FUNCTIONALIZED NANOSTRUCTURED CARBONS FOR FUEL CELL ELECTRODES

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Introduction

Bis-ortho-diyln arene or BODA monomers have been used to fabricate nanostructured carbon materials through their unique combination of excellent processability and high carbon yield. The enediyne functionality of the monomers undergo a thermal Bergman cyclodimerization reaction that yields reactive naphthalene diradicals which polymerize to form polynaphthalene. (Figure 1) The tetrafunctionality of the monomers allows for both a higher processing window due to extensive branching and ultimately the formation of network polymers. The high carbon yield results in less shrinkage of the polymer upon pyrolysis to the glassy carbon state. This allows for the faithful templating of carbon structures from a polymeric precursor.

Hydrogen fuel cell electrodes require several properties for optimum performance. An ideal electrode would have as high a surface area as possible with an uniform dispersion of nano-scale catalyst particles attached to the surface. The electrode must be electrically conductive and have good mass transport for products and reactants. Carbon supported platinum is the best known catalyst for the oxidation of hydrogen at the anode and the reduction of oxygen at the cathode of a proton exchange membrane fuel cell (PEMFC). The material also must have good compatibility with the material used for the proton exchange membrane in the membrane electrode assembly (MEA), usually a sulfonated fluoropolymer such as Nafion.

We have undertaken a study to prepare a high surface area carbon material through a BODA templating method which can then be functionalized with both well dispersed platinum nanoparticles to act as catalysts and fluorophilic groups to facilitate the compatibility of the membrane and electrodes in the MEA.

![Polymerization of BODA monomers](image)

Figure 1. Polymerization of BODA monomers

Experimental

Materials. All BODA monomers were synthesized as previously reported. H₂PtCl₆ was purchased from Strem Chemicals. Karstedt’s catalyst was purchased for GFS Chemicals. 4-acetamino-phenol was purchased from Avocado Research Chemicals. All chemicals were used as received, unless otherwise noted.

Fabrication. BODA derived carbon materials were templated with a disordered monolith composed of nanoparticles of silica synthesized from a sol-gel and sintered together at 900 °C. The BODA monomer was melted into the free space in the monoliths to replicate the disordered porosity of the template into the polymer. The polymer was fully cured by heating under nitrogen. Further heating leads to pyrolysis of the polymer network and glassy carbon formation. The template was then removed with HF.

Platinum Functionalization. Platinum functionalization was attempted by several different methods. The platinum particles can be preliminarily synthesized and adsorbed onto the carbon surface, or the particles can be formed from an adsorbed platinum precursor with in situ reduction methods. Further attempts have included the adsorption of Pt(0) species which theoretically would lose the organic ligands and coalesce into Pt(0) particles.

Method 1. Platinum sol formed from H₂PtCl₆ reduced with sodium citrate, then adsorbed onto carbon.

Method 2. H₂PtCl₆ adsorbed onto carbon then reduced with sodium borohydride.

Method 3. H₂PtCl₆ adsorbed onto carbon then reduced with sodium borohydride.

Method 4. H₂PtCl₆ adsorbed onto carbon then reduced under H₂ flow in tube furnace.

Method 5. Karstedt’s Catalyst [Pt[(CH₂)₃SiH₂O]) (1 ml 10 % in xylene) was adsorbed onto 0.029 g carbon, dried and heated under N₂ at 300 °C in a tube furnace for 1h.

Fluorine Functionalization. Incorporation of fluorine containing groups onto the surface of the carbon materials was attempted in several different ways. Direct fluorination of aromatic groups is possible using certain classes of electrophilic fluorine reagents. Alternatively, incorporation of fluorine containing groups can be achieved through reaction of carbon or functional groups on carbon. A few methods have already been attempted. N-fluorobenzene sulfonimide (NFSI) reacted with carbon samples from Aerogel and templated BODA samples. Diethylamino Sulfur trifluoride (DAST) was reacted with oxidized carbon aerogel sample (refluxed in HNO₃, 13h) at ~78 °C to room temperature. Carbon reacted with diazonium salt. Diazonium salts were all synthesized from their corresponding amines.

Surface Area Measurements. BET surface area measurements were performed using N₂ gas adsorption on a Micromeritics instrument.

Results and Discussion

BODA-Derived Carbon Foams. The carbon used in a fuel cell electrode must have high specific surface area for maximum efficiency in facilitating the redox reactions at the catalyst. BODA monomers were therefore templated with colloidal silica nanoparticles and thermally polymerized and carbonized in situ to yield an open shell three dimensional carbon foam with very high specific surface area (Figure 3). The templating fidelity of the monomers is dependent on its wettability with the template material. This can be controlled through the variability of the terminal group R on the monomer (Figure 2). Templated carbon materials were prepared using the same process from several different monomers. The BET surface area was then measured using N₂ gas adsorption. The results are summarized in Table 1. The carbon templated using monomer 1 yielded the highest specific surface area of 275 m²/g.

