Low Platinum Electrocatalysts for Oxygen Reduction at PEMFC Cathodes:

Atomic Structure and Electrocatalytic Activity

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Objectives

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

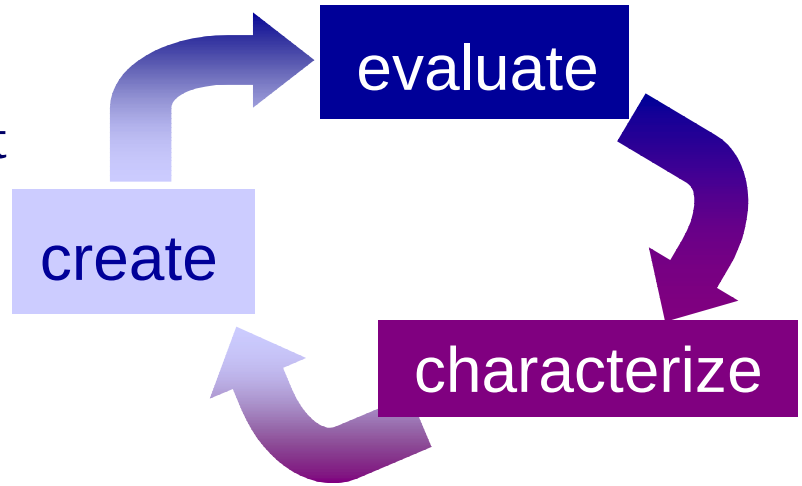
2. Improve oxygen reduction reaction (ORR) catalysis

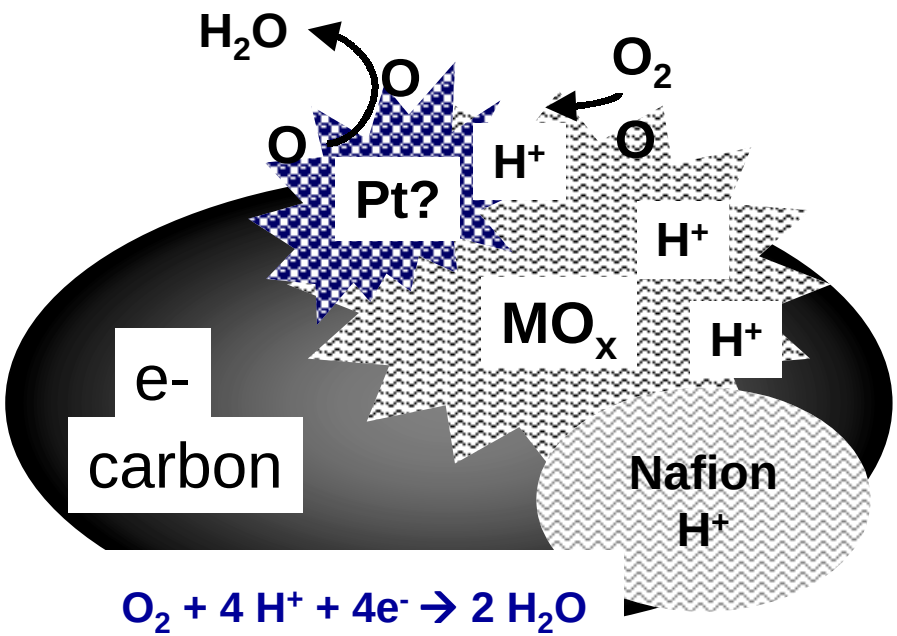
Major milestone:

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

Approach

Design efficient, low Pt electrocatalysts, which actively reduce oxygen, transport protons and electrons and water. Understand microstructural origins of the electrochemical activity and transport.



