

Topic Paper #23

The Development of Non-Precious Metal Catalysts for Oxygen Reduction in PEM Fuel Cells

On August 1, 2012, The National Petroleum Council (NPC) in approving its report, *Advancing Technology for America's Transportation Future*, also approved the making available of certain materials used in the study process, including detailed, specific subject matter papers prepared or used by the study's Task Groups and/or Subgroups. These Topic Papers were working documents that were part of the analyses that led to development of the summary results presented in the report's Executive Summary and Chapters.

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The NPC believes that these papers will be of interest to the readers of the report and will help them better understand the results. These materials are being made available in the interest of transparency.

Development of Non-Precious Metal Catalyst for Oxygen Reduction in PEM Fuel Cells

Abstract

Metal-free carbon-based catalysts for oxygen reduction is synthesized with high activity selectivity and durability. The catalysts were synthesized by introducing oxygen and nitrogen groups from various oxygen and nitrogen precursors. The nature of nitrogen surface groups and the effect of pyrolysis temperature on the activity of the catalyst have been evaluated. XPS indicates that higher concentration of pyridinic type nitrogen groups doped on nanostructures graphitic carbon increase the catalysts activity. The metal-free catalysts showed an onset potential close to 0.9 V (NHE) in 0.5 M H₂SO₄ solution, similar to that of Pt. The amount of hydrogen peroxide (H₂O₂) generated was less than 1 % indicating a complete four-electron reduction of oxygen to water. The fuel cell performance indicated a current density of 0.49 A/cm² at 0.5 V (catalyst loading of 2mg/cm²) and 2.0 A/cm² at 0.2 V with a maximum power density of 0.49 W/cm².

The nature of surface nitrogen groups has been examined. The XPS characterization studies indicated that on the carbon surface, only pyridinic and graphitic nitrogens act as catalytic sites for oxygen reduction: particularly, pyridinic nitrogen, which possesses one lone pair of electrons in addition to the one electron donated to the conjugated π bond, facilitates the reductive oxygen adsorption and eliminates H₂O₂ formation. Currently, our goal is to increase the catalyst activity by increasing the concentration of pyridinic and quaternary nitrogen on nanostructured carbon surface. More studies should be performed to decrease the hydrophilic character of the catalyst and to increase its durability.

Due to the high cost and limited availability of platinum, there has been a considerable research on non-precious metal catalysts. However, none of the catalysts reported in the literature fully meet the requirements of electrocatalysts for oxygen reduction in PEM fuel cells due to: (i) low catalytic activity, (ii) poor stability, (iii) low selectivity toward four-electron reduction of oxygen to water (large amount of hydrogen peroxide > 5 %) and (iv) high electronic resistance.

This review presents a new method for synthesis of nitrogen modified carbon-based catalysts for oxygen reduction in PEM fuel cells. The synthesis process involves the modification of the carbon surface with nitrogen-containing organic precursors followed by heat-treatment at elevated temperatures. An optimized nitrogen doped catalyst shows an onset potential for oxygen reduction as high as 0.9 V(NHE) in 0.5 M H₂SO₄ solution similar to that of platinum. The amount of hydrogen peroxide (H₂O₂) generated is less than 1 % indicating a complete four-electron reduction of oxygen to water. Such high selectivity of nitrogen modified carbons has not been reported before.

The current transient measured in PEM fuel cell at 0.4 V showed an initial increase of current density to approximately 0.12 A cm⁻² and then a steady-state current profile without showing performance degradation for up to 1000 h. The characterization studies indicated that pyridinic and graphitic nitrogens act as catalytic sites for oxygen reduction: particularly, pyridinic nitrogen, which possesses one lone pair of electrons in addition to the one electron donated to the conjugated bond, facilitates the reductive oxygen adsorption and eliminates H₂O₂ formation.

