Catalytic activity of Pt/graphene prepared by strong electrostatic adsorption technique for proton exchange membrane fuel cells

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Abstract. In the proton exchange membrane (PEM) fuel cell development, the catalytic activity requires the smaller particle size, the better metal dispersion, the higher conductivity and the longer durability. With these, platinum on graphene was synthesized using the strong electrostatic adsorption (SEA) technique. The pH shifts of graphene was evaluated and the point of zero charge (PZC) was obtained at pH about 5.2. This was a mid-low PZC, where the positive charge of Pt (i.e., platinum tetraamine, [NH₃]₄Pt²⁺ or PTA) was chosen as the metal precursor. The adsorption of PTA precursor on graphene was carried out at pH of 12 for one hour at room temperature. PTA on graphene was reduced in hydrogen environment, and transferred to Pt metal particle. The adsorption and reduction steps were repeat until the Pt metals percentage closed to 20% wt Pt/C (i.e., 19.3 % wt. for this work). The prepared Pt/graphene catalyst shows the smaller particle size that average particle size as 2.4 nm and highly better dispersion than the Pt/C-commercial. The Pt metal dispersion on the graphene support were inspected by transmission electron microscopy (TEM). The crystal structures and crystalline size were investigated by X-ray diffraction (XRD). Moreover, the electrochemical properties were tested using cyclic voltammetry (CV) and the accelerated durability test (ADT) was also carried out after 4000 cycles of reduction and oxidation reaction. Finally, the results were compared with the 20% wt. Pt/C-commercial catalysts. It was observed that the oxidation reduction reaction (ORR) activity in terms of mass activity (MA) and specific activity (SA) were better than Pt/C-commercial.

Keywords: Pt/graphene catalysts, Strong Electrostatic Adsorption, Platinum, PEM fuel cell

1. Introduction
Currently, the advance of technology makes fuel cells still being developed [1–5], although the electric power generation from hydrogen and oxygen gas has already done since 1839[6,7]. Fuel cell is an electrochemical device that converts chemical energy of a fuel directly into electricity with zero emissions and high efficiency. The proton exchange membrane fuel cells (PEMFCs) are considered as the best type of power conversion since their high power densities and relatively low operating temperature. PEMFC generates electricity using electrochemical reaction without a combustion process. The catalysts in the PEMFCs are one of the essential components. The general methods for preparing the catalysts are dry impregnation and wet impregnation but these methods are not controlled optimal.
pH value and low interaction between the support and the precursor that lead to less oxygen reduction reaction (ORR) activity. Recently, a new technique which relates to wet impregnation but more specific called Strong Electrostatic Adsorption (SEA). This method is based on the concept of electrostatic mechanism [8–12], where the interaction between the substrate and precursor solution are monitored and controlled by the functional groups on the support surface. With this technique, Nathali Job [13] investigated the effect of chlorine contamination on Pt/carbon xerogel. They found that chlorine was not completely removed during the precursor reduction, and suggested that the use of chlorine precursors needed to be avoided. In order to avoid chlorine contamination, the non-chlorinated Pt complexes were considered by using platinum tetraammine (Pt \( \text{[NH}_3\text{]}_4 \text{Pt}^{2+} \)) as the precursor, and the substrate must have a low PZC according to the SEA technique.

The point of this work is to prepare Pt onto graphene using the Strong Electrostatic Adsorption technique (SEA) for PEMFC. The PTA was chosen to avoid the chlorine contamination, where the high pH adsorption was proposed. Consequently, the average particles size and metal distribution will be inspected by the transmission electron microscopy (TEM) and x-ray diffraction (XRD). The electrochemical properties of Pt/C catalysts will be tested by the cyclic voltammetry (CV), the linear sweep techniques [14] and the ORR stability of Pt/graphene compared to commercial Pt/C.

2. Experimental

Graphene (GNPs Grade 3, 97% > 2 \( \mu \text{m} \), Cheap Tubes Inc.) with a surface area of 887 \( \text{m}^2/\text{g} \) were used for this study. Tetraamineplatinum (II) nitrate (Pt \( \text{[NH}_3\text{]}_4 \text{NO}_3 \text{]}_2 \), PTA, \( \geq 50 \% \), Sigma-Aldrich) was considered as the cationic Pt complex ([\( \text{NH}_3\text{]}_4 \text{Pt}^{2+} \]).