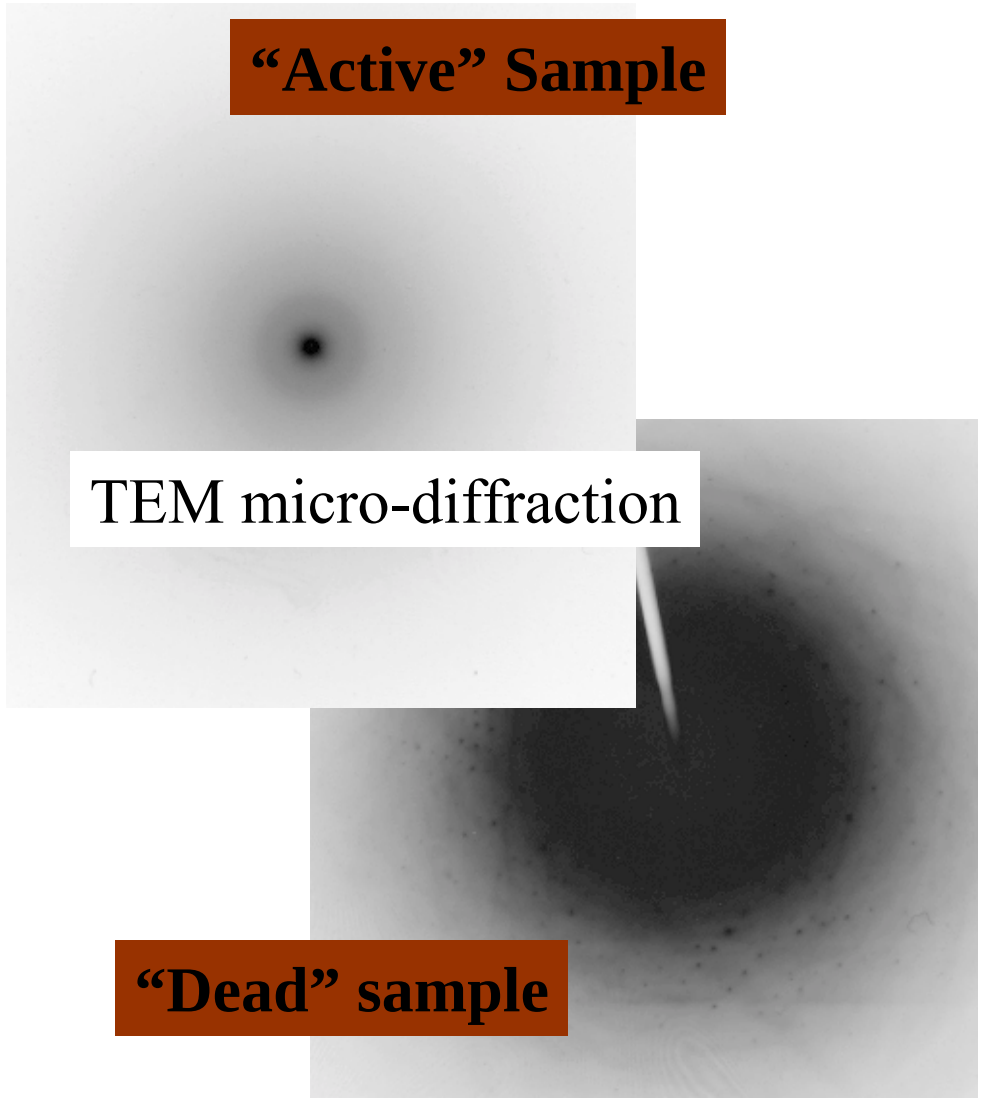


Leverage properties of hydrous transition metal oxides: efficient transport and chemical activity.

Use advanced characterization tools to identify structure property relationships

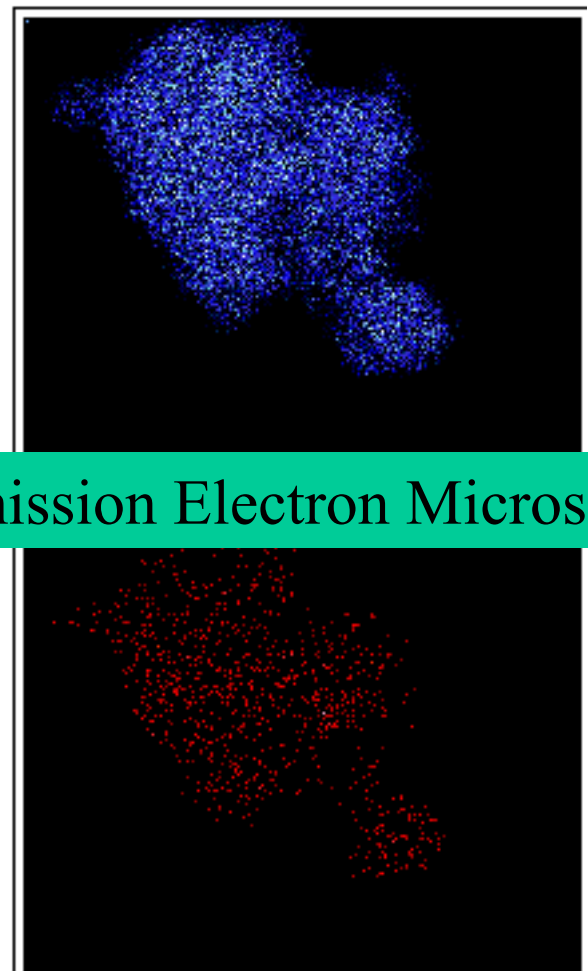
Importance of Atomic Structure

- What is the atomic structure of active catalysts?
- Which aspects of the structure are relevant for electrocatalytic activity?

