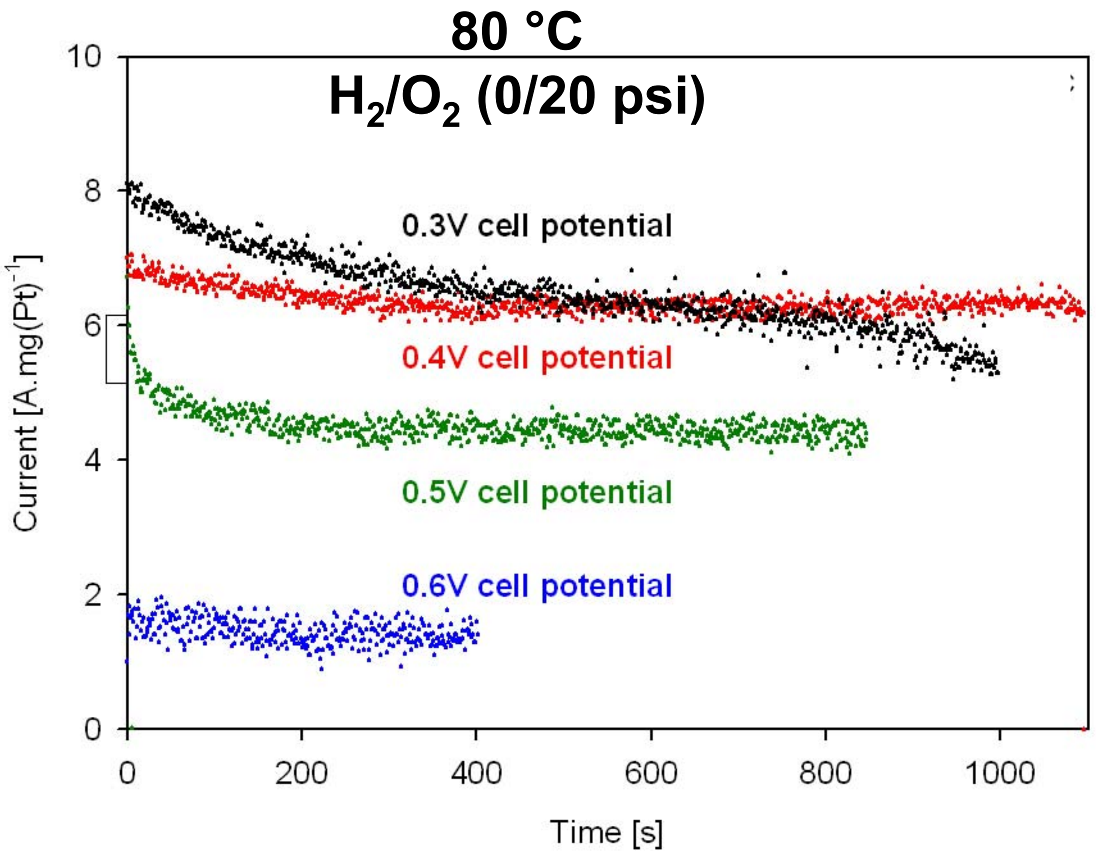
Normalized to Pt content: Pt-FePO$_x$ has >6× activity of 20%Pt-VC



60 °C 5 mV/s
0.1 M $HClO_4$
1600 rpm 100 ccpm O_2 flow
Tafel plots calculated from the difference of scans run under Ar and O_2 compared to 20% Pt/VC standard

Performance of Pt-FePO$_x$ MEAs

- Pt-FePO$_x$ compound holds a steady potential from 0.6 V to 0.4V - degrades at 0.3 V
- Note that this fuel cell had a low OCP
- Preparation of MEAs need optimization

