# Low-Platinum and Platinum-Free Catalysts for Oxygen Reduction at Fuel Cell Cathodes

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# Objective(s)

1. Reduce Pt loading in fuel cell cathodes by ***at least*** a factor of 20 (or eliminate all Pt)
   - ✯ Decrease cost of fuel cells to consumers
   - ✯ Lower national security risk

2. Improve oxygen reduction reaction (ORR) catalysis

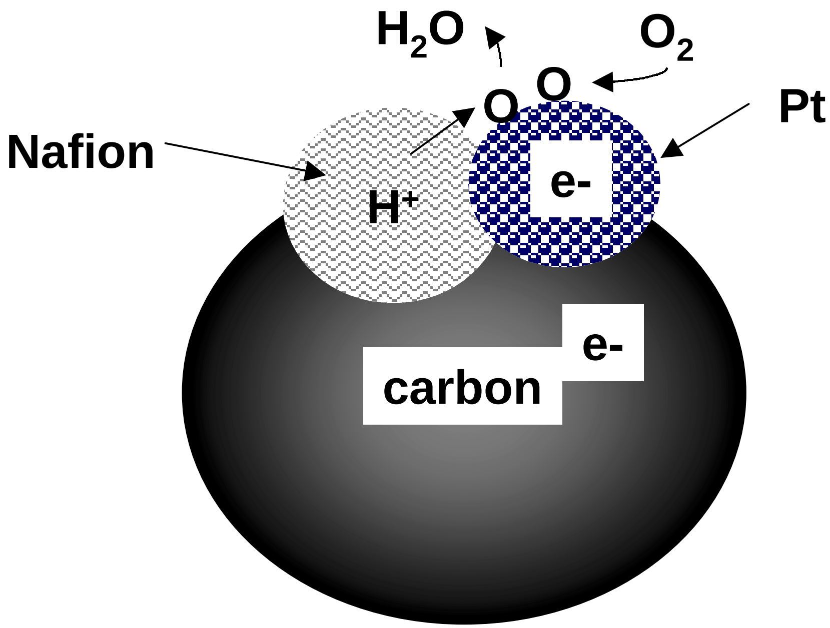
Major milestone:

Prove that our low-Pt catalysts can beat or meet the electrochemical performance AND stability of the standard 10 wt% Pt/Vulcan carbon in a working fuel cell