The most commonly accepted hypothesis regarding the catalytic site for oxygen reduction and the relevant reaction mechanism on non-precious metal catalysts is that the metal-N₄ center bound to the carbon support is catalytically active, and the central metal ion in the macrocycle plays a crucial role in the oxygen reduction reaction.¹⁻¹⁷ However, Yeager¹⁸ and Wiesener¹⁹ suggested that the transition metal does not act as an active reaction site for oxygen reduction, but rather it serves primarily to facilitate the stable incorporation of nitrogen into the graphitic structure during high-temperature pyrolysis of metal-nitrogen complexes. According to Maldonado and Stevenson²⁰, the strong basicity of N-doped carbons facilitates reductive O₂ adsorption without the irreversible formation of oxygen functionalities, thereby increasing the catalytic activity. This idea is strongly supported by our experimental findings on Co/C based catalysts.²¹⁻²⁸ The X-ray photoelectron spectroscopy (XPS) data indicated that the pyrolysis in the presence of Co increases the concentrations of two nitrogen functional groups on the carbon surfaces (pyridinic-type nitrogen and quaternary carbon-graphitic-type nitrogen). The subsequent dissolving out of Co metals from the heat-

treated Co-N chelates did not cause any loss of the catalytic activity; instead, the catalytic activity increased upon the chemical post-treatment for Co removal.

The experimental measurements of NH₃-treated Ketjen black in my laboratories indicated an onset potential for oxygen reduction of approximately 0.5 V(NHE) compared to that of 0.2 V(NHE) observed for untreated carbon. In the first and second step before treating the carbon with NH₃, the Ketjen black was treated in HNO₃ and HCl to remove all metals present as impurities. The quantum mechanical calculations on cluster models show that carbon radical sites formed adjacent to substitutional N in the NH₃-treated carbon are active sites for ORR.²⁸

In my laboratories, we have developed novel routes to synthesize nitrogen modified carbon-based catalyst without using nitrogen containing metal precursors. The active reaction catalytic sites and catalyst selectivity were optimized by optimizing the surface oxygen group, the nitrogen content, and the pyrolysis temperature. It is demonstrated that the modified carbon, upon chemical modification with nitric acid and treatment with nitrogen-rich precursors such as melamine, urea, thiourea, and selenourea is active for oxygen reduction exhibits very good selectivity towards the four-electron reduction of oxygen to water. Insight into the nature of the active reaction sites has been accomplished by various physical characterization techniques. Rotating ring-disk electrode (RRDE) technique and fuel cell testing were performed to evaluate the activity, selectivity and durability of the synthesized catalysts. After leaching the metal free catalyst 8 hours at 800C in H₂ SO₄ no heavy neither transition metals were detected in the solution. From our studies on the nature of the catalytic sites, it is conceivable that the nitrogen atoms are attached onto the surface of the oxygen-rich (oxidized) carbon in the form of pyridinic and pyrrolic structures. During the subsequent heat-treatment step, carbon becomes richer in pyridinic nitrogen that enhances the activity of the catalyst for oxygen reduction. The general conception is that pyridinic nitrogen groups co-ordinated with a metal atom is responsible for the activity of non-platinum catalysts. On the contrary we observed that pyridinic N-rich carbon is active for oxygen reduction. Our characterization study performed on the nitrogen modified carbon suggests that the pyridinic nitrogen facilitates reductive O₂ adsorption, thereby enhancing the catalytic activity and selectivity for four-electron oxygen reduction to water. This has been strongly supported by our experimental findings on Co-based catalysts.²⁷⁻²⁸ The X-ray photoelectron spectroscopy (XPS) data indicated that the pyrolysis in the presence of Co increases the concentrations of two nitrogen functional groups on the carbon surfaces (pyridinic-type nitrogen and graphitic-type nitrogen), when compared with the case of the pyrolysis in the absence of Co. The subsequent dissolving out of Co metals from the heat-treated Co-N₄ chelates did not

cause any loss of the catalytic activity; instead, the catalytic activity increased upon the chemical post-treatment for Co removal. From the extended X-ray absorption fine structures (EXAFS) study, we have also found that Co-N₄ chelates are not stable upon high-temperature pyrolysis above 800° C, and only the interaction between metallic Co atoms is observed.

Our experimental studies indicate that a strong Lewis basicity of carbons doped with pyridinic and graphitic nitrogens facilitates the reductive adsorption reaction of O₂ without the irreversible formation of oxygen functionalities, due to an increased electron-donor property of carbon.

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