

## Mitigating Phosphate Anion Resistance with Metal-Organic Framework based ORR Catalysts

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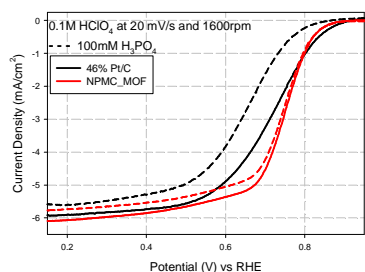
### Introduction

The oxygen reduction reaction is one of the most studied reactions in energy conversion systems due to the large overpotential engendered by the slow kinetics. Traditionally platinum based electrocatalyst have been used to facilitate ORR in acidic media, but these materials suffer poisoning effects from various anions that further inhibit this reaction. Phosphoric acid fuel cells (PAFC) presently operate at 80% combined heat and power efficiency, but the cathode materials suffer poisoning effects from phosphate ion adsorption ( $\text{H}_2\text{O}_4^-$ ) limiting the performance<sup>2</sup>. Anion adsorption is structure dependent and it has been shown that some Pt-alloys exhibit a heightened tolerance to phosphate poisoning<sup>3</sup>. Non-precious metal catalysts (NPMC) for ORR containing Fe and/or Co have been investigated for many years and recent progress in the synthetic strategy have now made these materials viable contenders with Pt-based catalysts for use in proton exchange membrane (PEM) fuel cells<sup>4</sup>. NPMCs are synthesized by combining metal ions, typically Fe or Co, with a source of carbon and nitrogen, followed by a heat treatment between 500-1000 °C to generate the active catalyst. NPMCs are typified by the source of the precursors used in the synthesis and can be further segregated by the type of gas used in the heat treatment. Our group has recently began investigating an alternative synthesis procedure in which the carbon support comes from a metal-organic framework (MOF) and is synthesized with the precursors in a one-pot technique that eliminates several steps from the typical procedure.

### Experimental

The rotating disk electrode (RDE) technique was used in 0.1 M  $\text{HClO}_4$  with varied concentrations of  $\text{H}_3\text{PO}_4$  (1 to 100 mM) to determine the effect of phosphate poisoning on the kinetic parameters of ORR.

In-situ X-ray absorption spectroscopy was used in conjunction with the electrochemical measurements with 0.1 M  $\text{HClO}_4$  with and without 100 mM  $\text{H}_3\text{PO}_4$  as a function of the potential. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) were measured. In addition, using the  $\Delta\mu$  XANES analysis procedure provided surface specific information



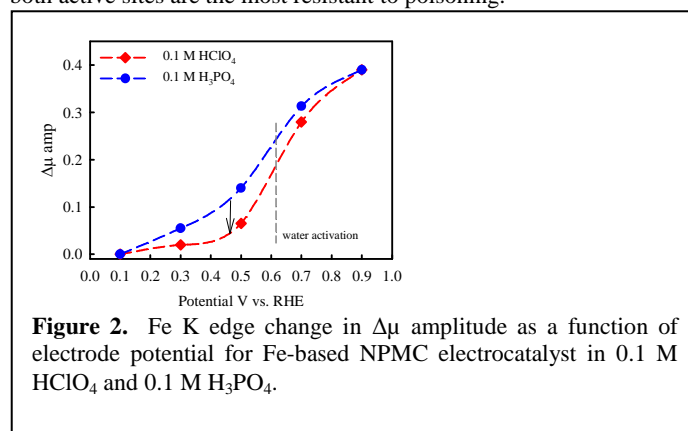
**Figure 1.** RDE voltammograms of ORR at Fe-MOF-NPMCs vs. Pt/C in 0.1 M  $\text{HClO}_4$  with addition of 100 mM  $\text{H}_3\text{PO}_4$ . Current density was based on normalization of voltammetric current to the geometrical area of the electrode. Rotation rate 1600 rpm. Scan rate 20  $\text{mV s}^{-1}$ .

about phosphate ion adsorption on the surface as a function of potential.

### Discussion

To determine the resistance of NPMCs to poisoning, RDE experiments were carried out with incremental addition of  $\text{H}_3\text{PO}_4$  to 0.1 M  $\text{HClO}_4$  represented in Figure 1. Both the onset potential, ~0.9 V vs RHE and well-defined diffusion limiting current was achieved by the MOF based NPMCs as in concert with Pt/C. Phosphoric acid was added in ten-fold increments, in contrast to Pt/C, which typically loses between 100-130 mV at  $E_{1/2}$ , the NPMC exhibited no unfavorable effect on the on-set potential and kinetic activity indicating immunity to phosphate ion adsorption.

In-situ XAS experiments were conducted in 0.1 M  $\text{HClO}_4$  and then repeated with the addition of 100 mM  $\text{H}_3\text{PO}_4$ . The EXAFS indicates two types of metal coordination present in NPMCs, M-N/O or a M-M coordination, which we attribute to the two active sites of these types of catalysts, M- $\text{N}_4$  or metal nanoparticles (NPs). The degree of each of these coordination environments present in NPMCs varies based on the synthetic pathway used. We looked at a variety of NPMCs with XAS and found varying differences in the XANES spectra between 0.3-0.7 V vs RHE when the phosphate ion is present in the electrolyte. We used the  $\Delta\mu$  XANES analysis procedure to investigate the surface interactions, an example of this is shown with a plot of the  $\Delta\mu$  amplitude vs applied potential in Figure 2. Based on the differences in the  $\Delta\mu$  amplitudes between the clean electrolyte and phosphate ion electrolyte it is possible that  $\text{H}_2\text{PO}_4^-$  binds preferentially with NPs and catalyst that possess a combination of both active sites are the most resistant to poisoning.



**Figure 2.** Fe K edge change in  $\Delta\mu$  amplitude as a function of electrode potential for Fe-based NPMC electrocatalyst in 0.1 M  $\text{HClO}_4$  and 0.1 M  $\text{H}_3\text{PO}_4$ .

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### References

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