

Role of nitrogen functional groups in nanostructured carbon catalysts for oxygen reduction reaction in PEM and direct methanol fuel cells

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Introduction

For more than 40 years, C-N catalysts have been studied as alternates to Pt oxygen reduction reaction (ORR) catalysts for fuel cells. The first C-N catalysts were macrocycles[1]. Later, these were heat treated to increase stability while maintaining activity[2,3]. To eliminate the expensive macrocycles, simple precursors of nitrogen, carbon and transition metals (such as ammonia, carbon black, and iron acetate) were heat treated together to also form active C-N catalysts[4]. At Ohio State, C-N ORR catalysts have been prepared using acetonitrile pyrolysis over oxide supports with or without metal doping [5-7]. The oxides and exposed metals were washed away after pyrolysis, leaving nanostructured CN_x catalysts. These were found to be active for ORR in both PEM[5-7] and DMFCs[8].

Today, the nature of activity of these C-N catalysts is unclear. Although, in general, it is believed that N plays a role, how it enhances activity is still debated. While some argue that the activity stems from metal-N₂ or metal-N₄ centers [9] others believe that metal does not play a role in the activity and that N in the graphitic structure is the source of activity[10-12]. Results from both schools of thought have shown that an increase in pyridinic-N correlates to increased ORR activity.

Materials and Methods

CN_x catalysts were prepared using acetonitrile pyrolysis over oxide supports[5-7]. Additional catalysts were prepared by growing carbon nanostructures with varying degrees of edge-plane exposure and then post treating with N-containing reactants including NH₃ and HNO₃. The resulting CN_x catalysts were characterized using X-Ray Photoelectron Spectroscopy (XPS), Transmission Electron Microscopy (TEM), BET surface area analysis, X-ray diffraction, laser Raman spectroscopy and Temperature Programmed Oxidation (TPO) experiments. These catalysts were tested for activity and selectivity to ORR using the Rotating Ring Disk Electrode (RRDE) technique. Catalysts were also tested for tolerance and inactivity to methanol using RRDE methods in the presence of methanol.

Results and Discussion

Through the development of CN_x catalysts made by acetonitrile pyrolysis, it has been found that both N-content and nanostructure play a significant role in ORR activity. As both the edge plane exposure (stacked cup nanofibers compared to multi-walled nanotubes, fig. 1) and pyridinic-N content (located on the edge plane of graphite) increase (fig. 2), the ORR activity increases.

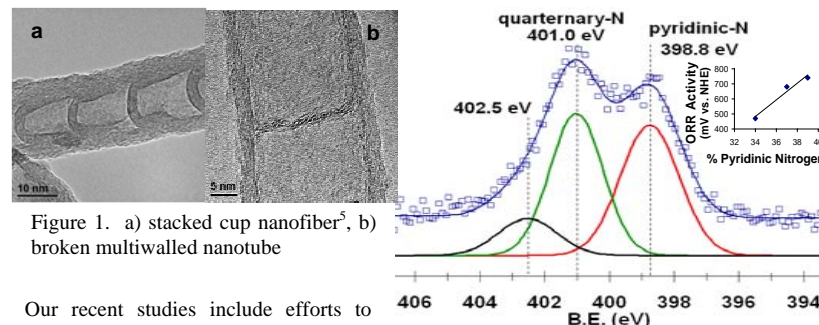


Figure 1. a) stacked cup nanofiber⁵, b) broken multiwalled nanotube

Our recent studies include efforts to decouple the effects of carbon nanostructure, and the location, abundance and the nature of nitrogen functional groups. To achieve this, carbon nanostructures with different edge plane exposures have been synthesized and *in-situ* or post-synthesis incorporation of nitrogen functional groups have been performed. To elucidate the nature of active sites, selective site blocking techniques using boron and phosphorus have also been used.

Significance

This study focuses on understanding the source of activity in CN_x catalysts. Once the nature of active sites is understood, targeted modification of CN_x catalysts will be possible to achieve the maximum ORR activity. Ultimately, this could lead to the replacement of Pt-based ORR catalysts with less expensive CN_x materials, especially in DMFCs where methanol crossover allows Pt to react with methanol and oxygen at the cathode, causing significant power losses. In our studies, CN_x catalysts are shown not to be affected by methanol crossover to the cathode[8].

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