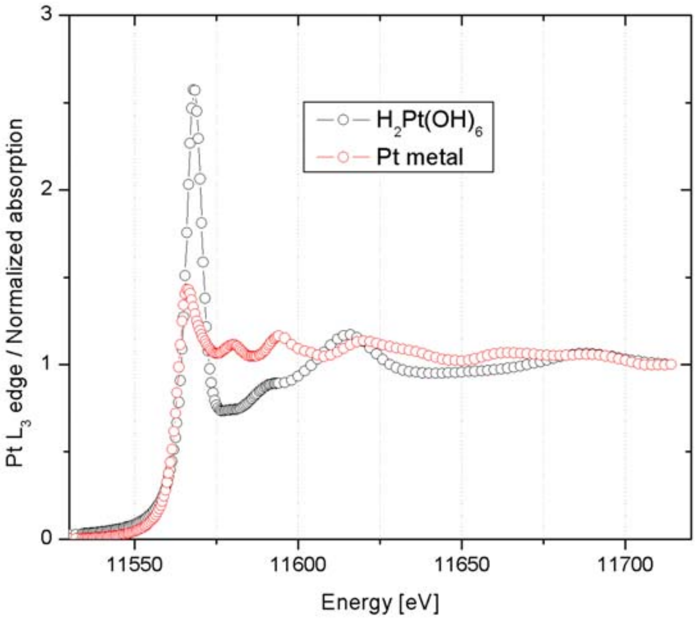


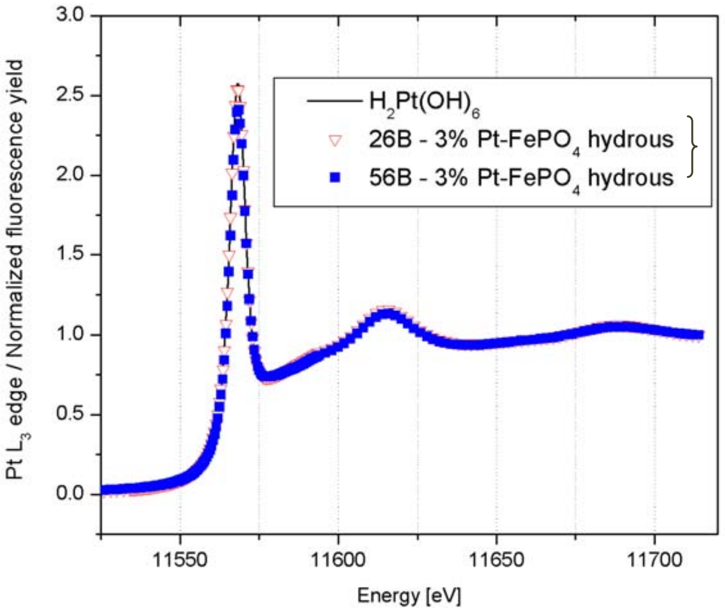
1.7% Pt-FePO$_x$- 80% VC cathode 0.013 mg Pt/cm^2

20% Pt-VC anode 0.08 mg Pt/cm^2

Oxidation state of Pt

Pt XANES measurements at the NSLS/X18B





Active $Pt-FePO_x$ catalysts

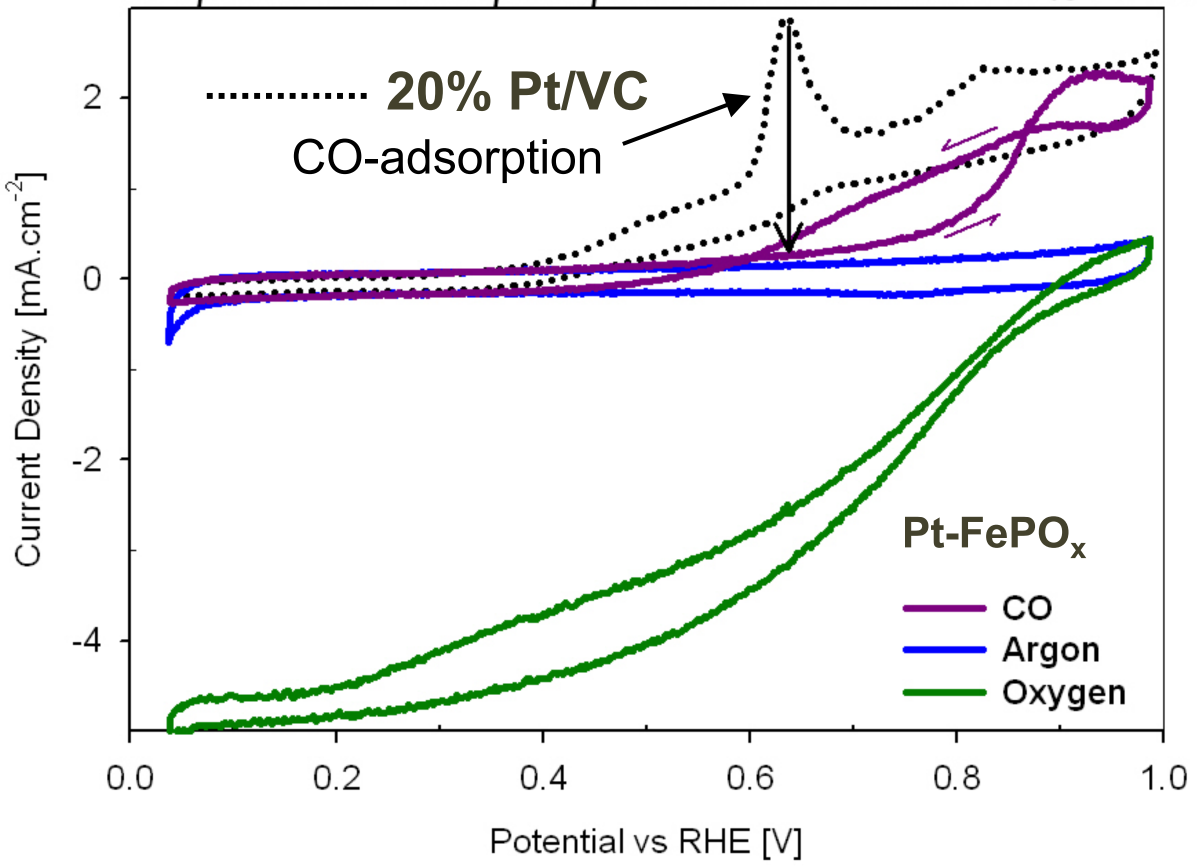
Pt is oxidized (~Pt^{4+}) and not metallic in $Pt-FePO_x$