# The Problem

Cathode

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

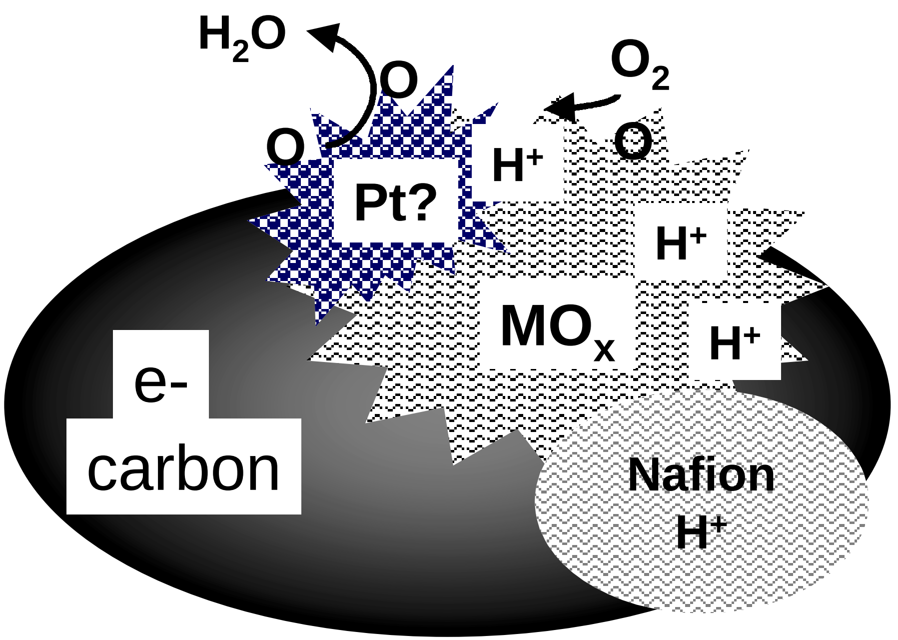



balance $\left\{ \begin{array}{l} H^+ \\ O_2 \\ H_2O \\ e^- \end{array} \right.$

**Reaction is transport limited**

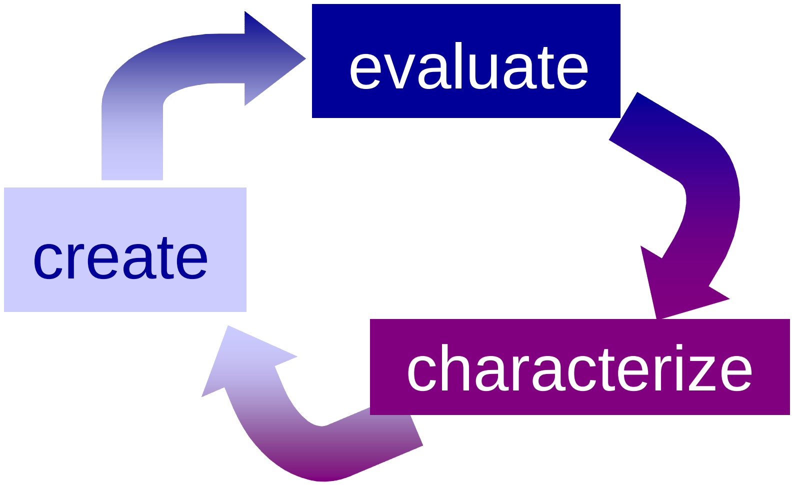
# Approach

**Design and understand new nano-composite catalysts having little or no platinum**




***Pt supported on $MO_x$•$H_2O$ supported on carbon***

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




- **Leverage properties of hydrous transition metal oxides**
  **✯High proton transport**
- **Select transition metals that adsorb and dissociate oxygen**
- **Use advanced characterization tools to identify structure property relationships**

# Timeline

April 01 Start Program

FY01 Lab review

FY02 Lab review

March 03 End Program

Observe 20 X catalytic activity of Pt-$FeO_x$ compounds

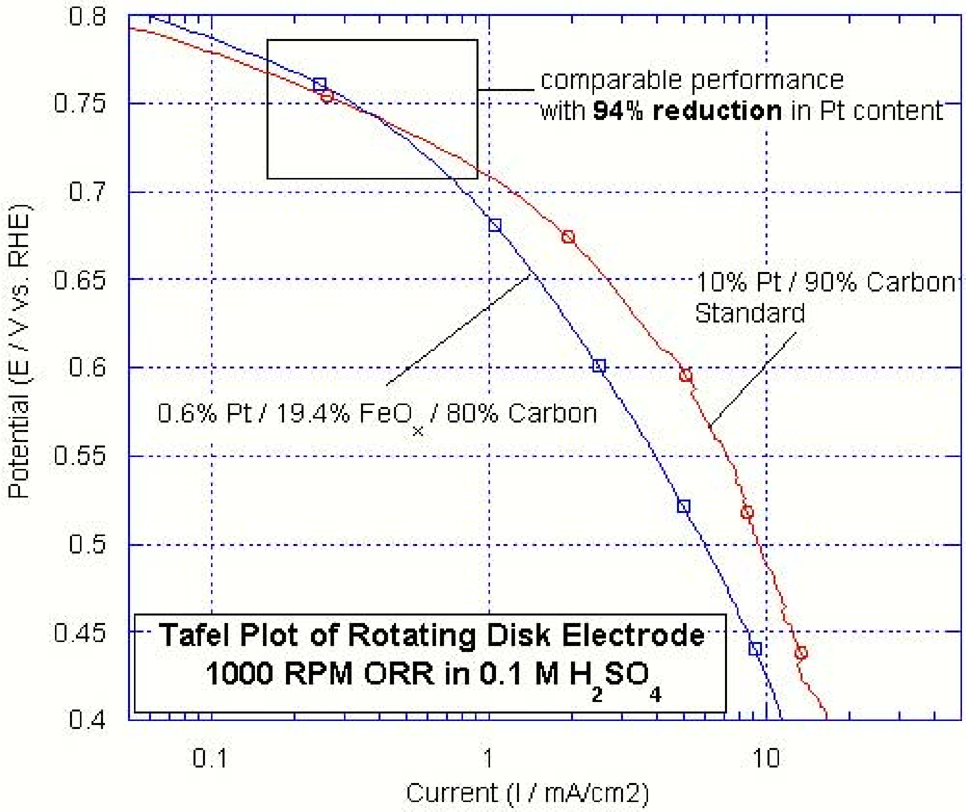
Receive LANL test results for Pt-$FeO_x$ catalyst performance in a PEMFC