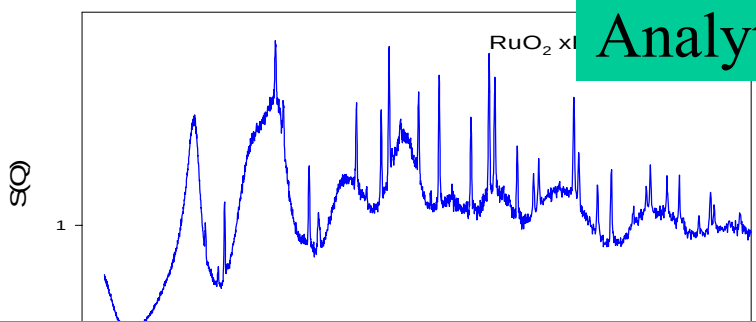


Materials and Techniques

Low Pt electrocatalysts for oxygen reduction at PEMFC cathodes: Pt-FeOx nano-mixtures show 20x ORR activity of standard 10%Pt-Vulcan carbon



Analytical Transmission Electron Microscopy



Synchrotron X-ray Scattering and Atomic Pair Distribution Function Analysis

Atomic pair distribution function (PDF) helps to elucidate the structure of complex materials.

Structure of important technological and scientific materials is not perfect! No nice "Bragg peaks" : they are disordered, inhomogenous and dirty.

PDF approach

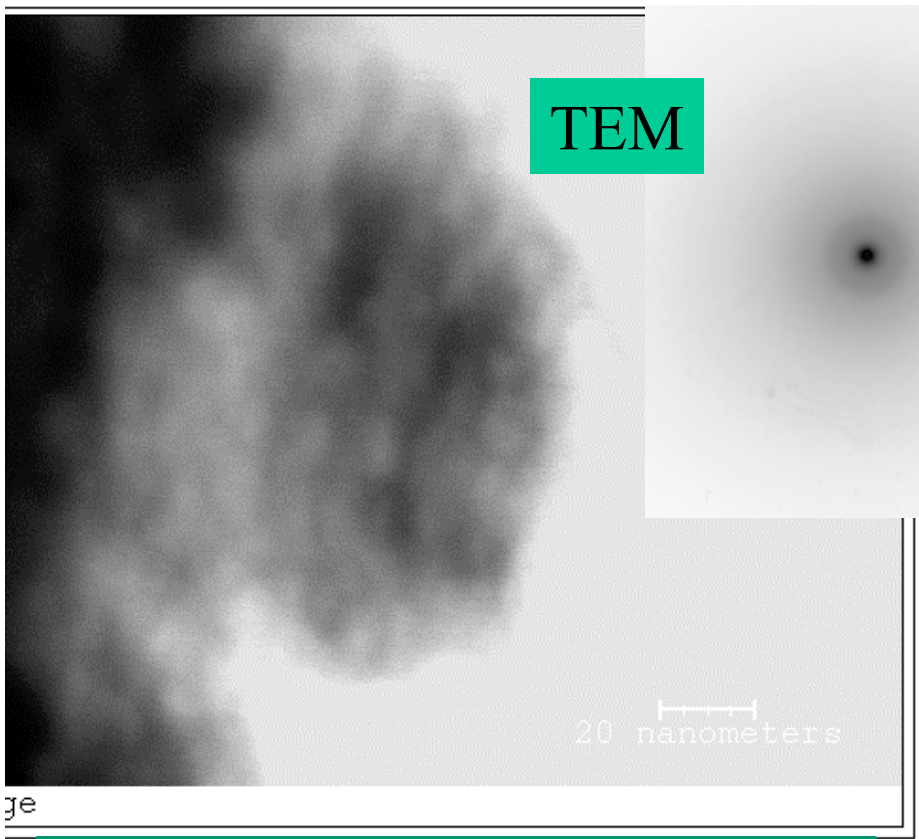
X-ray or neutron scattering is Fourier-transformed to give distribution of inter-atomic distances in a real space.