$FePO_x$ environment compresses metal-metal bond lengths, thereby changing the electronic states of the Pt and possibly making it a better catalyst

d-p bonding - occupied states at Pt modified

CO stripping of Pt-$FePO_x$

no specific CO adsorption peak as observed with 20% Pt-VC



- Pt-$FePO_x$ phase shows no evidence of CO adsorption
- Pt be less susceptible to poisoning in the phosphate structure

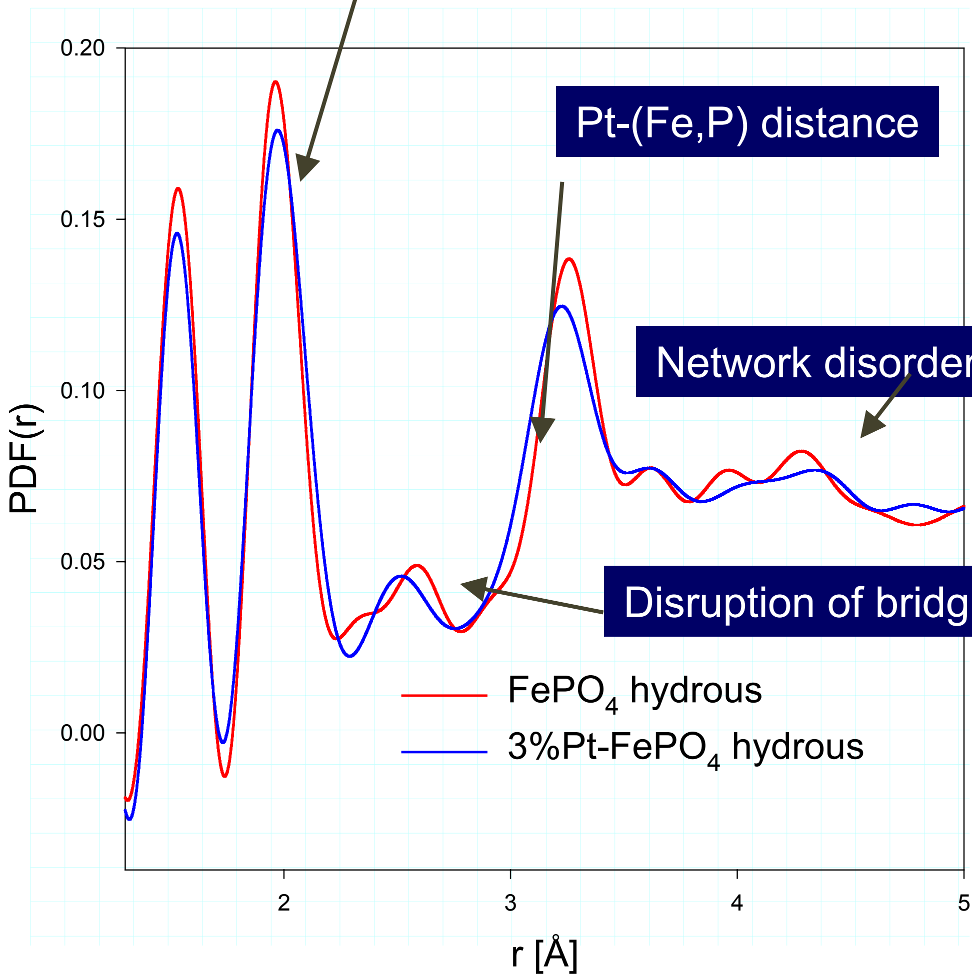
New results on acid stable Pt-$FePO_x$ phase

1.7% Pt-$FePO_x$- 80% Vulcan carbon

Structural analysis of Pt-$FePO_x$

Key structural elements of active material:

