

### Increased Poisoning Tolerance of Pt-MO<sub>x</sub> Oxygen-Reduction Catalysts

Peter J. Bouwman,\* Margaret Teliska,\*  
Wojtek Dmowski<sup>§</sup>, and Karen Swider-Lyons  
\*Code 6171, Naval Research Laboratory  
Washington, DC 20375-5320 USA

<sup>§</sup> Department of Materials Science and Engineering  
University of Tennessee, Knoxville, TN 37996

State-of-the-art proton exchange membrane fuel cells (PEMFCs) utilize platinum metal for the catalysis of the oxygen reduction reaction (ORR) at the cathode. Unfortunately, metallic platinum catalysts are sensitive to poisoning and therefore high quality oxygen or air is required to achieve proper performance. Yet, little attention has been directed to improving catalyst tolerance to contamination of the cathode.

We are developing catalyst materials in which the Pt is supported on a microporous oxide or phosphate structure to increase the efficiency of the active Pt-sites. The 'open' support structure provides pathways for fast proton and oxygen transport and influences the ORR catalysis mechanism. In addition to facilitating the ORR, the oxide supports appear to increase the poison-tolerance of the Pt. We have studied Pt-SnO<sub>x</sub> and Pt-MPO<sub>y</sub> materials with *M* = Fe, Nb, Ta and observed a decreased detrimental effect of Pt poisoning on the ORR performance, compared to the standard Pt-VC catalyst.

The hydrous Pt-MPO catalyst materials with *M* = Fe, Nb, Ta are prepared through wet-chemical synthesis and are dried at 150°C in air. The porous support materials exhibit surface areas on the order of 150 m<sup>2</sup>.g<sup>-1</sup> and their structures are ordered only to about 7 Å, according to pair density function (PDF) analysis of high-energy X-ray diffraction. The oxidation state of the Pt varies in the samples, and appears to be ionic (Pt<sup>2+</sup>/Pt<sup>4+</sup>) in the Pt-FePO, but is metallic in the Pt-SnO.

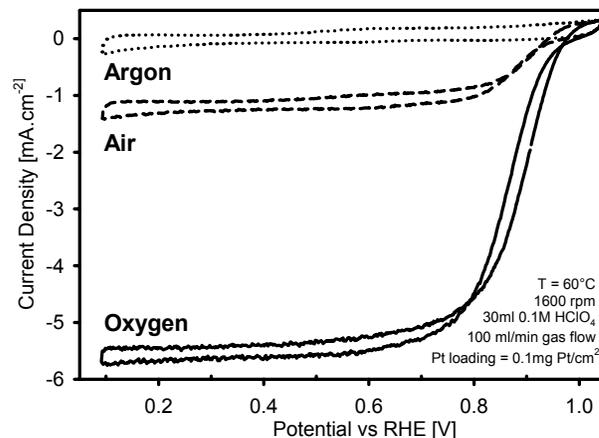
The catalyst materials are mixed with Vulcan carbon (VC) and Nafion for electrochemical characterization with rotating disk electrodes (RDEs) and in PEMFCs. Figure 1 shows the cyclic voltammograms of a 12 wt% Pt-FePO-VC on a RDE under argon, air and oxygen. No hydrogen adsorption peaks are observed at low potentials. Figure 2 shows the behavior of Pt-FePO in CO atmosphere compared to the standard Pt-VC RDE with similar Pt loading. The Pt-FePO shows CO oxidation activity, but does not adsorb CO. The Pt-VC shows a CO stripping peak under a subsequent Ar-purge, while the Pt-FePO shows no evidence of CO desorption with the same experiment.

The Pt-FePO also exhibits increased tolerance to SO<sub>2</sub> contamination. The influence is measured by pipetting a small amount of sulfurous acid solution into the electrochemical cell while monitoring the ORR rate. The HSO<sub>3</sub> is a precursor to the SO<sub>2</sub> poison found in air. The addition of 18 ppm SO<sub>3</sub> decreases the ORR activity significantly for both the Pt-FePO and the Pt-VC standard. With the second addition of 18 ppm SO<sub>3</sub>, the performance of the Pt-VC decreases another 10%, while that of the Pt-FePO stabilizes, indicating higher tolerance to SO<sub>2</sub> poisoning. Apparently the Pt-FePO has less sensitivity to poisoning or are able to recover more quickly. The sulfur-tolerance may be due to the high concentration of labile hydroperoxide species on the FePO.

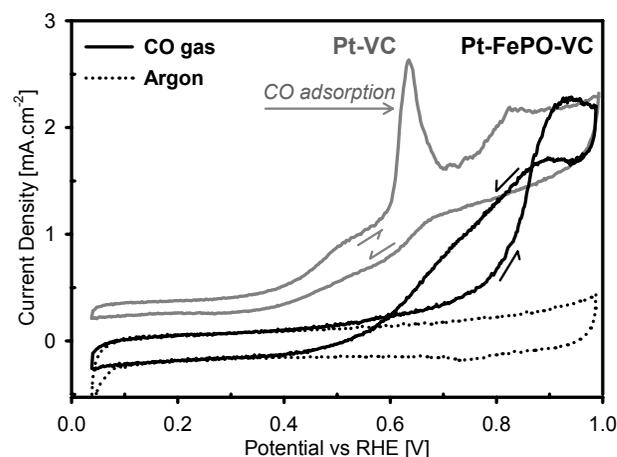
Possible mechanisms and properties of other Pt-MPO catalysts and Pt-SnO<sub>x</sub> will be discussed.

### Acknowledgements

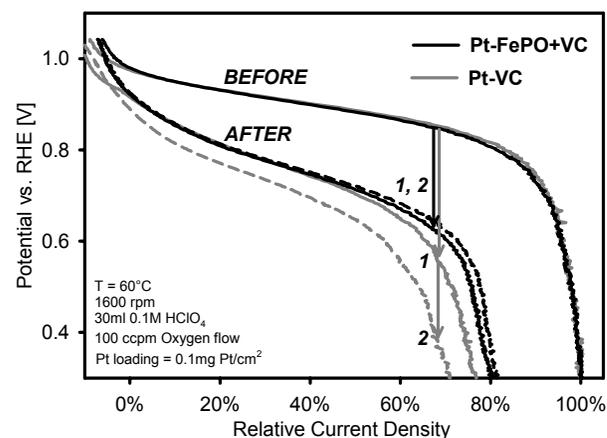
This work was supported by the Office of Energy Efficient Technologies of the Department of Energy and the Office of Naval Research.



**Figure 1:** Cyclic voltammograms of the Pt-FePO-VC RDE electrode in argon, air and oxygen.



**Figure 2:** Cyclic voltammogram of the Pt-FePO electrode and the Pt-VC standard in CO atmosphere (solid lines). In a subsequent Ar purge, the Pt-VC exhibits a distinct CO desorption peak (not shown), while there is no evidence of CO desorption from the Pt-FePO (dotted line).



**Figure 3:** Degradation of the ORR performance of Pt-FePO and Pt-VC with two additions of 18ppm SO<sub>3</sub>. Both materials show a decrease in performance with the first addition of SO<sub>3</sub>. Upon the second addition of SO<sub>3</sub> the Pt-VC performance decreases even further, while the Pt-FePO remains unchanged.