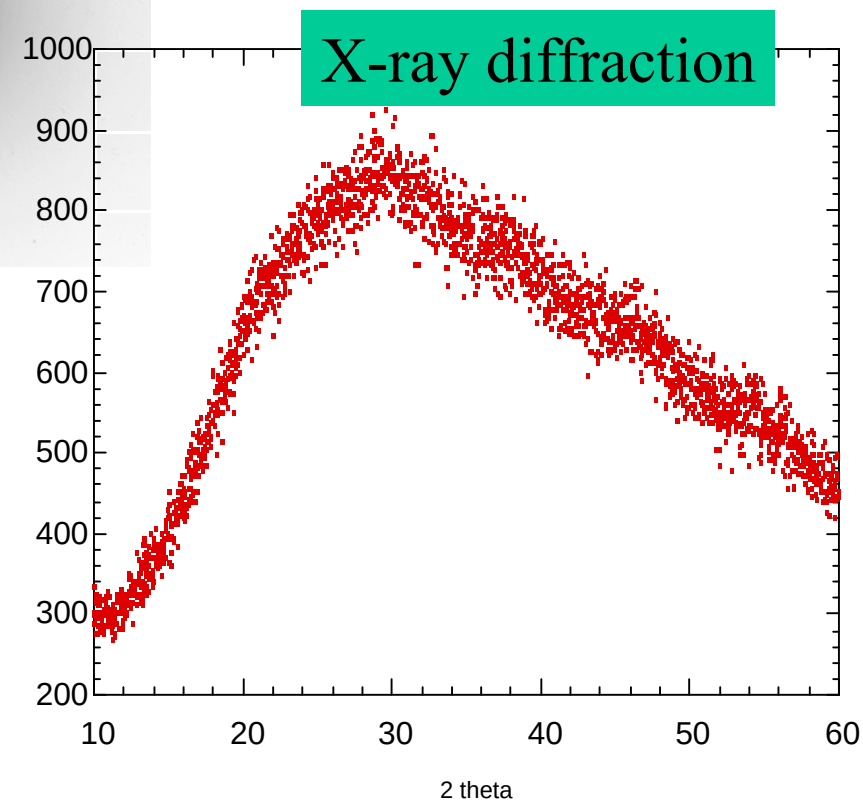
$$\rho(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^{\infty}[S(Q)-1]\sin(Qr)Qdq$$

$Q=4\pi \sin\Theta/\lambda$, S(Q) structure function (normalized diffraction intensity).

High energy, high intensity sources are essential to minimize errors and improve statistics.