Identify local structural differences between active and inactive Pt-$FeO_x$ catalysts

Observe high catalytic activity of Pt-$NbO_x$ compounds

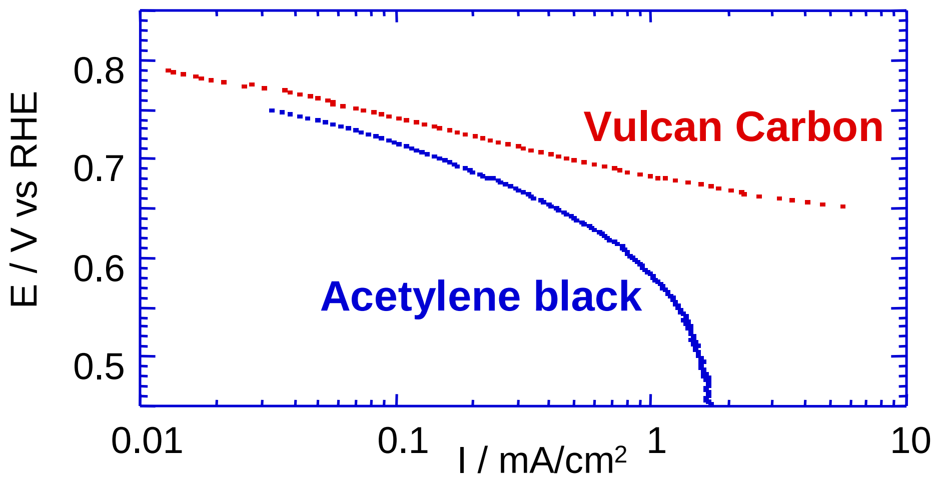
- Acquire fuel cell test station
- Identify new STABLE Pt-$MO_x$ catalysts
- Test stability of all active catalysts in fuel cells
- Determine structure-property relationships of catalysts

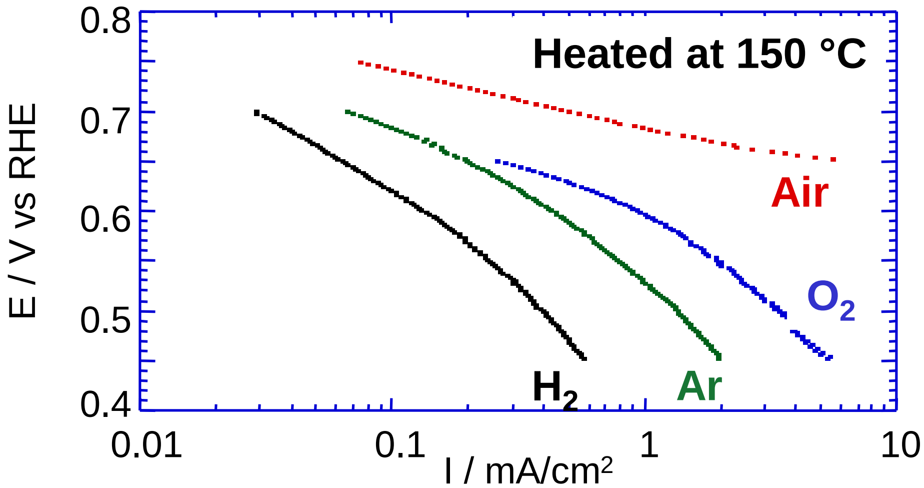
# Results - Pt-FeO$_X$




Amorphous composites of Pt and hydrous FeO$_x$ can perform with the same ORR activity as 10% Pt/Vulcan carbon, despite 20X less Pt

