

V.P.12 Investigation of the Oxygen Reduction Reaction Activity of Heteroatom-containing Carbon Nano-structures

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Objectives

The main goal of the proposed work is to undertake a fundamental investigation of the ways of modifying the nanostructure of precious metal-free carbon catalysts and their functional groups to enable their use as oxygen reduction reaction (ORR) catalysts in proton exchange membrane (PEM) fuel cells and direct methanol fuel cells (DMFC). The project targets investigation of the nature of active sites and the ways to create these active sites for oxygen reduction reaction by molecular tailoring of the carbon nanostructures and surface moieties.

Technical Barriers

Platinum supported on carbon is the current catalyst used for ORR at the cathode in PEM and direct methanol fuel cells. The cost and availability of platinum is a barrier in wide-spread applications of PEMFC and DMFCs. Carbon-based ORR catalysts offer an alternative. The role of heteroatoms and the nature of the active site in these catalysts are heavily debated and need to be better understood before increased activity, current density and stability of these catalysts can be achieved. The work we are doing aims to develop a better understanding of the role that heteroatoms play in these catalysts, especially in terms of the active site.

Abstract

Heteroatom-containing carbon nanostructures are being investigated as catalysts in the oxygen reduction reaction (ORR) for PEM and direct methanol fuel cells. Heteroatoms including nitrogen, phosphorus and sulfur are being incorporated into various carbon nanostructures to study the role that heteroatoms and nanostructure play in ORR activity and selectivity. It has

been found that sulfur can be used as a growth promoter in nitrogen-containing carbon nanostructures (CN_x), but does not participate in ORR and introduction of phosphorus can increase ORR activity in CN_x . Oxygen surface groups can increase the selectivity of CN_x catalysts. Additionally, nanostructure control is being developed to study the role of graphitic edge planes plays in ORR. Work is also ongoing in examining the corrosion characteristics of the catalysts developed. Full fuel cell tests with the most active catalysts are also in progress.

Progress Report

Investigation of the role of sulfur in CN_x catalysts.

Commercially, carbon nanofibers are produced using a sulfur growth promoter to increase yield. The impact of sulfur use on the end-use of nanofibers is not commonly discussed or understood. When we introduced sulfur, in the form of thiophene, into the acetonitrile pyrolysis feed used to produce nitrogen containing carbon nanostructure (CN_x) catalysts, the CN_x yield increased. Through X-Ray Photoelectron Spectroscopy (XPS), temperature programmed desorption (TPD) and temperature programmed oxidation (TPO) experiments, it was found that sulfur was both adsorbed to the CN_x surface and incorporated into the graphitic matrix. As long as acetonitrile was still in the fiber growth feed, ORR activity was unaffected by the growth promoter concentration or the amount of sulfur incorporated into the CN_x . These results also indicate that sulfur, as incorporated in this study, does not play a role in ORR activity. *This work is in press with Applied Catalysis B.*

Incorporation of phosphorus heteroatoms into CN_x .

Phosphorus, when incorporated into CN_x has the potential to impact the electrocatalytic ORR activity. Heteroatom incorporation may also affect physical and chemical characteristics, ORR activity and selectivity, as well as, stability. Phosphorus added to the growth media of nitrogen-containing carbon nanostructures was found to dramatically improve the electrocatalytic activity for oxygen reduction. Phosphorus doping was achieved by growing carbon-nitrogen-phosphorus catalyst (CN_xP_y) over triphenylphosphine- and iron acetate-impregnated magnesia support in N_2 saturated with CH_3CN at $900^\circ C$. Catalysts grown in phosphorus-containing media showed improved onset of activity, increased current density and higher selectivity for water formation. The incorporation of both phosphorus and nitrogen into graphite materials allows for the tailoring of the physical and electrochemical properties. *Initial results from this study have been submitted to Carbon.*