Atomic Structure of Low Pt Electrocatalyst



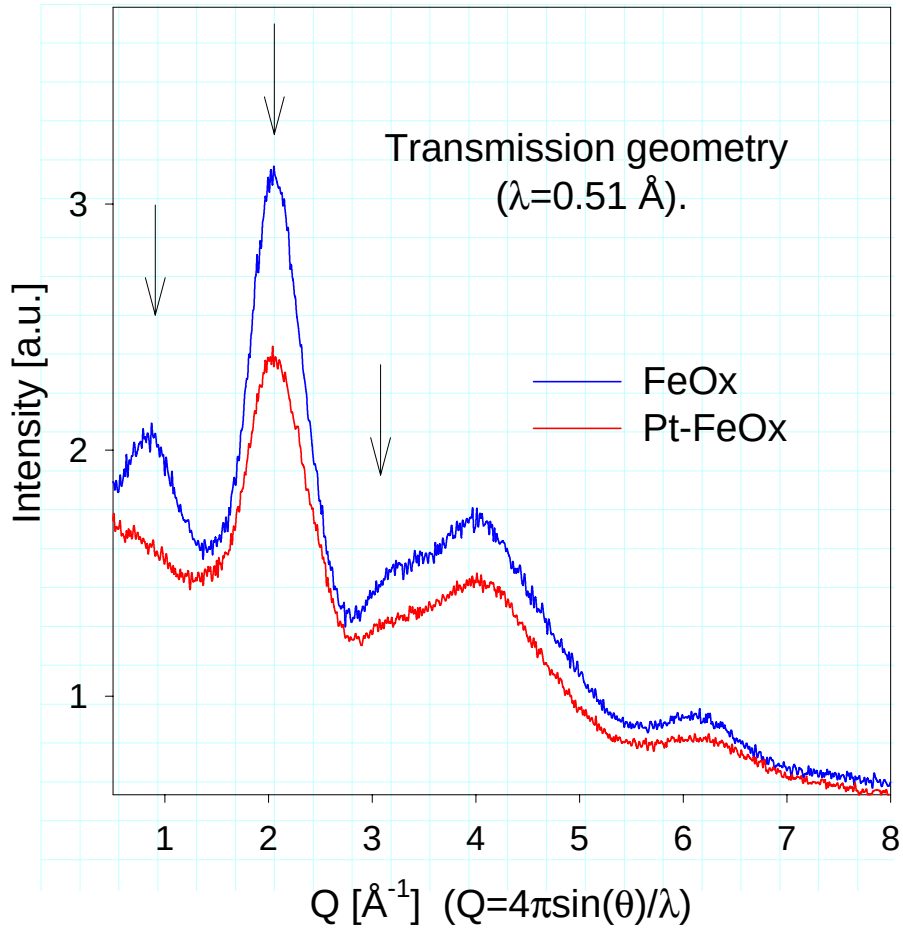


Structure of the active Pt-FeOx sample is glassy.
Can we say something more?

High Intensity High Energy X-ray Scattering

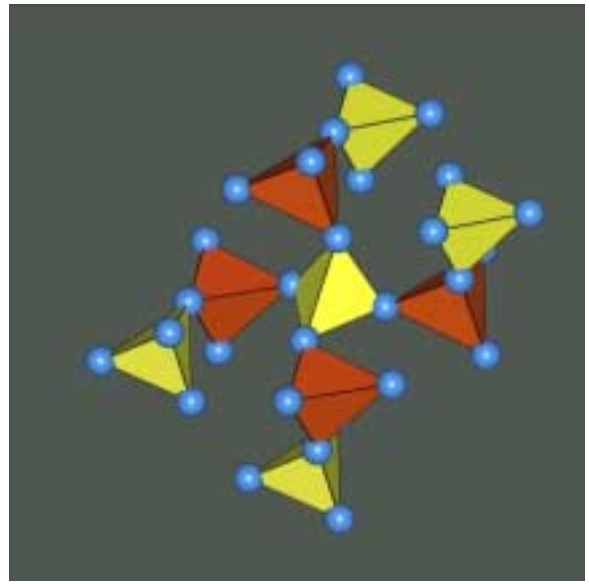
Diffraction pattern is consistent with Corner Linked Polyhedral (CLP) network (analogous to silica).

- First Sharp Diffraction Peaks indicate strong medium range order in the CLP network (arrangements of pseudo-atoms or voids).
- Addition of Pt modifies the structure.



Medium Range Atomic Structure

Glassy CLP networks have close counterparts with crystalline materials.
(For example silica is similar to quartz.)



We want to find out what kind of polyhedra are forming our glassy FeOx hydrous oxide and learn about Fe coordination.

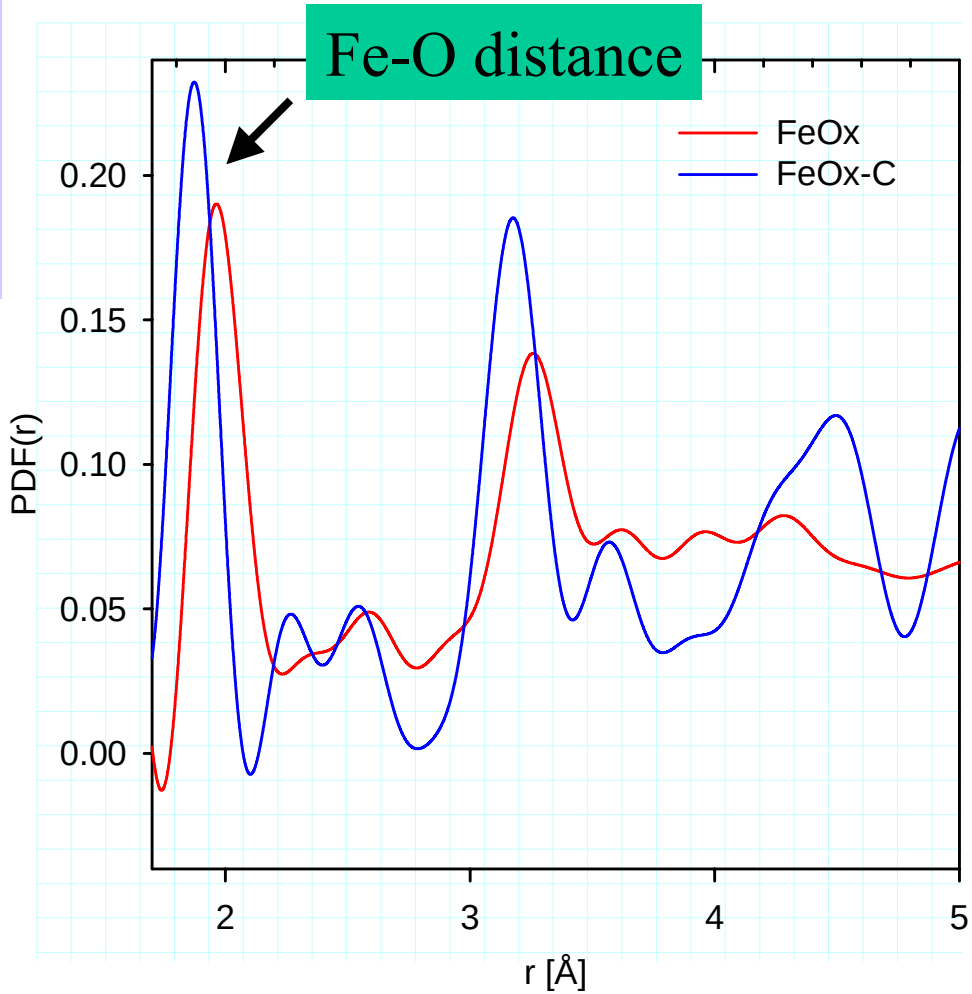
We compare the atomic pair distribution function of glassy (150-°C heated) and crystalline (600-°C heated) samples.