- Glassy network of FeO and PO tetrahedra – disordered α-quartz structure
- Fe is mixed valence
- Pt built-in as a "glass modifier"



Fe-O width increased

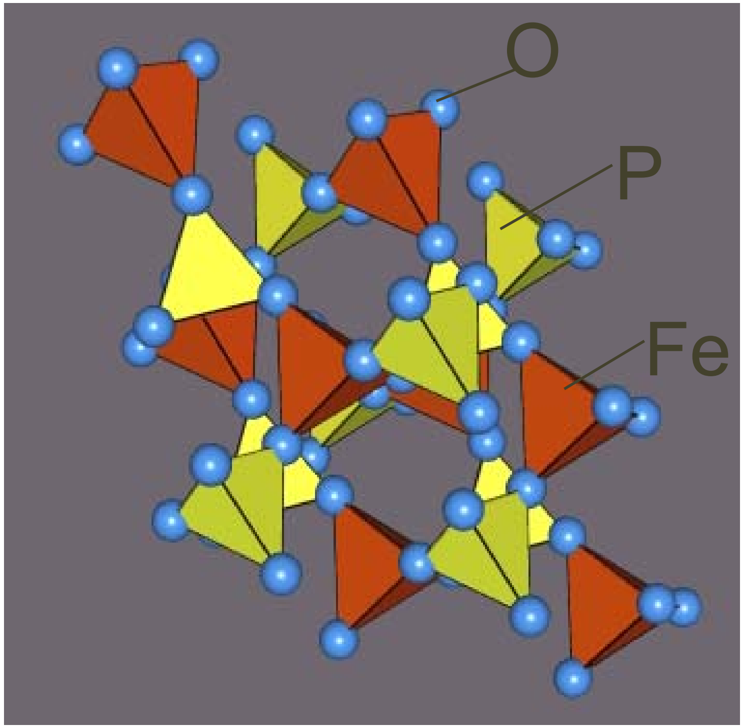
Pt-(Fe,P) distance

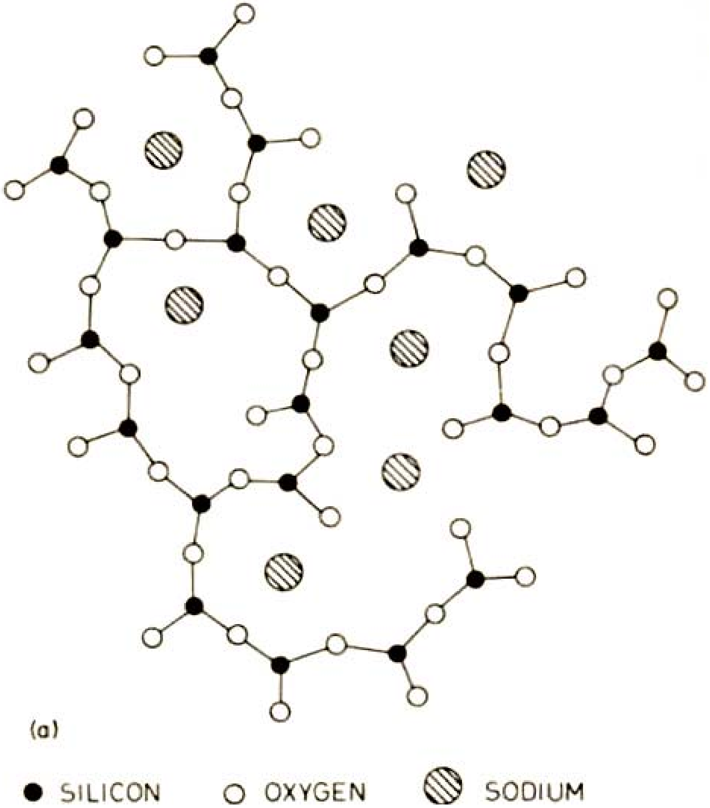
Network disordered

Disruption of bridging O atoms

Atomic pair density analysis (PDF) of high energy X-ray scattering reveals key structural elements of active material