Oxygen functionalities. Oxygen functional groups are commonly found on carbons when exposed to an oxidizing environment such as air. Oxygen functional groups affect properties critical for fuel cell catalysts, including hydrophilicity, elicit an activity increase and create anchoring sites for other functional groups or metals. CN_x was subjected to a nitric acid treatment in order to enhance the surface oxygen content and explore the role that oxygen functional groups have on ORR for CN_x catalysts. Nitrogen-containing carbon nanofibers were treated in HNO_3 to impart them with oxygen functional groups. With this treatment, ORR activity was found to increase slightly while selectivity to water formation markedly increased. Work continues with oxygen functional groups to identify the oxygen species that contribute to activity. *Preliminary results from this sub-area are published in Topics in Catalysis.*

Tailoring the catalyst nanostructure. The tailoring of nanostructure has been studied using different methods. The most active CN_x catalysts previously made by our research group had a mixture of nanostructures, but contained 60-70% stacked cup nanofibers. Studies were performed to increase the stacked cup nanofiber content. A solvothermal decomposition technique was used for preparing uniform 6nm iron oxide nanocrystals that were deposited on silicon wafers. CH_3CN pyrolysis was performed on the Fe nanoparticles. Unlike carbon nanofibers grown on Fe- or Co-impregnated VC, Al_2O_3 , SiO_2 , and MgO supports, which led to a mixture of carbon structures ranging from multi-walled nanotubes to nano-onions, this preparation gave exclusively “stacked-cup” structures. Since these stacked cup CN_x catalysts had very low yields because of the low surface area of the polished silicon wafer support, efforts are underway to prepare iron oxide nanoparticles on a silica support, by controlling the size and nanogeometry of the particles through organometallic synthesis techniques. Acetonitrile pyrolysis will, then, be performed, followed by washing, leaving behind the nitrogen containing carbon nanostructures.

Another avenue we followed was the synthesis of stacked platelets. This nanostructure was studied because of its increased edge plane exposure, hypothesized to be the location of the ORR active sites. Stacked platelets were made by passing a stream of $CO:H_2$ over an Fe:Cu unsupported catalyst. These stacked platelets were post-treated to incorporate oxygen and nitrogen functional groups into the nanostructure. They were oxidized in concentrated $HNO_3:H_2SO_4$ to add oxygen functional groups to the more active edge planes. The oxidized platelets were treated at two different temperature levels with ammonia to incorporate nitrogen into the nanostructure. It was found that oxidation of the platelets increased activity, but not as significantly as treatments in ammonia did.

Electrochemically accelerated carbon corrosion.

Accelerated electrochemical corrosion of CN_x catalysts was performed through a chronoamperometric hold of 1.2V vs. NHE in 0.5M H_2SO_4 electrolyte utilizing a rotating disk electrode system. The progression of carbon corrosion was monitored by measuring the intensity of an oxidation intermediate, the hydroquinone/ quinone electrochemically active redox couple. Half-cell testing of CN_x oxygen reduction catalyst materials showed superior carbon corrosion resistance compared to Vulcan carbon, the most commonly used material as cathode catalyst support. CN_x materials grown over an iron-impregnated support at 900°C in an acetonitrile atmosphere had a higher oxygen reduction activity than materials without an iron growth catalyst. When oxygen reduction activity was monitored before and after carbon corrosion testing, carbon corrosion resilience trended with oxygen reduction activity. Electrochemical ORR testing was observed to promote the corrosion resistance of highly active CN_x catalysts, but have no impact for materials that have low ORR activity. *This work has been submitted to Electrochimica Acta.*

Examination of the parameters that impact RRDE measurements. The parameters that impact the measurement of activity and selectivity through voltammetry techniques, such as rotating ring disk electrode (RRDE), were examined. The selectivity values measured using the RRDE technique for different catalyst loading levels on the disk were compared. A positive correlation between the selectivity and catalyst loading was observed for both CN_x catalysts and commercial Pt/VC.