PDFs of Glassy and Crystalline Samples

The first peaks in the PDFs are related, indicating similar short range atomic and chemical order.

Integration of the Fe-O peak gives < 4 oxygen atoms.

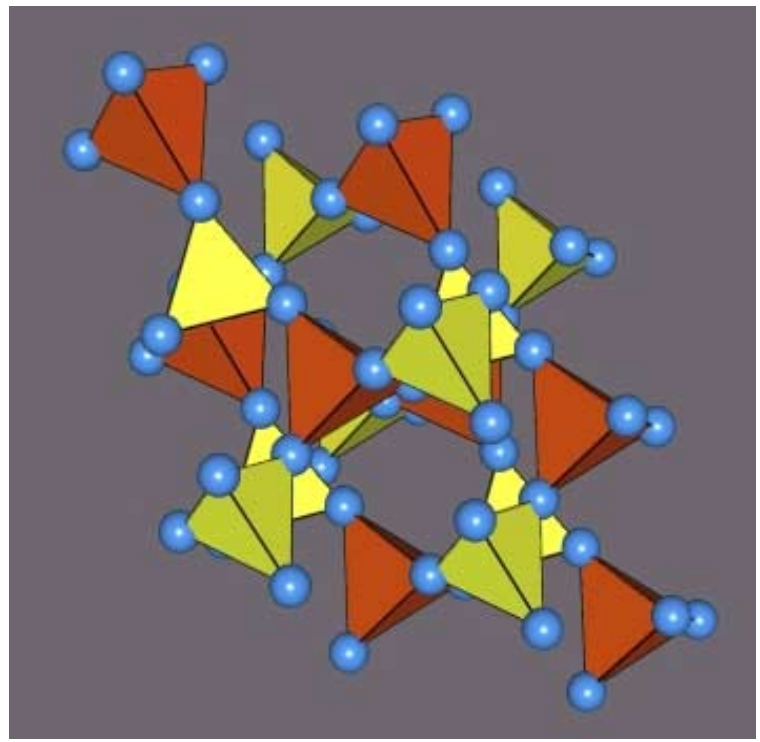
Corner Linked Tetrahedral Network



Corner Linked Tetrahedral Network

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

The PDF peaks of the glassy sample are shifted towards larger distances indicating structural swelling