Pt as a glass modifier

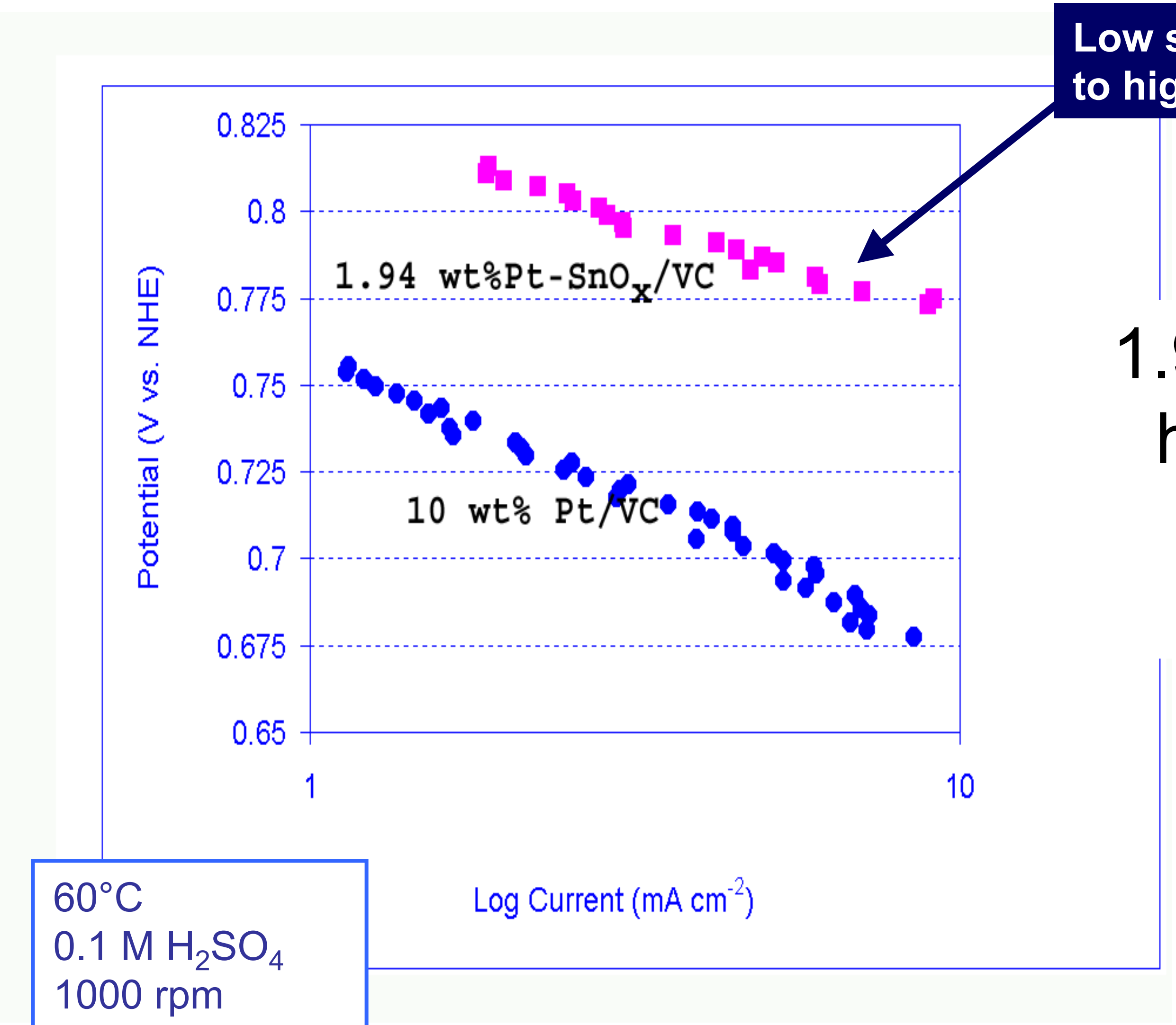




- Iron phosphate
  (berlinite) – α-quartz structure
- Pt modifies micropore sizes and long-range order

Example: Na modifies the structure of silicon oxide to form a glass

RDE performance of Pt-SnO_x



Low slope at high currents due to high H^+ conduction??

60°C
0.1 M H_2SO_4
1000 rpm
10 mV/sec

1.9 wt% Pt in SnO_x-VC has higher ORR activity than 10 wt%Pt-VC Despite ~5x lower Pt

