Chemical Modification of Carbon Surfaces to Synthesize Non-precious Metal Fuel Cell Catalysts

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New sources of power are of great interest as attempts to make smaller, more convenient and environmentally friendly sources are being investigated. Hydrogen fuel cells are a way to combine both an effective method of power supply, converting chemical energy into electrical energy directly, and a way to employ clean energy. Fuel cells involve the use of platinum (Pt) as a catalyst, for both the oxygen reduction and hydrogen oxidation reactions, which is both rare and expensive. As such, there is significant ongoing research towards the discovery of non-precious metal catalysts (NPMC) with activity comparable to that of Pt.

The Fe-N/C catalyst system is a promising alternative, though the exact structure of the active catalytic site is still debated. Active catalysts are typically formed by high temperature ($600 - 1000^{\circ}$ C) pyrolysis in an ammonia atmosphere of a carbon with adsorbed iron on the surface. Dodelet's¹ group has postulated that the active site consists of Fe bridging two graphitic crystallites that contain pyridinic nitrogen. Thus, catalytic activity is highly dependent on the nitrogen content achieved after heat treatment.

Our approach to these catalysts employs surface chemical methods to more systematically synthesize the active site in order to better relate structure and activity. The current nitrogen compound of interest is 5,6-diamino-1,10-phenanthroline (aphen) which was attached to a carbon support (carbon black pearls) using a diazonium coupling method (Figure. 1). This is a chemisorption process, as opposed to physisorption one, that allows for a clearer model of attachment of the aphen molecule.

In order to understand the effects of the precursor and the metal on active site density and activity many synthetic parameters were varied and measurements were taken at each step of the process. Aphen loading was investigated by preparing a series of samples with increasing ratios of aphen to carbon black pearls. Cyclic voltammetry was performed and indicated that there is a maximum effective amount of aphen that can be added to the materials (Figure. 2).

Iron uptake was also explored by using two different iron salts; iron(III) chloride and iron(II) acetate. In order to study solvent effects iron(II) acetate was prepared in both water only and a 50:50 water:isopropyl alcohol mixture. These experiments indicated that the catalyst activity was dependent on the amount of iron yielding poor results for higher concentrations.

The effects of the solvent, precursors and metals on the catalyst activity will be presented. Activity of the samples is compared using cyclic voltammetry while iron content was analyzed using thermogravimetric analysis. Alternate carbon supports, metal solutions and precursor molecules and their potential impact on activity will also be discussed.



carbon surface

carbon surface

Figure 1. Diazonium Attachment of Aphen to Carbon.^{2,3}



Figure 2. Cyclic Voltammogram comparing the activity of 4 samples prepared using different ratio of aphen to carbon black pearls (mmol aphen/g carbon).

Reference

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