![BODA monomers 1, 2 and Bisacetylene 3](image)

Figure 2. BODA monomers 1, 2 and Bisacetylene 3.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Monomer composition</th>
<th>BET Surface Area, (m²/g)</th>
</tr>
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<tbody>
<tr>
<td>100% 1</td>
<td></td>
<td>275</td>
</tr>
<tr>
<td>100% 2</td>
<td></td>
<td>135</td>
</tr>
<tr>
<td>80% 1, 20% 3</td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>100% 3</td>
<td></td>
<td>95</td>
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</table>

Table 1 Composition of Precursor BODA Polymer Network and BET Specific Surface Area of Templated Carbon Foams

![SEM of Templated BODA Carbon Material](image)

Figure 3. SEM of Templated BODA Carbon Material.

Platinum Incorporation. The platinum nanocatalyst syntheses can be divided into two basic paradigms: 1) pre-synthesis/adsorption and 2) in situ reduction. Methods 1 and 5 represent the pre-synthesis/adsorption route, where a Pt (0) species is adsorbed directly onto the surface of the carbon. This technique ensures that all of the platinum incorporated into the material will be surface bound and accessible for reaction in the fuel cell. Particle size is also better controlled and more monodisperse. Methods 2, 3, and 4 are all variations of the in situ reduction of a platinum salt method. This method involves immersing the carbon in a solution of a platinum salt and then using a chemical reducing agent to form the Pt (0) species within the framework of the carbon. This approach leads to a good dispersion of platinum particles over the entire surface of the carbon material.

Each method was attempted using enough platinum or platinum precursor to yield a final Pt loading of 20 % by weight with a carbon aerogel material. The samples were then analyzed using scanning electron microscopy (SEM) to determine catalyst size and dispersity and energy dispersive x-ray spectroscopy (EDX) for elemental analysis. The nanoparticles of platinum were not observed in any of the samples due either to too small of size for the resolution of the microscope or due to coalescence of the particles together on the surface. The EDX data, as summarized in Table 2 support the conclusion that the loading of platinum was too high for the surface area of the carbon and the size of particle formed. There is a greater that expected loading of platinum observed on the surface of the carbon for three of the methods. Method 1 seems to suffer from a poor adsorption of the platinum sol onto the carbon surface. The lack of control over loading is a major drawback for this method. Method 4 showed a platinum content very close to the expected platinum loading value. This indicates either good dispersity throughout the sample or a low yield of Pt (0) species from the precursor salt. In future experiments, the loading of the platinum should be related to the available surface area of the carbon support to prevent coalescence of the platinum nanoparticles on the limited surface.

The platinum nanoparticles may also be analyzed using wide angle x-ray scattering (WAXS) techniques, such as the pattern shown in Figure 4, which shows the platinum particles remaining after thermal oxidative removal of the carbon support. The large broad reflection indicates the presence of some carbon that was not fully removed. The sharp lines indicate the platinum that is left after the oxidation step. It is uncertain exactly what species is indicated. The peak width may be exploited to determine particle size. Unfortunately the particles are not visible in WAXS unless the carbon is removed, in a step which may also effect either the platinum species that exists or the particle size.

<table>
<thead>
<tr>
<th>Platinum incorporation method</th>
<th>C content (%)</th>
<th>Pt content (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>86.5</td>
<td>2.7</td>
</tr>
<tr>
<td>2</td>
<td>16.2</td>
<td>80.9</td>
</tr>
<tr>
<td>3</td>
<td>15.1</td>
<td>83.1</td>
</tr>
<tr>
<td>4</td>
<td>72.3</td>
<td>16.8</td>
</tr>
<tr>
<td>5</td>
<td>27.5</td>
<td>53.7</td>
</tr>
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Fluorine Incorporation. The incorporation of fluorine onto the carbon electrode material to aid in competitizing the electrode with the proton exchange membrane for close contact can be achieved by either the direct fluorination of the carbon material or incorporation of another fluorine containing functionality. Attempts at analyzing carbon materials with diamond ATR-IR have had only moderate success due partially to the inherent absorption of light by carbon. New peaks are detected around 1100 cm⁻¹ that may be attributable to new aromatic C-F bonds formed by the direct fluorination of carbon using DAST. No such peaks are visible for the other direct fluorination methods. The incorporation of fluorine may also be possible by including it with another group that can readily be attached to carbon such as a diazonium salt. Diazonium salts add to carbon materials, by dediazonation to form a reactive phenyl cation which then adds to the carbon. Several diazonium salts have been prepared as shown in Figure 5 with R = CF₂ and OCF₂CF₂. The latter species is a reactive species from which high molecular weight fluoropolymers may be grown from the surface of the carbon. This allows for high fluorine content to be achieved from even moderate carbon functionalization yields.

![Figure 5](image_url)

Figure 5. Synthesis of Diazonium Salts and functionalization of carbon support. a) NaNO₂, HCl, H₂O b) Carbon powder, H₃PO₄, 5 °C, 40 min.

Conclusions

Through the right combination of a suitable platinum nanoparticle formation technique, a suitable surface fluorine incorporation technique and the templated BODA carbon fabrication method, a very attractive approach for fabricating hydrogen PEM fuel cell electrodes should show promise for reducing some of the efficiency depriving faults in today’s fuel cell technology.

Acknowledgement. The authors would like to recognize the financial support of NSF/NER for funding the project. We would also like to recognize the assistance of Dr. K. Prasanna Perera, Dr. Suresh Iyer, Dr. Sibylle Glaser, and Dr. Chris Topping.

References