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Effects of reduction temperature and pH value of polyol process on reduced graphene oxide supported Pt electrocatalysts for oxygen reduction reaction

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ABSTRACT

Effects of the reduction temperature and the pH value of Pt precursor solutions of the polyol reduction process on the resulted Pt electrocatalysts supported on the reduced graphene oxide (Pt/r-GO) nanosheets for the ORR (oxygen reduction reaction) are investigated. The Pt/r-GO catalyst possesses Pt nanoparticles having an average size from 2 to 4 nm and a Pt loading from 13 to 20 wt%. The electrochemical performance of the Pt/r-GO catalysts is examined with the glassy carbon RDE (rotating disk electrode) technique in the O_2-saturated $HClO_4$ (0.5 M) solution. The Pt/r-GO catalysts have less ORR limiting currents near 3.5 mA cm^{-2}, but, in general, the more positive onset potentials than the commercial Pt/carbon black catalysts. The number of electron transfer in ORR over the Pt/r-GO catalysts is 3.85 in average, close to that of a 4-electron transfer process.

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1. Introduction

To decrease the emission of anthropogenic greenhouse gases that are mainly produced from burning of fossil fuels, the development of the alternative energy sources and the efficient utilization of these energy sources is of the utmost importance [1–4]. PEMFCs (proton exchange membrane fuel cells), which directly convert chemical energy from fuels such as hydrogen to electrical energy through the chemical reaction with oxygen, are attractive devices for various mobile and portable applications in recent years due to the lower pollutant emission, a higher energy efficiency, the quick startup and the lower operation temperature [5–9].

Briefly, the center of a PEMFC is the MEA (membrane electrode assembly) which contains proton exchange membranes sandwiched between the catalyst-embedded anode and cathode layers [10]. Adjacent to both electrode/catalyst layers, the GDLs (gas diffusion layers) commonly composed of a dense array of carbon fibers provide both gas (H_2/O_2) diffusion trails and electrically conductive pathways for current collection [2,11]. Next to GDLs and current collectors, field flow plate not only provide the mechanical support for the single cells in the stack, but also supply hydrogen and oxygen as well as a quick drainage to the excess produced water and generated heat [8,9]. If flooding, caused by trapped water, takes place in the cells, the PEMFC performance is degraded. Currently, serpentine design in flow channels are of the most common in PEMFC [8,9].

In PEMFCs, precious metals, such as Pt (platinum), are generally considered as the most effective catalysts. Consequently, Pt-based electrocatalysts are widely used in both anode and cathode composites for hydrogen oxidation and ORR (oxygen reduction reaction), respectively [7,11–27]. Practically, these electrodes are readily prepared from Pt and its alloy nanoparticles dispersed on conductive supports like carbon black and carbon paper with high surface area. Different engineering principles have been adopted to improve the electrocatalysis of these Pt-based electrodes in the ORR performance. In brief, these principles include the use of Pt and Pt-alloy nanoparticles with controlled size and configuration, as well as utilization of various supports and morphology to improve the catalyst's electrochemical activity. For example, in addition to Pt

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nanoparticles, different alloys nanoparticles of platinum, such as Pt-Rh [7], Pt-Ru [19] and Pt–Ti alloys [11], as well as configuration and geometric design of these nanoparticles, e.g. core–shell nanoparticles of Pd@Pt [20], Ni@Pt/C and Co@Pt/C [21] as well as Pt hollow nanoparticles [21] h have been utilized in electrode preparation. On the other hand, strategy using different supports to give better electronic conductivity on Pt catalysts has been adopted. Though TiN nanoparticles [16] and Sb-doped tin oxide [18] are been reported for the applications as electrode supports, carbon-based materials, such as carbon black, graphite, graphene and even carbon nanotube [12–19,24–27] are still prevailing. Moreover, the ORR performance of these Pt-based electrodes is profoundly influenced by the size of the Pt particles [22,23,28]. In general, the optimum size of the Pt nanoparticles on carbon supports for the ORR is found to be around 3–4 nm [22,23].

