

Oxygen Reduction at M-N_x and M/M_xO_y based Non-Noble Metal Centers: Investigation of Active Site Structure and Function

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Metal-nitrogen-carbon (M-N-C) systems are the most promising among non-precious metal-based catalysts for oxygen reduction reaction (ORR) in fuel cells. Several publications in recent years, have shown very well performing MNC catalysts [1-4], where high temperature pyrolysis has been found to be a crucial step of transforming metal-nitrogen-carbon-C precursors into ORR-active systems. However, profound understanding of the origin of ORR activity of these materials is needed to speed up process activity towards $\sim 1/10^{\text{th}}$ of the Pt/C mass activity (A/g_{Pt}) [5] and stability targets (5000 hrs) [6].

The high temperature pyrolysis being final synthesis step of MNC catalysts results in formation of several possible Metal-Nitrogen centers (described in earlier reports as M-N₂/C, M-N₄/C, M-N₂₊₂/C) incorporated into graphene plane, and/ or its edge [7-12]. According to density functional theory (DFT), the M-N_x coordination, especially M-N₄ has highly synergic effect in formation of stable defects in the graphene-like surface [8]. At higher pyrolysis temperatures ($> 800^{\circ}\text{C}$), part of the transition metal precursor transform into other forms including metal nanoparticles (M_{NPs}) and/or their oxides ($\text{M}/\text{M}_x\text{O}_y$). The $\text{M}/\text{M}_x\text{O}_y$ moieties stay intact even after several acid washing, and while exposed to hours-long electrochemical experiments in acidic environment. This stability has been attributed to the presence of protective graphene-like layers surrounding the metal nanoparticles [1]. The latest has been demonstrated in highly active PANIFeCo material developed by Wu et al [1].

While some argue that these metal nanoparticles play no role in catalytic MNC activity towards ORR [13], others insist otherwise [14, 15]. Olson et al. in one of their earlier publication proposed bi-functional mechanism, favoring two-step ORR pathways by presenting evidence for the second step to be facilitated by presence of metal nanoparticles coated with a thin layer of their native oxides $\text{M}/\text{M}_x\text{O}_y$ [14]. Catalysis of chemical disproportionation, and/or electrochemical reduction of peroxide intermediate by surface stabilized $\text{M}/\text{M}_x\text{O}_y$ species have been explored by other groups [14-16]. It is still questionable; however, which pathways involving peroxide intermediate take place following its formation in the 1st step of the ORR process, and what is the optimum structure of the active site/s in terms of long term stability.

A role/s of M-N_x and $\text{M}/\text{M}_x\text{O}_y$ moieties in MNC towards ORR activity have been further investigated employing electroanalytical methods such as rotating disc electrode (RRDE), cyclic voltammetry

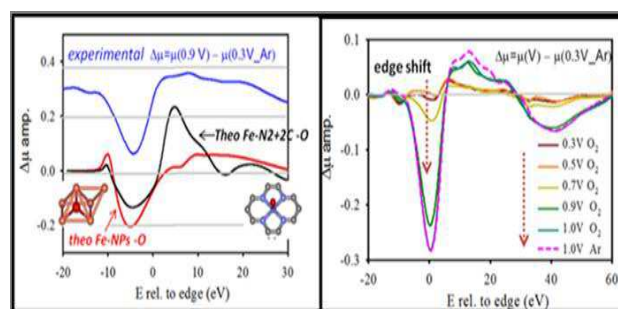


Figure 1: Delta Mu ($\Delta\mu$) spectra of NEU-FeNC collected in-situ at the Fe-K-edge representing changes on the Fe-surface as a function of potentials showing metal interaction with various oxygenated adsorbates. The figure (a) represents a comparative delta mu of theoretical $\text{FeN}_4\text{-O}$ ($\Delta\mu_{\text{Fe-N}_4}$, in black), and Fe-O in Fe-foil ($\Delta\mu_{\text{FeNPs-O}}$, in red) models with the experimental curve measured at 0.9 V vs. RHE shown in blue. (b) Shows the progression of the experimental spectra as a function of potential.

(CV), and chronoamperometry (CA) coupled with in situ x-ray absorption spectroscopy (XAS) and advanced subtractive technique referred to as ‘delta mu’ ($\Delta\mu$) [17-19]. The latter provides site-specific adsorption information on the nature of adsorption of various adducts from the electrolyte as well as reactants such as oxygen (Fig.1). Based on structural changes of selectively distorted MNC catalyst we will present strong evidence of single site ORR catalyzed by Fe-N₄ species in alkaline media and two-site ORR mechanism in acidic pH with evident supportive role of stabilized $\text{M}/\text{M}_x\text{O}_y$.

Acknowledgments:

Financial support for this work comes from the US-DOE-EERE fuel cell technology program: Development of Novel Non-PGM Electrocatalysts for PEM Fuel Cell Applications (S. Mukerjee, NEU, PI). The in situ XAS was run at Beamline X3B at NSLS located at Brookhaven National Laboratory (BNL) in Upton, NY, which is supported by the Department of Energy (DOE). Support from beamline personnel Dr. Erik Farquahar (X3B) is gratefully acknowledged.

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