2.1. Catalyst preparation

2.1.1. Determination of the concentration survey

The concentration survey was interested to determine the lowest initial PTA concentration that approved the highest level of adsorbed Pt salt on supported graphene. The optimal pH for strongest Pt adsorption was 12 [8,15]. The graphene at a fixed surface loading of 1,000 \( \text{m}^2/\text{L} \) was put into the bottle and shaken for 24 hrs. Then, PTA aqueous solutions with various concentrations varying from 200 to 1,200 ppm were added and shaken for 1 hour. The amount of Pt metal contents were examined by ICP-OES before and after contact with graphene. The metal uptake was calculated and determined as metal surface density, \( \Gamma_{\text{metal}} \), as described by equation 1.

\[
\Gamma_{\text{metal}} \left( \frac{\text{\mu mol}}{\text{m}^2} \right) = \frac{(C_{\text{metal, initial}} - C_{\text{metal, final}})(\text{\mu mol/L})}{\text{Surface loading} (\text{m}^2/\text{L})}
\]

2.1.2. Preparation of Pt/graphene catalysts

The Pt/C catalysts (Pt/Graphene) were prepared via the strong electrostatic adsorption (SEA) method, where PTA precursor was adsorbed by graphene electrostatically in 40 mL of aqueous solution at the initial pH of 12. Surface loading of aqueous solutions was fixed at 1000 \( \text{m}^2/\text{L} \). The slurry graphene and PTA solution were shaken for 1 hr. After shaking, 5 mL of solution was filtrated for ICP analysis. The metal surface density, \( \Gamma_{\text{metal}} \), was calculated as shown in equation (1). Then, the adsorbed Pt precursor on graphene was washed and dried in an oven at 100 °C for 24 hrs. After that, the catalyst was reduced in flowing 10% H\(_2\)/Ar (30 cm\(^3\)/min) at 300 °C for 1 hr. The adsorption and reduction steps were repeat until the Pt metals percentage closed to 20%wt.

2.2. Characterization

2.2.1. Physical characterization

Transmission electron microscopy (TEM) was used to analyze Pt particle sizes and size distributions of the Pt/graphene catalysts. The TEM images were taken using a JEM 2010 at 200 kV (JEOL). In the parts
of XRD, powder XRD measurements were made using a FE-SEM, JSM 6335 F (Rigaku, SmartLab) to investigate the lattice structures of the Pt crystalline and graphene spectra. The XRD patterns were compared directly with the JCPDS database.

2.2.2. Electrochemical characterization

The electrochemical active Pt surface area of the catalyst was determined by cyclic voltammetry analysis (CV) (PINE research, E6R2 Series, USA). The experiment was carried out on a thin active layer (AL) of Pt/Graphene catalysts, which were deposited onto a glassy carbon electrode, having a surface area of 0.1962 cm$^2$. The catalyst ink was fixed around 20 μg/cm$^2$. The catalyst ink was prepared by mixing about 10 mg of Pt/graphene powder with 5 mL of Nafion solution (5%wt. Nafion in IPA with EW of 1,000 from DuPont) and sonicated for 60 minutes. All cyclic voltammetry experiments were conducted in 0.5 M H$_2$SO$_4$ solution as the supporting electrolyte, which was purged with the argon gas flowing rate of 30 mL/min. CV measurements were performed from -0.15 to 1.2 V to measure the electrochemical surface area (ECSA) of catalysts at a scan rate of 50mV/s.

The oxygen reduction reaction (ORR) experiments were performed by running the CV for 4,000 cycles called accelerated durability test (ADT) from 0.4 -1.2 V (SHE) at a scan rate of 50 mV/s under O$_2$-saturated in 0.5 M H$_2$SO$_4$ solution. The linear sweep (LSV) was carried out before and after ADT in the same 0.5 M H$_2$SO$_4$ solution from 0.6 – 1.2 V (SHE) at the sweeping rate of 5 mV/s and 1600 rpm rotating speed. Through these sweeps, the specific activity (SA) and mass activity (MA) were calculated [16].

3. Results and discussions

3.1. PZC of graphene and optimal Pt uptake

Due to the PZC of graphene was about 5.2 [17], it is the mid-to-low pH of the PZC. The adsorption of Pt metal salt onto graphene prefered to conduct at higher pH. Therefore, the Pt salt should have cation compound such as Pt amine complex (PTA), where the adsorbed condition was set at the pH of 12.

For figure 1 shows the metal densities surface area ($\gamma_{\text{Pt}}$ with the unit of μmol/m$^2$) versus the initial metal concentration (ppm) for graphene surface loading of 1000 m$^2$/L at pH 12. This indicates that the adsorption of Pt metal salt onto graphene was saturated at the concentration around 600 ppm, the uptake likely constant at around 0.78 μmol/m$^2$. The Pt percent weight was about 12.2%wt. However, for PEM fuel cell application, the percent weight Pt loading should have at least 20.0%wt. Therefore, the second uptake is required.

![Figure 1. Platinum uptake at surface area 1000 m$^2$/L for final pH 12 versus PTA.](image-url)
3.2. Catalysts synthesis and characterization

3.2.1. Physical characterization

The TEM image shown the first uptake in figure 2(a) is the 8.5 % wt. Pt/graphene. In figure 2(b) is the second uptake with the total Pt loading of 19.3 % wt. and figure 2(c) shows the image of commercial Pt/C catalysts with 20%wt. These TEM images have the same magnification of 200K. The images observe that the dark small spots are Pt particles, where the bright-bigger circles represent the graphene as the support. The particle sizes of Pt are also evaluated and the average particle size of Pt/graphene is about 2.4 nm (figure 2(e)-the gray bar). This is smaller than the commercial Pt/C catalyst (3.6 nm). Moreover, the size distribution of Pt/graphene is narrower than that of commercial Pt/C and exhibits better Pt distribution over the support control corresponding to the SEA technique.