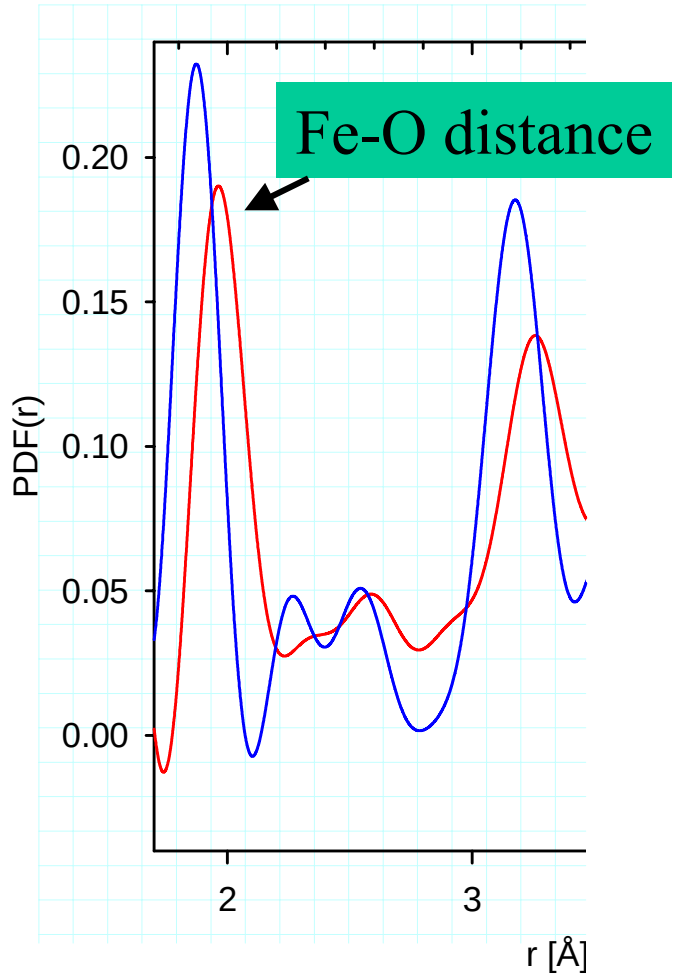


Coordination of Fe Atom in a Tetrahedron

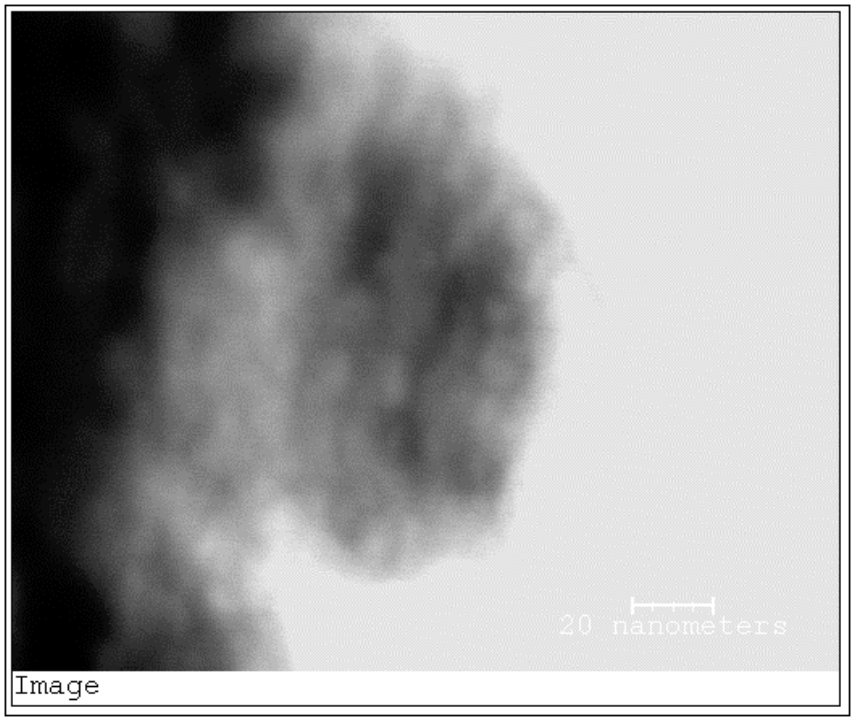
Fe-O average distance is larger in the glassy, hydrous sample (red line PDF).

Nominal valence of Fe atom is lower.

Charge can be easily disproportionated.



Inclusion of Pt in the CLT Network of FeOx



Microscopic and corresponding Z-contrast image of the 3%Pt-FeOx particle indicate uniform Pt distribution.

