Understanding Electrocatalytic Pathways in Complex Organic and Inorganic Composites in Aqueous and Non Aqueous Environments’

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Recent advances in our understanding of alternative active sites for oxygen reduction has provided for the basis of its molecular design. This presentation put these developments in the context of more than two decades of effort devoted to engendering such non noble metal electrocatalysts. In this presentation we will present our latest data on the most active analogs which comprise of a FeNₓ coordinated active site in close concert with Fe nano-particles either present in some polymer composite or more ideally as edge defects close to the Fe-Nₓ coordinated structure. We will show how these active sites evolve on carbon supports as graphene defect structures. Such active site determinations are made with the use of a special in situ synchrotron x-ray absorption method using the near edge spectra referred to as x-ray absorption near edge structure (XANES), in a subtractive mode wherein the signal contribution from the bulk is successfully subtracted from the effect of the surface adsorbed species. When combined with our ability to simulate the same signatures using models with specifically adsorbed moieties, a powerful tool emerges to study electrochemical interfaces under actual in situ and operando conditions. This technique, commonly called the ‘Delta Mu (Δµ) Technique’ has been applied to a wide variety of transition metal surfaces and alloys (1-2) including non-Pt based metal electrocatalysts with element specificity. EXAFS data taken concurrently provide information on the changes in short range atomic order around the absorber atom thereby providing structural information such as bond distances and coordination numbers (thereby information on average cluster size, homogeneity and surface segregation etc.). We will describe (a) the important distinction of new emerging materials as distinct form past efforts in this arena where materials were derived from N₄ containing macrocycle. (b) We will present the emergence of highly active sites in the context of a wide range of preparation methods and nature of precursor materials. Such distinction is manifest in the comparison of pyrolyzed Fe-Tetraphenyl porphyrin (Fe-TPP) where the starting material contains existing N₄ coordination and those where the active material emerges as a function of a metal polymer composite pyrolysis. Comparison shown in Fig. 1 where in situ Fourier transform (at Fe K edge) is shown for a Fe-TPP catalyst under a potential of 0.3 V with corresponding spectra of the as received catalyst (ex situ) and Fe foil reference. Important points to note is (a) the presence of two separate peaks corresponding to Fe-N/Fe-O and Fe-Fe interactions in the as received sample and he complete removal of the Fe-Fe interactions in the sample measured in situ at 0.3 V vs. RHE. This is expected to happen when considering the pH of 1 expected with 0.1 M HClO₄. The N-coordinated Fe however remains stable. On the other hand the Fourier transforms for catalyst prepared using Fe-polymer composites (Fig 2) shows that both the Fe-N and Fe-Fe interactions are maintained in the catalyst on exposure to the electrocatalyst. This is shown using a Fe-PANI (Fe-Polyaniline) catalyst obtained from Los Alamos National Laboratory.

In this presentation among other things we will provide a picture of the electrocatalytic pathways in aqueous (at both the extreme edges of the pH scale) and non-aqueous environments. The technological consequence of such materials in power generation, electrolysis and energy storage will be described.

References