![Figure 2](image)

**Figure 2.** TEM images (a) the first uptake yielded 8.5 % wt. Pt/Graphene, (b) the second uptake yielded 19.3 % wt., (c) commercial catalyst of 20.0 % wt. Pt/C, (d) XRD pattern comparison, and (e) particle size comparison between XRD and TEM technique for all samples.

The XRD patterns in figure 2(d) shows four major peaks at the Bragg angle of 39.8°, 46.2°, 67.5° and 81.3° correspond to diffractions from the (111), (200), (220) and (311) planes of the face-centered cubic(fcc) lattice of platinum, respectively. In addition, the diffraction of (002) carbonized carbon planes show a broad peak at around 26.6°. This result clearly confirms that Pt nanoparticle prepared by SEA is very small due to the XRD pattern shown the peak of Pt (111), which is broader than the commercial Pt/C catalyst. It is found that the average particle sizes of Pt/graphene catalysts from this work are smaller than the commercial catalysts for both XRD analysis and TEM images. This indicates a good dispersion of Pt over the graphene surface due to SEA.
3.2.2. Electrochemical characterization

The cyclic voltammetry (CV) was performed to evaluate the ECSA as shown in figure 3. The ECSA is calculated by integrating charge under the hydrogen desorption peak [18]. For the initial cycle, The ECSA of 19.3%wt. Pt/graphene (i.e. 417 m²/gPt) has higher than 20% wt. Pt/C commercial (i.e. 135 m²/gPt). The CV results show that Pt/graphene exhibited a larger double layer than commercial catalysts because of the high specific surface area of graphene[19–21]. Sato[20] found that the smaller particle size of the graphene (i.e. larger specific surface area) gave a broader double layer.

![Figure 3. Cyclic voltammograms (CV) comparison of 19.3 %wt. Pt/graphene (solid line) with 20%wt. Pt/C commercial (dashed line) obtained at 0.0-1.2 V vs. SHE in 0.5M H₂SO₄ solution saturated by He-gas at a scan rate of 50 mV/s.](image)

3.2.3. Oxygen reduction reaction(ORR)

The accelerated durability test (ADT) of catalysts was also performed by running the CV for 4,000 cycles, by using a linear sweep voltage (LSV) with scan rate of 5 mV/s in an O₂-saturated 0.5M H₂SO₄ solution. With the results from the LSV in figure 4(a), it can be seen that the LSV of ORR on both catalysts are negative shift of potential after ADT. In the part of SA and MA figure. 4(b), activity before ADT are observed that both SA and MA of Pt/graphene catalysts at 0.9 V yielded much better ORR activities (around 1.5 folds) than that of Pt/C commercial catalysts. After 4,000 cycles, both SA and MA are decreased for both Pt/graphene and Pt/C commercial catalysts. ADT results indicate that an overall ORR activity is loss due to the Pt nanoparticles agglomeration during the electrochemical reaction. In addition, the decreasing rate of the both SA and MA activity are obviously different on two catalysts (40 % loss for Pt/graphene and 60 % loss for Pt/C commercial). This indicates that Pt/graphene catalysts had higher stability during the electrochemical reaction, probably due to the better interaction between substrate (graphene) and Pt particles according to the strong electrostatic.

![Figure 4. ORR activity (a) The linear sweep voltage(LSV) for 19.3 %wt. Pt/graphene and 20 %wt. Pt/C commercial before(solid lines) and after dashed lines) ADT in O₂-standard from 0.6-1.0 V vs. SHE with](image)
5 mV/s at rotation speed of 1,600 rpm and (b) Comparison specific activity (SA) and mass activity (MA) before and after ADT at 0.9 V vs. SHE for 19.3 %wt. Pt/graphene and 20 %wt. Pt/C commercial.

4. Conclusion
Strong electrostatic adsorption (SEA) technique was used to prepare the Pt onto graphene. The Pt/graphene catalyst had narrower size distribution, and yielded higher ORR activity than commercial catalysts. Pt/graphene catalysts had the crystal structure verified from the XRD spectra. The ECSA of 19.3%wt. Pt/graphene had higher than 20%wt. Pt/C commercial (around 3 folds). After the electrochemical reaction for 4,000 cycles, the SA and MA were evaluated and had the activity loss of about 40%, which inferred the superior stability particularly for the electrochemical oxygen reduction than the commercial catalysts (60% loss). Consequently, catalysts prepared from SEA technique performed better durability and are hopefully able to operate in fuel cell with a longer lifetime.

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