Pt in the CLT Network of FeOx from PDF

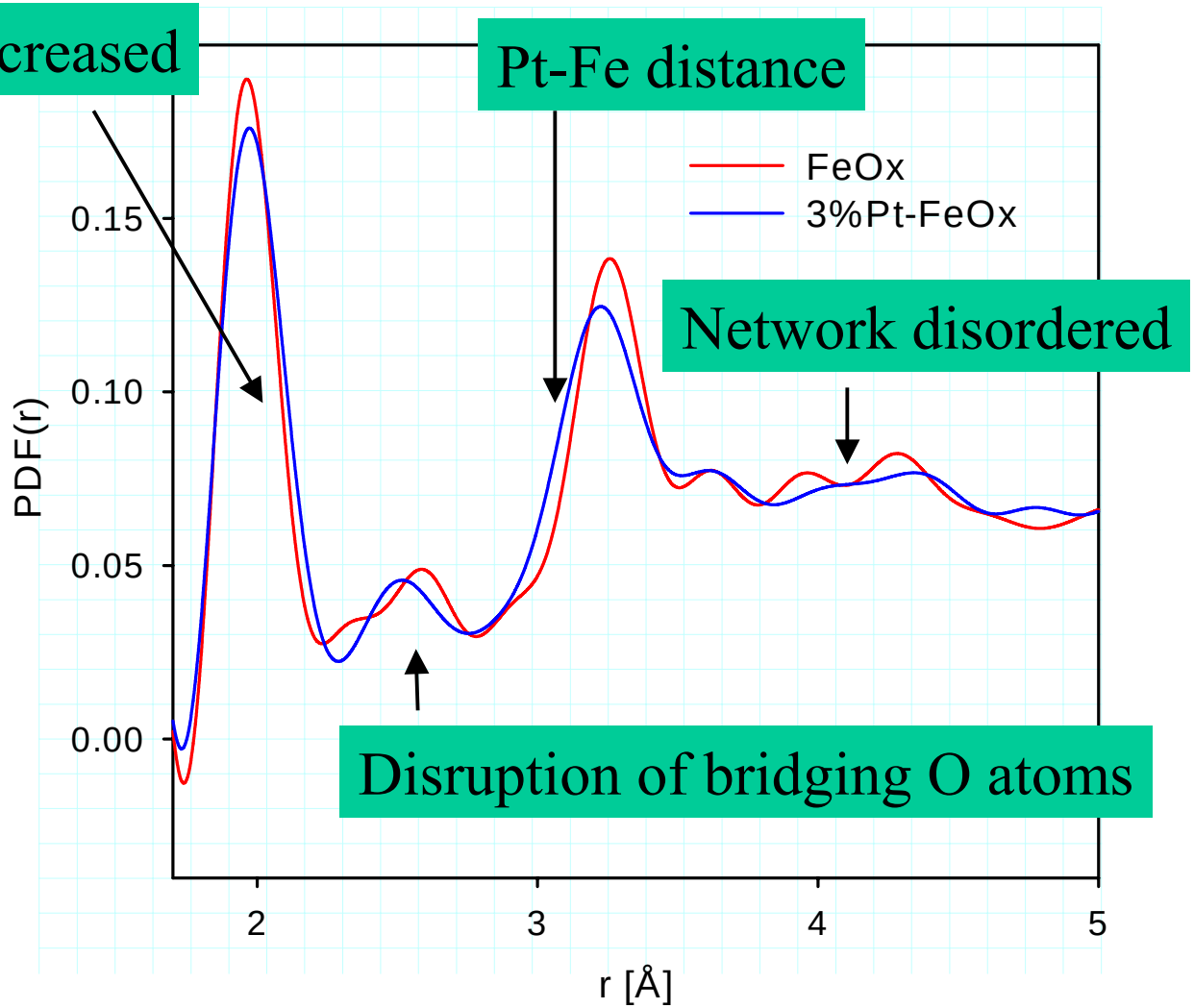
Fe-O width increased

Pt-Fe distance

Network disordered

Disruption of bridging O atoms

Pt behaves in a CLT network as a glass "modifier".



Atomic Structure of Pt-FeOx Electrocatalyst

The atomic structure of the Pt-FeOx electrocatalysts can be described as a glassy corner linked tetrahedral network.
Fe atoms have tetrahedral coordination.

Fe atoms have lower nominal valence/charge disproportionation.

Partial crystallization (H_2, O_2, or heating at high temperature) deteriorates electrocatalytic activity.

Key Structural Aspects for Low Pt Electrocatalyst

Efficient transport.

Open framework structure that can absorb water.

Electrocatalytic activity.

Fe (or other transition metal) charge disproportionation.
Fe/M to Pt proximity.

Additional Experiments and Acknowledgement

1. Small angel scattering to probe microscopic porosity.
2. High resolution XANES to investigate charge disproportionation
3. Examine other Pt-Mox structures (non-Fe) with high electrocatalytic activity

We gratefully acknowledge…

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