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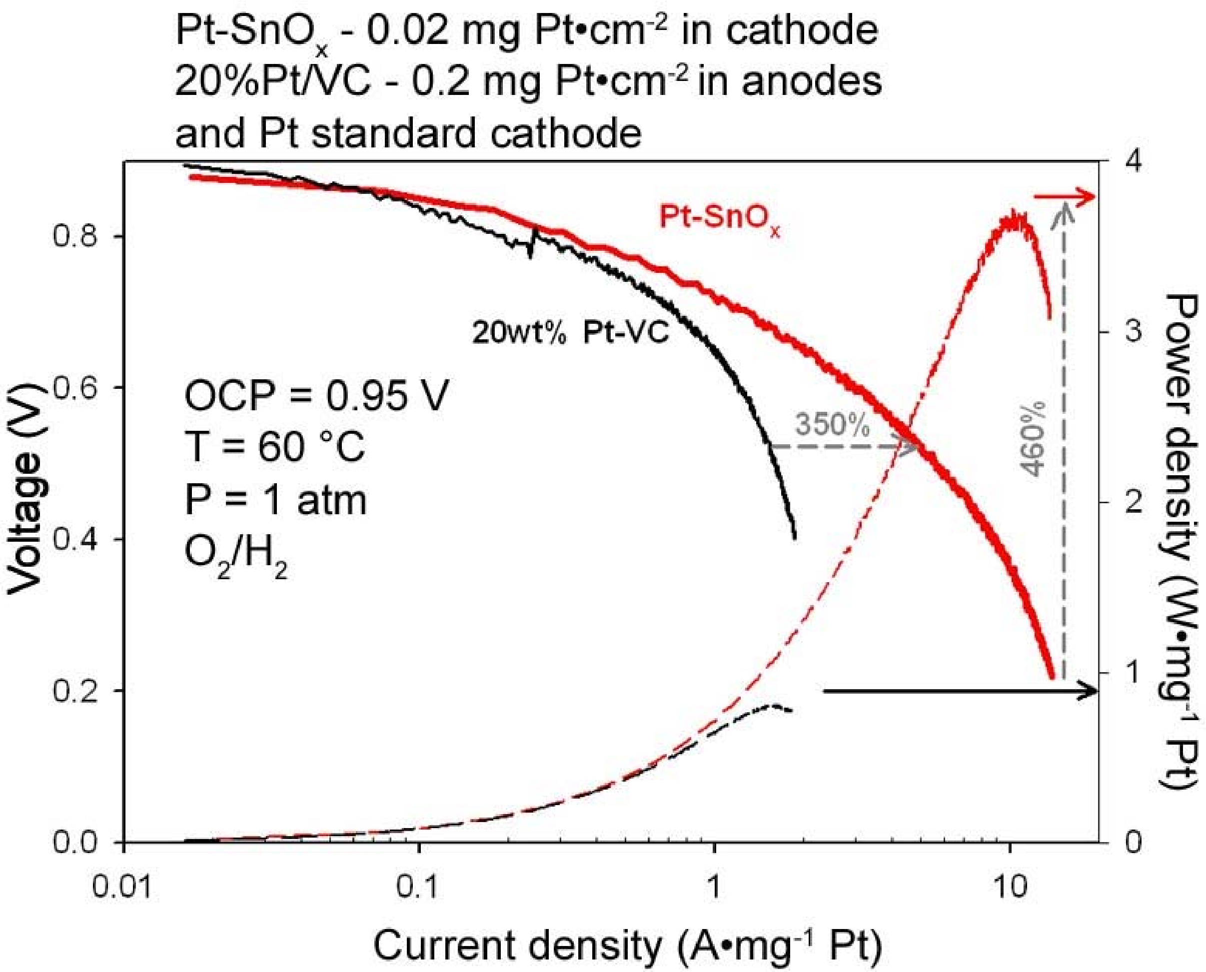
Pt-SnO$_x$ cathode performance in a PEMFC

- Fuel cell performance of Pt-SnO$_x$ is 3.5× better per wt% Pt in first-generation MEAs
- Improvements needed in MEAs (e.g., thinner catalysts layers)
- Performance at 80°C same as that at 60°C - under investigation



