## Structure and Reactivity of Fe-N-C Non-PGM Cathode Catalysts Derived by the Sacrificial Support Method

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One rapidly developing class of the state-of-the-art nonplatinum group metal (non-PGM) catalysts for oxygen reduction reaction (ORR) is represented by complex nanostructured materials composed of a transition metal, nitrogen and carbon, thus often abbreviated as M-N-C.<sup>1</sup> There are several ways to synthesize those materials, either through pyrolysis of macrocyclic compounds or through heat treatment of mixture of transition metal precursor (usually a salt) and source of carbon (often a carbon black) and a nitrogen source that could be ammonia, cyanamide, urea or amines of various types, or a polymer containing nitrogen.

Since 2000 UNM has been developing an original method of catalyst synthesis that is based on tinplating of mono-dispersed of hierarchically structured silica particles: the *Sacrificial Support Method* (SSM. This method allows producing catalysts with an open-frame morphology at the meso-scale and at the same time eliminates the "formal" support, thus the entire catalyst is the "active material".<sup>2</sup> During the pyrolysis the support ensures the catalyst dispersion and is responsible for the resulting high-surface area. After the pyrolysis, silica (the sacrificial support) is removed by dissolving in KOH or HF, resulting in self-supported M-N-C catalyst. We have demonstrated catalysts made by SSM derived from porphyrins<sup>2-5</sup>, heteroamines<sup>6,8</sup> and polymers.<sup>7</sup> We have studied these catalysts intensely by XPS<sup>2</sup> and EXAFS/XANES<sup>4</sup> and have made suggestions on the ORR mechanism.<sup>5,8</sup>

Exceptionally active catalysts were developed based on the SSM and derived from Fe salt and N-containing organic salts. These cathode catalysts meet DOE-EERE non-PGM targets of performance in PEMFC single MEA tests: 0.8 V at 0.1 A at 1.5 Bar total pressure.

Understanding of the nature of active sites in non-PGM catalysts is difficult due to high heterogeneity of such materials. It should be noted, however, that both XPS and EXAFS/XAN studies are converging on the fact that most catalysts of this class, regardless of the precursors used, when optimized for performance in ORR, display a similar set of Fe and N moieties incorporated in a carbonaceous matrix. SSM provides a unique opportunity to study the structure and reactivity of M-N-C catalysts as there is no "support effect" and the activity exceeds the state-of-the-art in non-PGM.

All the M-N-C catalysts display plurality of active sites that have reactivity in ORR. Some of these sites support oxygen reduction to peroxide, some are active in peroxide reduction to water, some are active in both reactions and some may support a 4e<sup>-</sup> reduction of oxygen to water. In the actual catalyst a plurality of such moieties is presents and they all contribute to the integral activity. In this work we introduce the approach of interpreting the structure of the active sites as *defects in graphene*.

Detailed XPS and EXAFS/XANES analysis revealed correlations between chemical species and ORR activity providing sufficient information on the nature of active sites. We will report on the role of the in-plane Fe-N<sub>4</sub> and Fe-N<sub>3</sub> defects; Fe-N<sub>2</sub> and Fe-N<sub>2+2</sub> edge defects; metal-less N and O moieties as well as reduced metal and metal oxide nano-phases and will show their correlation with the catalyst activity in ORR individual reactions. Relative contributions of these different active sites to the overall cathode process will be assessed.



**Fig 1:** XPS N1s spectra of Fe-carbendazim derived catalyst showing a suggested composition of several N moieties. The same moieties are schematically drawn as in-plane and surface defects in a graphene sheet and are conceptually related to the morphology of the catalysts, which is supported by HR-TEM observations.

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