# Effects on Electrocatalyst Performance



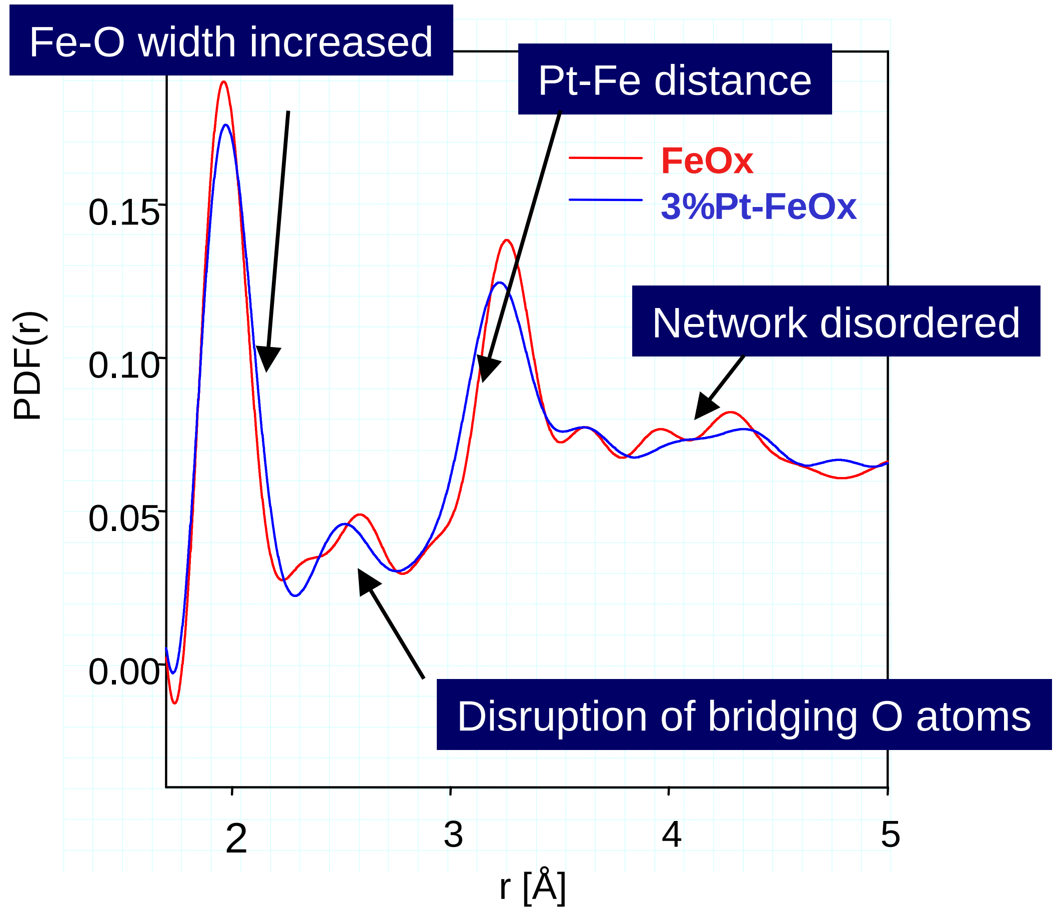

**Catalyst performance is sensitive to processing conditions**

- **Carbon type**
  - ✯ **Vulcan carbon is best**
- **Heating atmosphere**
  - ✯ **Air is best**
- **Heating temperature**
  - ✯ **150 °C is best**

Conditions: rotating disk half-cell reactions
0.1M $H_2SO_4$, 60 °C, 1000 rpm, Ar vs $O_2$

