Research Article

Polyol-Free Synthesis of Uniformly Dispersed Pt/Graphene Oxide Electrocatalyst by Sulfuric Acid Treatment

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Polyol-free synthesis of highly loaded Pt catalysts on sulfuric-acid-treated graphene oxide (SGO) was reported. Sulfuric acid treatment increased the surface hydroxyl groups on graphene oxide (GO), which contributed to the reduction of Pt precursors in the absence of external reducing agent. By adjusting pH during the Pt reduction, we can get uniformly dispersed 2.5 nm size Pt nanoparticles on GO surface even at 50 wt% Pt loading amount. Cyclic voltammetry showed that increased pH resulted in increased electrochemical surface area.

1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is regarded as one of the best candidates for the future energy sources as it can generate the electricity in a carbon-free way through the carbon dioxide free electrochemical reaction. Generally, only hydrogen and oxygen (or air) are used as the fuel gas and the oxidant gas, respectively. Moreover, the product generated during this reaction is only pure water, which will not cause any harms to the environment and also can be used as the essential ingredient for human and nature [1]. Nevertheless, its high cost impedes the commercialization. To reduce materials cost by improving the catalyst performance, robust catalytic supporting materials must be developed to achieve high dispersion, utilization, activity, and stability [2]. Recently, the majority of the catalyst support research has focused on the use of graphitic materials such as carbon nanotube and graphene [3–5].

Graphene is extensively studied due to its excellent properties such as a large theoretical specific surface area, high intrinsic mobility, high Young's modulus and thermal conductivity, and its optical transmittance and good electrical conductivity [6–9]. There are several pathways to fabricate graphene nanosheets including chemical vapor deposition, mechanical exfoliation, and chemical exfoliation; among them chemical exfoliation is regarded as the most suitable one for fuel cell application due to its versatility

of their surface modifications, unique defect behaviors, functional groups, and advantages associated with low cost and easy scale up [10].

The Pt catalyst for PEMFC can be prepared by impregnation, polyol, and colloidal method [11, 12]. Generally, wet impregnation followed by reduction by gaseous hydrogen atmosphere at high temperatures or the chemical reduction of the metal precursors using reducing agents can be used but achieving small particle size and uniform size distribution of Pt in this ways is very difficult especially at high Pt loading amount. Instead, the colloidal method using diverse stabilizing agents that prevent the Pt agglomeration can be used alternatively but the residual organic materials can deteriorate the fuel cell properties. Recently, polyol process is preferred due to its several advantages but it still needs chemicals such as ethylene glycol as reducing agent [13]. In this paper, we report a facile polyol-free synthesis of graphene oxide (GO) supported Pt catalyst at high loading condition. By modifying GO surface with sulfuric acid and controlling pH of catalyst loading process, we can successfully get as small as 2.5 nm Pt size even at very high Pt loading amount (45 wt%). We also used X-ray photoelectron spectroscopy (XPS, Thermo Fisher), X-ray diffraction (XRD, Rigaku) and Transmission electron microscope (TEM, JEOL) to verify the chemical and physical structures of fabricated catalysts and cyclic voltammetry (CV) to see the Pt size effect on the electrochemical activity.

FIGURE 1: TGA curves of Pt/SGO catalyst.

FIGURE 2: (a) XRD patterns of Pt/SGOs fabricated at different pH. TEM images of Pt/SGOs fabricated (b) at pH 8 and (c) at pH 11, respectively. The inset of (b) is AFM image of GO.

FIGURE 3: X-ray photoelectron C1s spectra of (a) GO, (b) Pt/GO, and (c) Pt/SGO. (d) Area ratio between C-C bond and sum of others including C-O and C=O related bonds.

2. Experimental Details

GO was prepared according to the modified Hummer's method from expandable graphite (Grade 1721, Ashbury Carbon) described in previous works [14, 15]. The sulfuric acid treated GO (SGO) was prepared by immersing GO to 4 M H_2SO_4 (aq.) solution for 24 h at 60°C. During that process, carbonyl and epoxy functional groups can be converted to hydroxyl group by the keto-enol tautomerism and acid catalyzed ring opening reactions [16]. The Pt/GO and Pt/SGO catalysts were synthesized by reacting Pt salt precursor, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich Corporation) and GO or SGO in the water at 90°C for 2 h. Different amounts of NaOH were added to adjust the pH of the solution. The product was collected by filtering and washing with ethanol and deionized water followed by vacuum drying for 2 h at 60°C. The final loading amount of Pt was 45 wt% when

measured with thermogravimetry analysis (TGA) as shown in Figure 1.