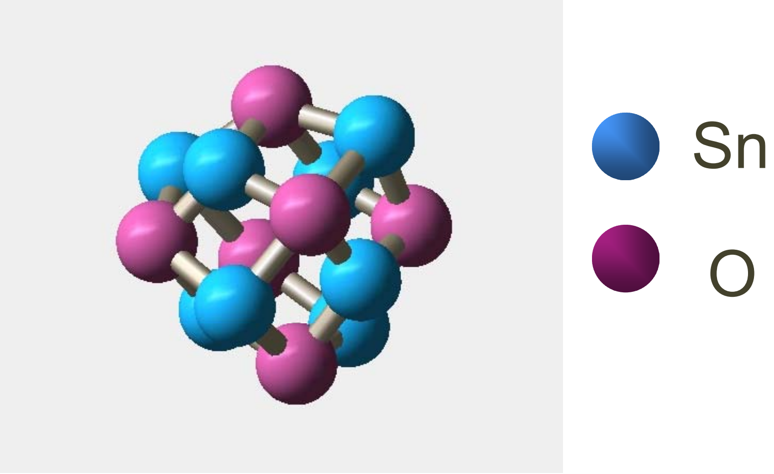
Structural analysis of Pt-SnO_x

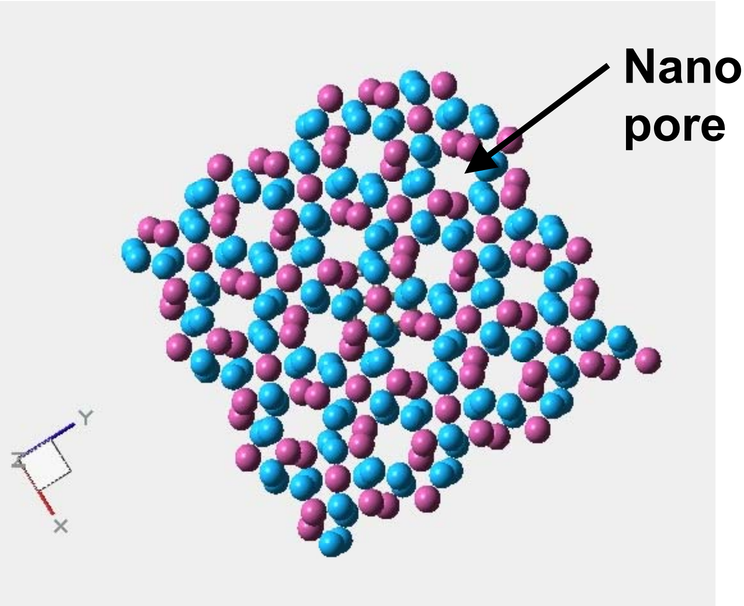
with conventional XRD and high energy XRD/PDF analysis

hydrous SnO_x - as prep is crystalline - $Sn_6O_4(OH)_4$ *(BCC packing of Sn_6O_8 clusters)*