# Physical characterization of active catalysts

***PDF-XRD of Pt-FeO$_x$ vs. FeO$_x$***



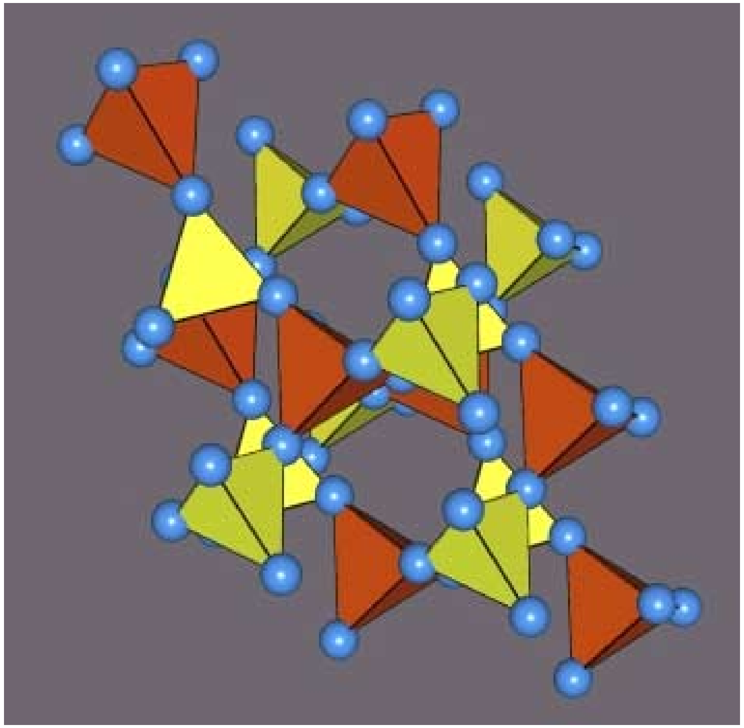

**Atomic pair distribution analysis of high energy X-ray scattering reveals key structural elements of active material**

- **Glassy network of FeO$_x$ polyhedra**
- **Pt built-in as a "glass modifier"**

**Neither TEM nor XPS show detectable differences between characteristics of active and inactive catalysts**

# Structure-property relationships in Pt-$FeO_x$

- **The atomic structure of the active Pt-$FeO_x$ electrocatalysts are best described as a glassy corner-linked tetrahedral network.**
- **Fe atoms are tetrahedrally coordinated in all of the $FeO_x$ structures**
- **Fe atoms in active catalysts have lower nominal valence/charge disproportionation (to $2^+$ and $3^+$)**
- **The Pt atoms have close proximity to the Fe sites in active catalysts**
- **Partial crystallization is observed in inactive catalysts (those heated under $H_2$, $O_2$, etc)**



The tetrahedral framework is relatively open: front view shows pores that can easily accommodate water and provide efficient transport of protons.

# Results of LANL Fuel Cell test

- Pt-$FeO_x$ catalysts cast into MEAs using LANL inking procedures
- NRL catalysts performed poorly in LANL fuel cells
- LANL also got very poor cyclic voltammetry results for NRL catalysts

NRL catalysts were clearly dead 

<u>What happened??</u>

- LANL inking process takes longer than NRL's method so full degradation had not been observed at NRL
- LANL cyclic voltammetry results repeated at NRL confirming that both labs have uniform testing methods
- NRL Pt-$FeO_x$ catalysts decompose in Nafion

