



# Durable platinum/graphene catalysts assisted with polydiallyldimethylammonium for proton-exchange membrane fuel cells



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## ABSTRACT

High performance and electrochemically stable Pt/graphene catalysts assisted with polydiallyldimethylammonium (PDDA) have been synthesized for PEM fuel cells. The preparation procedure and properties of the catalysts are investigated in detail. With the introduction of PDDA molecules, Pt nanoparticles can be well-dispersed on graphene support, resulting in improved electrochemical surface area and enhanced electrocatalytic activity. The corresponding electrochemical surface areas (ECSA) of catalyst layers calculated from the hydrogen desorption peak on cyclic voltammogram curves are 78.3, 72.5 and 73.6 cm<sup>2</sup> g<sup>-1</sup> for catalyst layers with Pt/graphene, Pt-PDDA/graphene, and Pt/graphene-PDDA catalysts, respectively. Both PDDA modified Pt nanoparticles and PDDA modified graphene supports also exhibit high durability toward electrochemical oxidation cycles compared with the conventional produced Pt/graphene catalyst at the same conditions. After 3000 cycles, only 23.52% of the initial ECSA remains for Pt/graphene electrocatalyst whereas 43.04% and 37.7% of the initial ECSA for the Pt/graphene-PDDA and Pt-PDDA/graphene catalysts remain, respectively.

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## 1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) are attractive low-emission power sources for electrically powered vehicles and distributed power generation. The major barrier that limited their further practical applications is the durability. This is especially the case when the fuel cell is operated for transportation applications with extreme or cyclic changes in load [1–3]. The integrity of the catalyst support is one of the most crucial factors affecting the lifetime of fuel cells because it functions as both anchor of the catalyst and electron conductor of the electrochemical reaction. The commonly employed carbon black supports suffer from oxidation to surface oxides, and eventually to CO<sub>2</sub> at the cathode during long-term operations in oxygen-rich environment, high operating-potentials, and low pH [4–9]. It is also possible for the

cathode to attain high potentials for short periods of time during start-up and shut-down. Practically, repeated start-up/shut-down cycles can lead to short-term potential excursions of the cathode to 1.2–1.5 V, causing accelerated carbon corrosion [10–12].

In the past several years, many efforts have been geared toward the development of alternative, chemically stable catalyst support for PEM fuel cells. It was reported that durability of the carbon black supports subjected to potential cycling between 0.6 and 0.9 V could be improved by covering with inorganic oxide such as silica [13]. However, the coverage of the whole surface of the catalysts with silica layers produced electrochemically inactive Pt catalysts. Graphene is recently deemed as a potential candidate for fuel cell catalyst supports because of the stable physical properties in comparison to active carbon, and larger surface area in comparison to other sp<sup>2</sup> bonded carbon materials, e.g. carbon nanotubes (CNTs) [14–16]. The surface and structure of the catalyst support have strong influence on size and morphology of catalyst particles. Compared with carbon fibers, the three-dimensional graphene used as a free-standing electrode support can result in improved catalytic activity due to its three-dimensionally interconnected seamless porous structure, high surface area, and high conductivity [17].

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Recently, Hsieh et al. developed a palladium/graphene catalyst by pulse electrodeposition [18]. The results demonstrated that the presence of graphene sheets facilitates the dispersion of metallic Pd clusters, ionic diffusion, and charge transfer. However, the inert surface of the graphene resulted from the  $sp^2$  hybridization is a concern for nanoparticle deposition and star-like Pd clusters consisting much of primary size of the cluster have been observed.

Nitrogen doped graphene could improve defects on the graphene for catalyst deposition. It is demonstrated that nitrogen plasma treatment could create pyrrolic nitrogen defects, which acted as good anchoring sites for the deposition of platinum nanoparticles and resulted in increased electrical conductivity and improved carbon-catalyst binding [19]. Intercalation with high surface area conductors, such as carbon black, is another effective method to improve the nanocatalyst deposition on graphene. Recently, carbon black was added as the spacer between two-dimensional graphene sheets in the catalyst layer. The results showed more Pt nanoparticles available for electrochemical reaction and better mass transport in the catalyst layer if carbon black was added [20,21].

The smooth surface of the graphene can also be improved by wrapped with carbon nanotube. The wrapped structure, which was constructed by chemical vapor deposition or chemical functionalization [22–24], could act as anchoring sites for the homogeneous deposition of platinum nanoparticles. Thus, proton exchange membrane fuel cell with the graphene wrapped-MWNT hybrids as catalyst support showed higher performance compared to the pure catalyst-support-based fuel cells because of enhanced electrochemical reactivity and great surface area.

Organic cations exhibited important role for depositing nanoparticles on inert graphene. Sheng et al. developed highly dispersed ultrafine platinum nanoparticles supported on graphene sheets with the assistance of oleyamine [25]. In this study, we report a high performance and electrochemically stable Pt/graphene catalyst assisted with polydiallyldimethylammonium (PDDA) for PEM fuel cells. The preparation procedure and properties of the catalysts were studied in detail. The results show that PDDA can improve Pt nanoparticles dispersion on the graphene support, thus improve the electrochemical surface area and catalytic activity. The PDDA modified Pt nanoparticles and graphene also presented high durability toward electrochemical oxidation cycles, in comparison with the conventional produced Pt/graphene catalyst at the same condition.