The cyclic voltammetry (CV) analysis was performed at 25°C with a three-electrode system using 0.5 M H_2SO_4 (aq.) as the electrolyte, Ag/AgCl reference electrode, and Pt counter electrode. The scan range was $-0.2 \sim 1.0$ V and scan rate was 50 mV s^{-1} , respectively. To prepare catalyst ink, each catalyst was mixed with 5 wt% Nafion ionomer dissolved in isopropanol (IPA) solvent. Polarization curves of a unit cell with 5 cm^2 MEA were measured at a cell temperature of 70°C under ambient pressure, using H_2 and air to the anode and cathode, respectively.

3. Results and Discussion

The thickness of GO used in this study was around 1 nm when measured with Atomic force microscope (AFM) as

FIGURE 4: Cyclic voltammograms of Pt/SGOs fabricated at different pH. The scan rate was 50 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte.

FIGURE 5: Polarization curves of Pt/SGO fabricated at different pH.

shown in inset of Figure 2(b). The mean particle size of Pt was calculated from XRD patterns by Scheerer's formula based on the Pt (111), (200), (220) and (311) peaks [17]. As shown in Figure 2, when SGO used as catalyst support the Pt size decreased to as low as 2.5 nm as the pH of the solution increased to 11 in the absence of any external reducing reagents such as ethylene glycol. On the other hand, when unmodified GO was used, the Pt size remained around 9 nm even at high pH condition (inset of Figure 2(a)). TEM image shown in Figure 2(c) clearly demonstrates the uniform distribution of small Pt particles on SGO surface fabricated at pH 11. This result indicates that sulfuric acid treatment enhanced the reaction between GO and Pt precursor by the effect of formation of large amount of hydroxyl group. The relation between pH and particle size is known due to the glycolates, the reaction intermediates produced during reaction between ethylene glycol [18, 19] and similar relation in this study exhibits similar reaction path as conventional

polyol synthesis. The reaction mechanism between ethylene glycol and Pt precursor involves the following reactions:

At first reaction, the interaction of $-\text{OH}$ groups of ethylene glycol with Pt-ion sites results in the oxidation of the alcohol groups to aldehydes. These aldehydes are not very stable and undergo further oxidation to carboxylic acid at second step, which may again be oxidized to CO_2 or carbonate in alkaline media, finally. The electrons donated by oxidation reactions result in the reduction of the Pt metal ions. The large amount of surface hydroxyl group of SGO after sulfuric acid treatment is believed to act like ethylene glycol and might undergo above reactions with Pt precursors.

This can be confirmed by the XPS data after Pt loading on GO or SGO surface as shown in Figure 3. The XPS C1s peak of GO at 284.3 eV corresponds to the C–C bonds of the graphite carbon, and the peaks at 285.5, 286.5, 287.5, and 288.6 eV can be attributed to C–S, C–O, C=O, and O–C=O bonding, respectively. Initially, GO contained large amount of surface functional groups, but after reaction with Pt precursor without external polyol, loss of functional groups was observed both GO and SGO. As shown in Figure 3(d), more loss of functional group in SGO over unmodified GO was seen and especially C–O bond which includes hydroxyl (–OH) and epoxy (C–O–C) decreased a lot. As the large amount of epoxy group exists in unmodified GO instead of hydroxyl group, there is limited loss in C–O related functional groups during the first reaction. We think that larger amount of hydroxyl groups in SGO generated by sulfuric acid treatment contributed better reaction with Pt precursor, which resulted in the smaller Pt size on SGO surface and more loss of oxygen related functional groups.

To see the electrocatalytic activity of Pt/SGO catalysts at different pH, the CV was performed and the results were shown at Figure 4. The Pt/SGO catalyst prepared at higher pH showed larger electrochemical surface area ($13.4 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ at pH = 11 and $5.2 \text{ m}^2 \text{ g}^{-1}_{\text{Pt}}$ at pH = 8), which might be due to the smaller Pt size of catalyst fabricated at higher pH. As shown in Figure 5, Pt/SGO fabricated at higher pH showed better fuel cell performance than that prepared at lower pH. This is presumably due to the smaller Pt particle size and larger Pt active area of Pt/SGO prepared at higher pH.

4. Conclusion

In this study, we successfully fabricated uniformly distributed 2.5 nm size Pt catalysts supported on graphene oxide (GO) without any external reducing agent such as ethylene glycol. By treating GO with sulfuric acid, we can increase the population of surface hydroxyl groups on GO surface which can act as polyol and reduce Pt precursor to metallic Pt nanoparticles. XRD and TEM data showed that Pt supported on sulfuric acid treated GO exhibited smaller Pt size than that fabricated unmodified GO. XPS data showed that large amount of hydroxyl groups generated by sulfuric acid enhanced the Pt reduction. Cyclic voltammetry showed that as the pH increased the electrochemical surface area increased. We believe that this facile and environmentally friendly approach can provide new way to commercialize the grapheme-based PEMFC devices in near future.

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