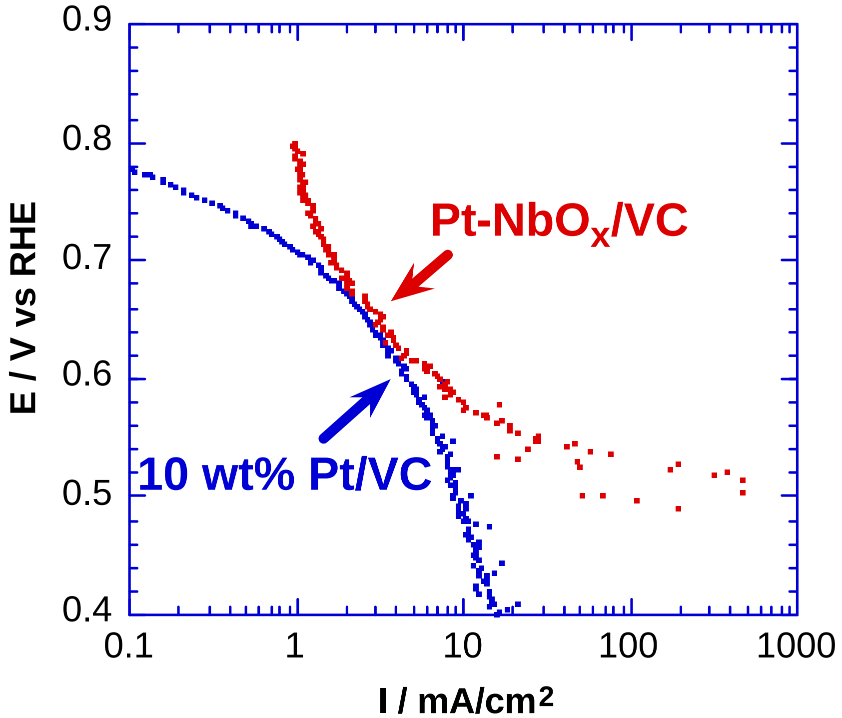
<u>Solutions to problem</u>

- Use LANL inking process at NRL
- Test CV of catalyst inks over time at NRL

# Some things we have learned

- Oxygen reduction reaction activity can be significantly increased when Pt is combined with appropriate nano-structured hydrous metal oxide
- The ORR activity of the catalysts is sensitive to the local structure of the hydrous metal oxides
- Open-framework structures provide the best supports for the Pt catalysts
- High ORR activity measured when Pt and Fe have close proximity in structures (like alloys)
- Stability/durability is the biggest problem with these materials
- Avoid transition-metal oxides that have $2^+$ and $3^+$ oxidation states under cathode conditions (e.g., Fe, Co, Ni)
- Avoid transition-metal oxides that form volatile oxides under cathode conditions (Ru)

# Pt-NbOx




**ONLY 0.06 wt% Pt in $NbO_x$ sample is comparable to 10 wt%Pt/VC (~150x lower Pt)**

- **Niobium is VERY stable to dissolution**
- **High ORR activity observed when surface of $NbO_x$ phase is decorated with Pt**
- **Electrocatalytic activity of Pt-$NbO_x$ very sensitive to $NbO_x$ preparation method**
- **Stability testing underway at NRL**

# External collaborations/support

- ONR provided financial support toward purchase of fuel-cell test station
- LANL tested Pt-$FeO_x$ catalysts and transferred method to make fuel-cell inks
- $H_2$Gen Innovations Inc. entered into catalyst characterization program with NRL

# Response to FY01 reviewers

**Range of positive and negative comments - reviewers either liked the program for being different or criticized it for being too unconventional**

## Approach

R: Some reviewers liked our new approach which others thought we should use a more conventional approach and look at bimetallic alloy systems

U: We did not change our approach because we were too early in the program a year ago to make this decision

## Progress

R: Program too young to assess

U: We think we have made a lot of progress this year, let us know what you think

## Collaborations

R: Work with LANL and UPenn

U. We did and it worked out well

R = reviewers
U = us

## Recommendations

R: Determine stability of Pt-FeOx catalysts

U. We did, and they aren't stable, but we learned a lot and now we can make more stable catalysts

# Summary and Outlook

- Low-Pt catalysts supported on nanostructured hydrous transition-metal oxides meet DOE FreedomCAR goals for low Pt-loading and cost
- Stability and durability are the major issue for this class of catalysts and efforts are underway to solve this problem
- Structural characterization of catalysts by UPenn is guiding design of new electrocatalytically active materials
- Capability to test the fuel-cell performance of catalysts internally at NRL will greatly improve progress in next year

*We gratefully acknowledge…*

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