## 2. Experimental

### 2.1. Synthesis of graphene oxide (GO) and graphene-PDDA catalyst supports

The graphene oxide was synthesized from natural graphite powder (99.99%). In the typical experiment [30], 6 g of graphite (purity  $\geq 99.99\%$ , Aldrich), 5 g of  $K_2S_2O_8$  (AR, SCRC) and 5 g of  $P_2O_5$  (AR, SCRC) were added into 24 mL of concentrated  $H_2SO_4$  (98%, SCRC) under strong stirring at  $90^\circ C$  for 6 h. After the solution was cooled down to room temperature naturally, 0.5 L of deionized (DI) water was added into the above solution and aged for 15 h. The suspension was filtered, washed and dried to obtain the black solid. The black solid was mixed with 240 mL of concentrated  $H_2SO_4$  and 30 g of  $KMnO_4$  (AR, SCRC) in an ice bath below  $20^\circ C$ , and then was transferred to a water bath and magnetically stirred at  $30^\circ C$  for 4 h. The resulted dark-brown paste was further diluted with the slow addition of 500 mL of DI water and then stirred for 4 h. 40 mL of  $H_2O_2$  (30 wt% in water, SCRC) was slowly added to quench the solution to produce a golden-brown solution. After the mixed product was centrifuged, the sample was washed with HCl (AR, 37 wt% in water, SCRC) and DI water, respectively, until the

pH of the washed solution was ca. 6. Finally, the product was dried at  $60^\circ C$  in vacuum to obtain the GO sample.

To prepare graphene-PDDA supports, the graphene oxide powder was firstly transferred into PDDA (polydiallyldimethylammonium chloride, Mw  $\sim 5000$ , 1 wt% in water, Aldrich) solution to graft positively charged groups. The pH of the solution was adjusted to 2 by the addition of  $0.5 \text{ mol L}^{-1} H_2SO_4$ . After immersing for 24 h, the graphene oxide powder was filtered and washed by solution was Milli-Q water until the pH of the washed solution was ca. 6.

### 2.2. Synthesis of Pt/graphene, Pt/graphene-PDDA and Pt-PDDA/graphene catalysts

The Pt electrocatalyst supported on graphene or graphene-PDDA supports were prepared by a pulse-microwave assisted polyol route [26,27]. For detail, 0.35 g graphene or graphene-PDDA was added into 100 mL chloroplatinic acid solution ( $0.0077 \text{ mol L}^{-1}$  in ethylene glycol, the Pt content was 0.15 g, SCRC) at stirring speed of  $2000 \text{ r min}^{-1}$ . The pH value of the mixed suspension was adjusted to 10 by drop-wise addition of NaOH/EG solution ( $1.0 \text{ mol L}^{-1}$ , SCRC). After dispersed with high speed stirring and ultrasonication for 30 min, the Pt ions in the suspension were reduced to  $Pt^0$  by intermittent microwave-heating in a microwave oven (Panasonic NN-GF352M) at power of 1000 W with pulses every 5 s for three times. After the reduction, the pH value of the suspension was adjusted to 2 by HCl (AR, 37 wt% in water, SCRC) to promote the adsorption of the Pt nanoparticles onto the supports. The resulting electrocatalyst powders were filtered, washed and dried at  $80^\circ C$  for 10 h in a vacuum oven.

For preparing Pt-PDDA/graphene catalysts, 0.35 g graphene oxide powder were firstly added into 50 mL PDDA solution (2 wt% in ethylene glycol). Then 50 mL chloroplatinic acid solution ( $0.0154 \text{ mol L}^{-1}$  in ethylene glycol, the Pt content was 0.15 g) was added into the mixture. The pH value of the mixed suspension was adjusted to 10 and the Pt ions in the suspension were reduced to  $Pt^0$  by intermittent microwave-heating at power of 1000 W with pulses every 5 s for three times. The as-result catalysts were then filtered washed and dried at  $80^\circ C$  for 10 h in the vacuum oven.

### 2.3. Structure characterization of the catalysts

Pt content in the as-prepared catalyst was determined using atomic absorption spectroscopy (AAS, Perkin Elmer 5100 spectrometer). Before the tests, 0.2 g of samples was treated with 30 mL mixing concentrated nitric acid and hydrochloric acid (volume ratio 1:3). Then the suspension was dried and 20 mL of water was added. The mixture was filtered and the filtrate was analyzed by AAS.

Transmission electron microscopy (TEM) was carried out on a JEOL 6300 at an accelerating voltage of 100 kV. Samples for TEM measurements were dispersed in absolute ethanol by vibration in the ultrasonic pool. Then, the solutions were dropped onto a copper grid coated with amorphous carbon films and dried in air before measurements.

The XPS spectra were collected using a Physical Electronics (PHI) Model 1600 XPS system equipped with a monochromator and an Al  $K\alpha$  source ( $h\nu = 1486.8 \text{ eV}$ ) operating at 350 W beam power. Ejected photoelectrons were detected by a hemispherical analyzer that provided both high sensitivity and resolution. The operating pressure in the sampling chamber was below  $5 \times 10^{-9}$  Torr. A neutralizer beam was used during XPS measurements to compensate for peak shifting that occurs due to charging of samples during X-ray exposure. All high resolution spectra were collected using pass energy of 46.95 eV. The step size and time per step were chosen to be 0.025 eV and 100 ms, respectively. Samples were scanned at different locations and the peak intensity and composition at different

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