Another parameter which affects the RRDE measurements is the aging of the catalyst ink before being applied to the electrode. A dramatic decrease in the ring current with ink aging coupled by a more modest increase in the disk current was observed with RRDE ink aging. The onset of activity does not appear to change with ink aging. When experiments were repeated with Pt/VC catalysts, similar changes in selectivity were observed, indicating that this was not a phenomenon specific to CN_x catalysts. *This work is in review with Electrochemical and Solid-State Letters.*

Full PEM fuel cell testing of heteroatom-doped carbon materials. Procedures for fabricating membrane electrode assemblies (MEAs) have been modified from those used for Pt-based catalysts reported by Los Alamos National Laboratories for our CN_x catalysts. Method optimization for enhanced performance for non-noble metal catalysts is ongoing. With the addition of an Arbin 50W hydrogen/direct methanol fuel cell test stand, CN_x catalyst MEA performance and stability are being explored.

Initial computational chemistry studies: Computational exploration of heteroatoms in graphite materials. As a collaborative effort with Professor Christopher Hadad, density functional theory (DFT) calculations have been initiated for nitrogen 1s orbital energies in polycyclic aromatic hydrocarbons (PAHs), which have a similar electronic structure to carbon-nitride catalyst materials. A strong correlation between DFT B3LYP method N 1s energies and experimental XPS N 1s energies was established for the PAHs studied. Additionally, experimental ionization potentials trended strongly with the DFT adiabatic ionization potentials. This calibration will be extended to larger and more complex molecules that are more like CN_x catalysts.

Correlation between activities of CN_x catalysts in ORR and ODH reactions. There have been reports in the literature citing the activity of carbon-based materials in oxidative dehydrogenation (ODH) reactions. Although the source of activity in these materials was not clear, the pre-treatments that involved O_2 , N_2O and HNO_3 suggested possible oxygen and nitrogen functional groups playing a role in catalyzing the reaction. While some research has been conducted connecting carbon nanostructure to ORR activity, there is far less literature connecting carbon nanostructure to ODH activity. We initiated a study to examine the activity nitrogen-containing carbon nano-structures in oxidative dehydrogenation of lower alkanes and explore if any correlations existed between the ODH and ORR activities over this group of catalysts. There was a strong correlation between ODH and ORR activities observed. XPS analysis demonstrated that ORR and ODH activity trends between catalysts followed the percentage of oxygen present as quinone groups as well as the pyridinic nitrogen groups. The correlation may suggest a shared active site between the ORR and ODH reactions although alternative explanations cannot be ruled out. *This work is in press with Catalysis Letters.*

Future Plans

Work on all sub-areas mentioned in the above progress report will continue. Some specific areas of particular interest are listed here:

- **Determination of the role of phosphorus carbon-nitrogen nanostructures:** Phosphorous was shown to impact the electrocatalytic ORR activity when incorporated into CN_x . The phosphorus content and local bonding environment will be probed to ascertain what the role of phosphorus is.
- **Poisoning CN_x catalysts:** The nature of activity in non-noble metal CN_x materials is still debated in the literature. To determine if the activity is imparted by a Fe- N_x type active site, activity testing will be performed on the CN_x material before and after exposure to several common catalyst poisons that bond strongly to iron.

- **X-ray Absorption Spectroscopy (XAS) characterization.** The XAS techniques are powerful tools to provide information about the coordination chemistry, formal oxidation state of a selected element being studied as well as the species, distances and coordination number of the atoms surrounding it. These techniques can be very useful in elucidating the molecular structure of the CN_x catalysts. Heteroatom-containing carbon nanostructures grown on different transition metals will be characterized using XAS techniques. Our recent proposal to Advance Photon Source (APS) of Argonne National Laboratory was accepted and we are given beam time at Sector 10.
- **Computational chemistry studies to complement the experimental work.** A collaborative effort is in progress to gain insight into the oxygen reduction reaction over the nitrogen-doped carbon catalysts using computational chemistry. It is planned to use both cluster models and periodic boundary models to explore the possible ORR mechanism over the nitrogen-doped carbon catalysts in acidic solution. Experimental techniques will be used in tandem to refine the ORR mechanistic pathway.

Publications acknowledging the grant

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