CHAPTER 3

PLATINUM ON OXIDIZED GRAPHENE SHEETS FOR USE AS ELECTROCATALYST FOR PROTON EXCHANGE MEMBRANE FUEL CELL

3.1 INTRODUCTION

Graphene has sparked overwhelming research activities in recent years. Preliminary experiments already indicate much promise for Pt/Graphene electrocatalysts in proton exchange membrane fuel cells and direct methanol fuel cells (Vinayan et al 2012; Aravind et al 2011; Neetu et al 2011; Chen et al 2011; Seger & Kamat 2009; Yoo et al 2009; Kou et al 2011; Guo, Dong & Wang 2010). Carbonaceous materials and nanostructured forms of carbon are widely used as catalyst supports (Auer et al 1998; Planeix et al 1994; Tang et al 2004) because of their high surface areas, good electrical conductivity, resistance to corrosion, and structural stability. Although considerable progress has been made in developing better electrode materials, the catalytic activity and stability of the electrode still need to be improved. Currently, the states of the art in electrocatalysts are Pt and Pt-based alloys supported on carbon black. Many different carbon based materials such as nanotubes, and graphitic nanofibers, have been used as electrocatalyst supports in fuel cells.

Recently, a spate of advances in synthesizing graphene-based nanomaterials have opened up exciting possibilities for the development of
graphene supported metal catalysts (Yoo et al 2009; Li et al 2010; Kou et al 2009; Seger & Kamat 2009; Zhong et al 2010). Replacing carbon with graphene is an approach researcher has been experimenting with to stabilize the catalyst. Graphene’s mechanical strength, crystalline structure bonds strongly with platinum nanoparticles and it demonstrates the durability. The unique property of graphene including high surface area and excellent conductivity, its unique graphitic basal plane structure prompted researchers to investigate the electrochemical activities of Pt/Graphene electrocatalyst. Compared with standard Pt/Carbon black catalysts, Pt/Graphene composites display enhanced catalytic activity, tolerance to CO poisoning and long term stability.

In the present work, Pt/Graphene electrocatalyst were synthesized using wet impregnation method with hexachloroplatinic acid as platinum precursor. Platinum particles were dispersed on the highly conductive graphene oxide (EC2) sheets and the catalysts were evaluated for activity towards hydrogen oxidation and methanol oxidation reaction.

3.2 EXPERIMENTAL

3.2.1 Synthesis of Reduced Graphene Oxide Sheets

Graphene oxide was prepared from 1g of Exfoliated Graphite (EG) and 50mg of potassium dichromate in 25ml of concentrated sulphuric acid subjected to vigorous agitation. The mixture was stirred for several hours maintaining a temperature less than 20°C. The mixture was washed copiously with water and dried. The graphene oxide was reduced by sodium borohydride by adding the reducing agent drop wise to the suspension of graphene oxide resulting in mildly oxidized graphene sheets (EC2).
3.2.2 Synthesis of Pt/Graphene Electrocatalyst

The synthesis of the catalyst was done by polyol method. The schematic diagram of the synthesis procedure is shown in Figure 3.1. The graphene oxide was dispersed in ethylene glycol and sonicated for 3 hours. The graphene suspension was put on constant stirring and required amount of hexachloroplatinic acid is added to it slowly. The pH of the suspension is maintained at 10 by adding aqueous Sodium hydroxide (NaOH) solution. The solution is heated to 130°C and maintained for 3hrs, followed by cooling till room temperature. The mixture is then washed until the pH is 7 and dried. The percentage of platinum was kept 40% with that of the support. Pt/Graphene catalyst would be termed Pt/G hereafter. The Pt/G catalysts were then post treated at 100°C in Ar/H₂ (5%) atmosphere. The sample without post treatment is Pt/G_A. The sample post treated for 1hr and 3hrs are labelled as Pt/G_B and Pt/G_C respectively.

Figure 3.1 Schematic of Pt/Graphene electrocatalyst synthesis using polyol method
3.3 RESULTS AND DISCUSSION

3.3.1 Physical Characterization

3.3.1.1 TEM characterization

Figure 3.2 gives the TEM images of the Pt/G catalyst showing uniform dispersion of platinum particles on graphene sheets. The SEM images of all graphene samples are transparent and rippled at the edges. The appearance of “kinked” sheets of graphene, and transparency implies that the graphene sheets are very thin to disrupt their normal planar structure. The wrinkles observed were attributed to the oxygen functionalized groups and the resultant defects, during the preparation of graphene sheets. TEM images reveal the presence of ample platinum nanowires in a low magnification image. The nanowires have an average cross sectional diameter of 2-3nm as determined by manually measuring randomly selected sections of the wires. At higher magnification the nanoparticles are seen to interconnect to form large three dimensional porous wire networks on the graphene sheets. The percentage of Pt was found to be 40wt% from the EDX analysis (Figure 3.4c; Section 3.3.1.2).