⇒Hydrous SnO_x heated to 150 °C is amorphous

⇒Hydrous Pt-SnO_x heated to 150 °C has short-range order



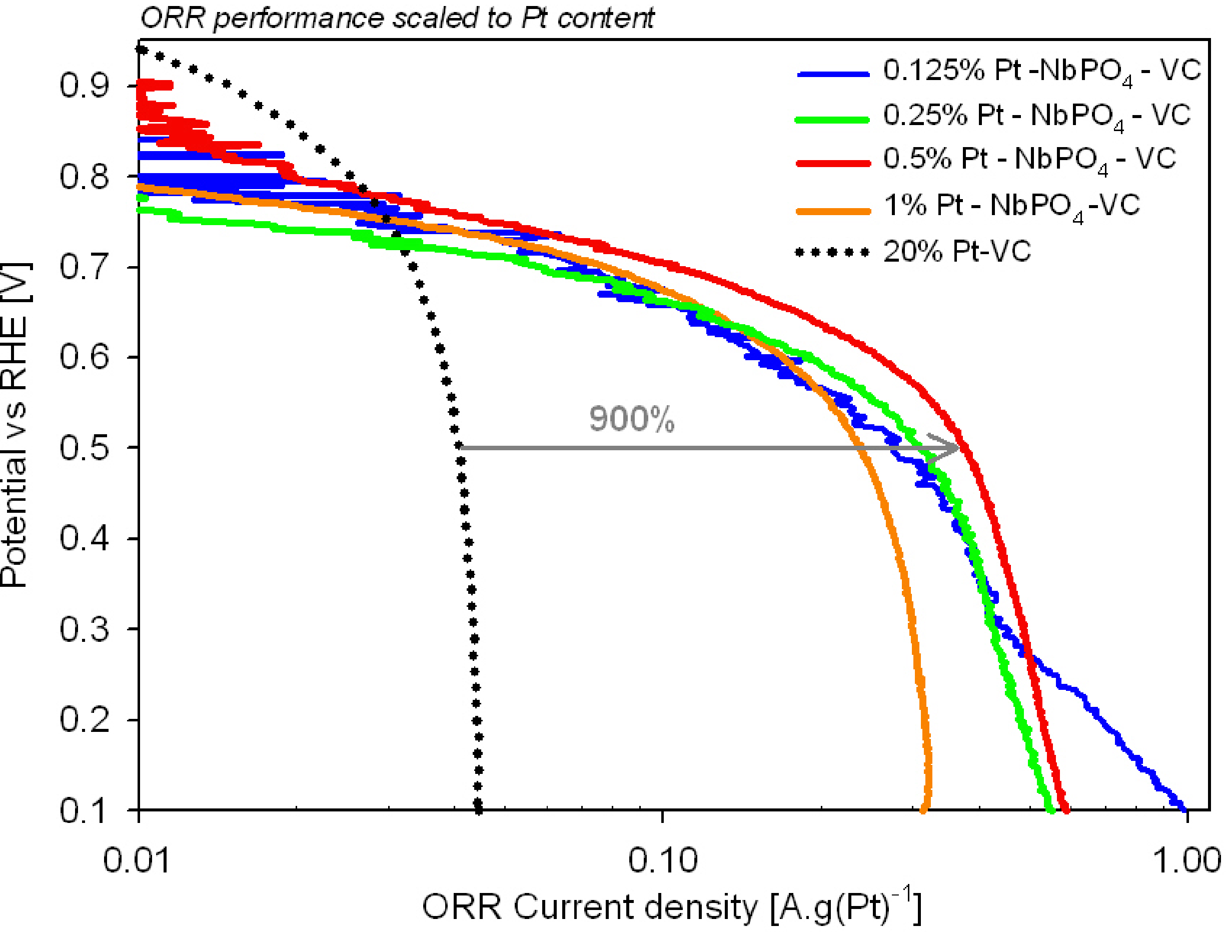


Nanoscale pore

Addition of Pt and 150 °C heat treatment results in changes both within cluster and inter cluster arrangements, but the microporous structure is retained

TEM indicates that Pt distribution is non-uniform

RDEs of Pt-$NbPO_x$



- $NbPO_x$ doped with various levels of Pt - best *relative* performance from 0.5 wt% Pt in $NbPO_x$
- 9× improvement in activity per mass Pt
- OCP of Pt-$NbPO_x$ materials is lower than expected ~0.8 V vs H
- MEAs have not yet been made successfully

60 °C 10 mV/s
1600 rpm 0.1 M H_2SO_4
100 ccpm O_2 gas flow

Collaborations

- LANL - NU and PB traveled to LANL to make state-of-the-art Pt/Vulcan carbon MEAs
- General Motors - H. Gasteiger and S. Kocha traveled to NRL and shared expertise in fuel cell and RDE evaluation. KSL, PB and NU will travel to GM in late May.

Materials transfer agreements being signed with:

- ✓ GM
- ✓ E-TEK
- ✓ RPI - Benicewicz (PBI membrane fuel cells)

Response to DOE Tech Barriers

Metal	**Relative costs**
Pt	100%
Fe	0.12
Nb	2.4
Sn	0.14

estimated based on costs of metals in Alfa-JM 2003 catalog

Can these catalysts be useful for high T MEAs??

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

0.02 mg Pt/cm^2 and 3.7 W/mg Pt (for Pt-SnO_x)

Assume $15/g Pt

--> $4/kW for Pt-$SnO_x$ cathode

P: Durability (5000 h)

Catalysts are stable in sulfuric and phosphoric acid

Pt distributed in oxides will be less prone to ripening than metallic particles, so there is opportunity for longer lifetime

Q: Electrode performance (reduce high overpotentials at cathode)

Under investigation

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Goals for 2003-2004

- Isolate active Pt-phosphate and/or Pt-oxide phases
- Improve MEA development via internal research and collaborations
  - ✓ Modify catlyst morphology (surface area & particle size)
  - ✓ Identify optimal deposition methods and processing conditions
- Improve electronic transport in metal oxides via doping with appropriate metals
  - ✓ $FePO_x$ doped with Mo
  - ✓ $NbPO_x$ doped with W
  - ✓ SnO_x doped with In or Sb
- Understand structure of active catalyst
  - ✓ In situ XANES and PDF-XRD studies
- Investigate carbon-support interactions
  - ✓ Nitrogen functionalities on carbon may enhance Pt-iron phosphate activity
- Continue stability evaluation of catalysts in acids and in fuel cells

Response to reviewers

A lot of constructive criticism from last year - we responded to all practical suggestions

- ✓ Validate results from RDE measurements by testing materials in MEAs in fuel cells
  - Our RDE and MEA results correlate to the ORR (but not for HOR)
  - MEA development needed to maximize benefits of new materials
- ✓ Justify approach to work on iron oxides
  - Iron phosphates have unique properties and are stable in acid with Pt
- ✓ Evaluate materials' stability
  - Preliminary stability studies have been completed and stability must be evaluated in a fuel cell
- ✓ Expand collaborations with industry
  - Collaborations with industry will expedite progress in 2003 - 2004

Summary

- Low-Pt catalysts can be prepared by dispersing Pt in metal oxide supports
- Choice of metal-oxide support is critical

  naturally-forming microporous oxides have good attributes for fuel cells

- Pt-impregnated oxides and phosphates can be stable under the acidic conditions of fuel cells
- Pt present as ~Pt^{4+} and may be less easily poisoned
- Oxidized Pt atoms can be active catalytic sites with the appropriate oxide environment (electronic and ionic effects)
- Structural analysis of new catalysts performed EARLY

  PDF of XRD is an excellent tool for analysis of materials with nanoscale features

- “Amorphous” can be a function of your analytical method