

## Investigation of C-N containing ligands on the ORR activity of Fe-based catalysts

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### BACKGROUND

In a PEMFC, the catalytic materials typically consist of Pt nanoparticles (NPs) distributed on a high surface area carbon support. However, there are still kinetic losses seen at the cathode during the oxygen reduction reaction (ORR) (1) and the high cost of Pt is another drawback. For these reasons, research is being increasingly directed towards the development of less costly non-precious metal (NPM) catalysts for the ORR, such as heat-treated Co and Fe based macrocycles (2,3) on carbon, and mixtures of low cost transition metal compounds heat-treated in various gaseous atmospheres (4,5).

Our previous work has focussed on the fabrication of NPM catalysts from a Fe or Co oxide sol or gel and then adding a low cost N-containing ligand (e.g., phenylenediamine or aniline), followed by mixing with carbon powder and heat-treatment. The hypothesis behind this synthesis has been that the viscosity of the gel would ensure that a reasonably thick layer of metal-ligand would remain on the carbon support surface to ultimately form the catalytic layer. Indeed, it is found (5) that the metal content is relatively high, from 2-5 wt %, and the N content is also high, up to 5 wt %. It is evident from our earlier work (6,7) that this type of synthesis ensures the formation of metal-nitrogen complexes bonded to the carbon surface, likely forming polymeric species during the synthesis step. Our catalysts have exhibited high ORR catalytic activities and low H<sub>2</sub>O<sub>2</sub> % yields compared to many other NPM catalysts reported in the literature (8).

The present work is focused on the evaluation of a range of nitrogen (N)-containing ligands, such as diaminotoulene, aniline, and others, some of which can thermally polymerize after adsorption onto carbon powder (5-7). These ligands were mixed with an Fe-based salt and carbon, and then thermally treated. with the results compared to those obtained with phenylenediamine (pda). The primary goal of this work has been to determine whether a polymeric intermediate is key to producing a high performance and durable NPM-based ORR catalyst.

### METHODS & RESULTS

FeCl<sub>3</sub>.6H<sub>2</sub>O was dissolved in absolute ethanol and ethyl acetate, refluxed under Ar, and then an exact volume of the nitrogen-containing ligand solution was added drop-wise to the Fe precursor solution. These solutions were then loaded onto Vulcan XC-72R carbon with sonication, then

gravity filtered and ground to achieve good mixing and a smaller particle size. Heat-treatment of the carbon powder supported catalyst was carried out under a stream of N<sub>2</sub> in a tube furnace at a range of temperatures (from RT to 1100°C). The catalysts were then mixed with a 1% Nafion solution, applied to the electrode surface, and air-dried. Electrochemistry was carried out using a glassy carbon rotating ring disc electrode (typically at 1000 rpm), coated with the catalyst, and using a Pt ring to monitor hydrogen peroxide production. Cyclic voltammograms were collected in a N<sub>2</sub> purged 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, followed by studies in O<sub>2</sub>-saturated conditions.

It was found that the best ORR catalysts were formed from ligands that yield a polymeric phase during the heat-treatment process, as seen particularly clearly from the CV response (in the absence of O<sub>2</sub>) for catalysts heated to roughly 500°C (5). A detailed analysis of the electrochemistry of these materials will be presented as a function of their heat-treatment temperature. Finally, the effect of the ligand, as well as how it was thermally treated, on its resistance to dissolution in acidic media will also be discussed.

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