Figure 3.2 (Continued)
3.3.1.2 HR-TEM, EDX and SAED

Figure 3.3 shows the HR-TEM images of Pt/G catalyst. The platinum particles were highly crystalline with the interfring spacing of 0.19nm. The elemental mapping (Figure 3.4(a) and 3.4(b)) of the Pt/G catalyst shows dispersion of Pt particles on graphene sheets. The HR-TEM image of graphene and Pt/G with the corresponding electron diffraction (ED) pattern is shown in inset of Figure 3.3. The selected area diffraction (SAED) pattern is matching well with the diffraction pattern of fcc Pt crystals.
Figure 3.3 HR-TEM image of (a) Pt/G_C and (b) High magnified image of Pt/G_C with inset showing the corresponding SAED pattern
Figure 3.4  (a) DF-TEM image (b,c) elemental mapping and EDX pattern of Pt/G_C catalyst (Carbon is in given in blue colour and Pt is given in red colour)
3.3.1.3 AFM analysis

Atomic force microscopy (AFM) in the non-contact mode was employed to characterize the topography of the Pt/G_C sample. AFM topographic images acquired for regions surrounding the edges of Pt/Graphene samples on glass substrates are shown in Figure 3.5. The height distribution over the 2X2µm² regions of the surfaces is presented. From the image it was observed that there are also plenty of wrinkles in the graphene sheets. The graphene sheets are fluctuant rather than identically flat. The heights of the Pt particles were found to be approximately 4nm from the graphene surface. This matches with the particle size of platinum particles as observed form TEM (Section 3.3.1.1).

Figure 3.5 AFM image of Pt/G_C with the line scan for height analysis of the image along with the 3D AFM image of the catalyst taken in an area of 2X2 µm²
3.3.1.4 XRD pattern

The structural analysis of graphene oxide (EC2) and Pt/G has been done by using Powder XRD and is given in Figure 3.6. The d-spacing of graphene oxide has been increased to 8.36Å after functionalization (Section 2.3.7). It is obvious that the position of the (002) diffraction peak (d-space 0.34nm at 2θ=26.23) moves slightly to higher angle after deposition of Pt nanoparticles on the graphene sheets, which indicates that graphene oxide is further converted to the crystalline graphene, and the conjugates graphene network (sp2 carbon) has been re-established due to the reduction process. Along with the (002) plane of the hexagonal carbon, peaks corresponding to metal nanoparticles are also visible in the corresponding powder XRD pattern. The strong diffraction peaks at 2θ = 39, 46, 67, 81 and 85 can be assigned to the characteristic (111),(200),(220),(311),and (222) crystalline planes of Pt, respectively, which possesses face centered cubic (fcc) structure. The crystallite size of the metal nanoparticles was found to be 5nm for Pt/G.

![Figure 3.6 Powder XRD patterns of graphene oxide (EC2) and Pt/G catalyst](image)
3.3.1.5 FT-IR analysis

The functional groups present in the mildly oxidised graphene (EC2) and Pt/G_C catalyst were determined by FT-IR spectroscopy and are shown in Figure 3.7. Graphene oxide consists of covalently attached oxygen containing groups such as hydroxyl, carbonyl, epoxy and carboxyl groups. The oxidized graphene consists of a broad –OH peak from 3600 to 3000 cm\(^{-1}\), strong C=O peak at 1720cm\(^{-1}\), and strong C-O peak at 1230 cm\(^{-1}\). A weak –OH bending at 1410cm\(^{-1}\) shows the presence of epoxy groups. These functional groups act as anchoring sites for the platinum particles onto the graphene sheets during the synthesis of Pt/Graphene electrocatalyst for PEMFC electrodes. These functional groups are utilized for the anchoring of platinum nanoparticles.

![FT-IR spectrum of graphene oxide (EC2) and Pt/G_C catalyst](image)

Figure 3.7 FT-IR spectrum of graphene oxide (EC2) and Pt/G_C catalyst
3.3.2 Electrochemical Characterization- Hydrogen Oxidation Reaction

3.3.2.1 Cyclic voltammetry

Figure 3.8(a) shows a typical cyclic voltammogram of the adsorption/ desorption reaction of Pt / Graphene. The voltammogram exhibits peaks associated with both the oxidation and the reduction reactions. Each peak is indicative of the adsorption onto or desorption from a particular crystal index of platinum. The ECSA of Pt/C, Pt/G_A, Pt/G_B, and Pt/G_C are estimated to be 54, 55, 56 and 58 m$^2$.g$^{-1}$ respectively. The high ECSA of Pt/G is the effectiveness of 2D support such as graphene in dispersing Pt nanoparticles but also implies the ease of charge transfer at the Pt and mildly oxidized graphene interface. The results indicates that the Pt/G is a good catalyst for PEMFC with high ECSA which can be attributed to the uniform dispersion of Pt particles on the hybrid nanostructures and good accessibility of these sites for hydrogen adsorption and desorption reactions.

The durability of the Pt/G electrodes was tested for 4000 cycles and is shown in Figure 3.8(b). After 4,000 cycles of cyclic voltammetry measurements, Pt/Graphene catalyst lost only 20% of the Pt initial ECSA, whereas the degradations of Pt/Carbon catalyst was quite severe, with 65% loss under identical operating conditions. These results indicate that the Pt/G catalyst is 3 fold more stable than the Pt/C commercial catalyst and the durability can be attributed to the uniform dispersion of Pt particles on the graphene and good accessibility of these sites for hydrogen adsorption and desorption reactions.
Figure 3.8 (a) Cyclic voltammetry and (b) Accelerated durability test of Pt/C and Pt/G catalyst at a scan rate of 15mV.s$^{-1}$ in 0.5M H$_2$SO$_4$
3.3.3 Membrane Electrode Assembly Fabrication and Single Cell Test

Catalyst ink consisting of electrocatalyst with ionomer, 10% Nafion dispersion from Dupont denmour was spread uniformly in the gas diffusion electrode of 30 sq cm area. Three MEAs were fabricated using Pt/G_A, Pt/G_B and Pt/G_C catalyst on both anode and cathode labeled as MEA1, MEA2 and MEA3.

A single cell test fixture was employed for evaluating the catalyst performance for \( \text{H}_2 / \text{O}_2 \) based Polymer Electrolyte Membrane (PEM) fuel cell. The fabricated MEA was inserted between two graphite blocks, which had a multichannel serpentine flow pattern. Two fiber reinforced Teflon gaskets of thickness 0.22 mm were introduced between the membrane and electrodes. Tie rods with end plates and bolts for proper compaction and leak prevention held the whole assembly. A uniform torque was applied to each of the bolts used to assemble the cell. The fuel cell polarization experiments were conducted by using a test station, which was equipped with a bubble type gas humidifier, a mass flow controller, a temperature indicator and controller. Humidified hydrogen and oxygen gases were fed into the cell and an electronic load box is used to get the current-voltage (I-V) characteristics of the cell.
Figure 3.9  Polarization curves of MEAs using Pt/G catalyst

Figure 3.9 shows the polarization curves with the anode and cathode containing Pt/G electrocatalysts acquired at cell temperature 50°C without back pressure. The fuel cell exhibited good open circuit voltage of 0.9V. However at 50°C, at cell voltage of 0.2V the maximum current density was found to be 1644mA cm$^{-2}$ for MEA3. On comparing polarization curve analysis one can see that there was an improvement in the performance of Pt/G catalyst with Ar/H$_2$ treatment compared to that of MEA with untreated Pt/G. The improvement in the performance may be due to the increase in the conductivity of the graphene after Ar/H$_2$ treatment and the reduction of the unreduced Pt ions as well. The dispersion of the platinum particles in the form of network structure on graphene has been found to be useful for achieving higher performance in fuel cells. The present results show a higher ECSA of 58m$^2$.g$^{-1}$ and power density of 600mW.cm$^{-2}$ compared to the previous results on Pt supported on graphene.
3.3.4  Electrochemical Measurements- Methanol Oxidation Reaction

3.3.4.1  Cyclic voltammetry

The electrocatalytic performance of the Pt/G electrocatalyst, for the methanol oxidation reaction (MOR) was also studied. Figure 3.10 shows the CV curves of the MOR for the Pt/G and Pt/C in a 0.5 M H₂SO₄ solution containing 0.5 M methanol. All CV profiles consist of two strong anodic peaks: the forward peak and the backward peak, which are known to originate from the electro-oxidation of methanol and the intermediate carbonaceous species, respectively. The onset potential of methanol oxidation for the Pt/G was 0.2 V, while that for Pt/C was 0.4 V. In principle, with respect to the mechanism of alcohol electro-oxidation on the Pt catalyst, the onset potential is related to the breaking of C–H bonds and the subsequent removal of intermediates such as COₐd by the oxidation with OHₐd supplied by Pt-OH sites or other sources. This reveals that the Pt/G exhibited higher performance for the promotion of C-H breaking and COₐd tolerance in the methanol electro-oxidation. The methanol oxidation current density for Pt/C, Pt/G_A, Pt/G_B, and Pt/G_C were found to be 226, 409, 473 and 526 mA.mg⁻¹ respectively. Moreover, the significantly higher methanol oxidation currents in both the forward and subsequently in the reversed scans also for the Pt/G catalyst, which clearly demonstrate a higher mass activity of Pt in the Pt/G catalyst, mainly due to the higher utilization of Pt supported on the graphene surface compared to conventional carbon supported catalyst.

The ratio of the forward peak current (Iₚ) to the reverse anodic peak current (Iᵦ), Iₚ/Iᵦ, can be used to evaluate the catalyst tolerance to the intermediate carbonaceous species accumulated on the electrode surface. The Iₚ/Iᵦ ratio was estimated to be 1.29, 1.32, 1.06 and 0.95 for the Pt/G_A,
Pt/G\textsubscript{B}, Pt/G\textsubscript{C} and Pt/C, respectively. This result suggests that Pt/G sheets have less carbonaceous accumulation and hence are much more tolerant towards CO poisoning. The superior electrocatalytic activity of the catalyst can be attributed to the surface of the Pt, which may offer more active sites in the electro-oxidation and the 3D nanostructures of the Pt/G thus leading to a high electrocatalytic activity.

![Graph showing cyclic voltammograms for Pt/C, Pt/G\textsubscript{A}, Pt/G\textsubscript{B} and Pt/G\textsubscript{C} in H\textsubscript{2}SO\textsubscript{4} (0.5M) containing CH\textsubscript{3}OH (0.5M) at scan rate of 50mV.s\textsuperscript{-1}]

**Figure 3.10** Cyclic voltammograms for Pt/C, Pt/G\textsubscript{A}, Pt/G\textsubscript{B} and Pt/G\textsubscript{C} in H\textsubscript{2}SO\textsubscript{4} (0.5M) containing CH\textsubscript{3}OH (0.5M) at scan rate of 50mV.s\textsuperscript{-1}

### 3.3.4.2 Linear sweep voltammetry

The oxidation potential of Pt/G were lower than those of Pt/C as indicated by the green dotted line, suggesting the ease of methanol oxidation as observed from the linear sweep voltammetry (LSV) curves shown in Figure 3.11.
3.3.4.3 Chronoamperometry measurements

The long-term stability of the Pt/G and Pt/C were evaluated by chronoamperometric measurement under a constant potential of 0.65V. The polarization currents at Pt/G, and Pt/C catalysts decrease rapidly at the initial stage as observed in Figure 3.12, which is due to the formation of intermediate species during methanol oxidation reaction. However, the anodic current of the Pt/G_C electrode (80 mA.mg$^{-1}$) is still considerably higher than those obtained at Pt/C (15mA.mg$^{-1}$), at a time of 3000s, indicating that the electrocatalytic stability of the Pt/G_C catalyst for the MOR is higher than that of the Pt/C catalyst. These results are consistent with the voltammetric measurements shown in Figure 3.10, further confirming the better tolerance to the intermediate species and higher catalytic activity of Pt/G electrocatalyst than Pt/C electrocatalysts. This shows that activity of the catalyst has good...
tolerance against poisoning species generated and good stability towards methanol oxidation reaction as well.

![Mass normalized chronoamperograms recorded at 0.65V for methanol oxidation](image)

**Figure 3.12** Mass normalized chronoamperograms recorded at 0.65V for methanol oxidation

### 3.4 CONCLUSION

Knowledge of graphene oxide’s chemistry provides valuable insight into its reactivity and properties, as well as those of graphene that are derived there from. The preparation of oxidized graphene supported Pt electrocatalyst by a simple approach was demonstrated. This method has the advantage of making uniformly dispersed network of nanoparticles, because the significant number of oxygen defects prevents particle agglomeration, which is often a considerable challenge in synthesis of electrocatalyst for fuel cell applications. The Pt/G showed a high ECSA of 58m²g⁻¹ and power density of 600 mWcm⁻² when used as both anode and cathode catalyst. Thus
the combination of nanomaterials opens up a new approach to advanced catalyst for energy conversion. The electrocatalyst prepared using graphene as support materials exhibited a high current density of 526mA.mg$^{-1}$ towards methanol oxidation reaction. The catalyst showed better CO tolerance and stability compared to commercial Pt/C catalyst.