Due to the good electrical conductivity, the larger accessible surface area and a higher chemical stability, carbon materials, such as carbon black, graphite and graphene, have attracted more and more attention in electrochemical devices and applications [24,25,29]. However, carbon black materials, commonly used fuel cell catalysts, could not provide satisfactory electrochemical performance in PEMFC [25]. Alternatively, graphene, usually a one-atom-thick layer of carbon atoms arranged laterally in honeycomb lattice, was proposed in the applications as PEMFC catalyst support [24,25,29]. Graphene has unique physical properties, such as high surface area (2600 $m^2 \cdot g^{-1}$, theoretically), excellent electric conductivity, superior mechanical strength and thermal stability [24,30,31]. The graphene could be readily synthesized from the reduction of graphene oxide that has a layer structure with oxygen-containing functional groups such as hydroxyl, epoxide and carboxyl groups on planes and edges [29,32], and, thus, is often referred as r-GO (reduced graphene oxide). The common reducing agents used to obtain the reduced graphene oxide nanosheets include hydroquinone [31], hydrazine [33], and $NaBH_4$ [34]. These r-GO nanosheets can be conveniently prepared from natural graphite by the Hummers method [35]. Notably, the r-GO is known to have better conductivity and stability than GO [32,36]. Notwithstanding, the use of r-GO and graphene nanosheets in PEMFC electrodes is still relatively less popular than that of carbon black and graphite [25].

Recently, contradictive results on the electrocatalytic improvements by r-GO and graphene, in lieu of CB (carbon black), were reported [24–27]. For example, Xin et al. [24] and Park et al. [27] observed a lower ORR limiting current on Pt/r-GO than Pt/CB. Conversely, a slightly higher ORR activity on Pt/r-GO than Pt metal supported on commonly used carbon substrate was reported [26]. Briefly, the controversy could be ascribed to the final assembly structure of carbon materials, as well as the average size and the degree of dispersion of Pt nanoparticles on carbon supports [25]. Certainly, this controversy poses a curiosity with scientific interests to be explored. Therefore, in this work, the usage of graphene, instead of carbon black and carbon paper, as an effective support for Pt-nanoparticle electrocatalyst is attempted and studied with a goal to have the enhanced activity of ORR (oxygen reduction reaction) on the cathode.

There are various methods to grow Pt nanoparticles on catalyst support materials for electrochemical applications such as electrodes in PEMFCs. These methods, in general, but not subject to, include the polyol process [26,37], the microwaved-assisted polyol process [38–40], the chemical reduction by using stronger reducing agents such as $NaBH_4$ [12,39] or hydrazine [32,41], the electrochemical deposition [42], and the thermal decomposition [43]. Out of these numerous reduction processes, the polyol process using EG (ethylene glycol) as the reducing agent is more popular to deposit Pt nanoparticles on carbon support, mostly on carbon black [26,37–40,44]. Nevertheless, graphene has great tendency to aggregate together owing to the strong van der Waals interactions and, thus, leading to the failure to fully reach its predicted properties [25]. Consequently, it is important to uniformly disperse graphene in solutions containing Pt precursor [45]. Hence, in this work, a nonionic surfactant is selected both to retain well dispersion of graphene and to avoid any influence pounding on the polyol process.

It is also reported that the reduction temperature and the pH value of the Pt precursor solution of the polyol process might affect the size distribution of Pt nanoparticles, the dispersion of Pt particles and the aggregation of r-GO nanosheets [26,38]. That is, the electrocatalytic performance of the obtained Pt/r-GO catalysts could be affected, accordingly [22,23,26,38,44]. Therefore, in this work, these influential factors to the preparation of the Pt/r-GO catalysts and the electrocatalytic performance of the Pt/r-GO catalysts on the ORR activity are carefully examined with an aim to shed lights on the improved design of the cathode used in the PEMFCs.

2. Experimental

2.1. Chemicals and reagents

Sulfuric acid (Sigma–Aldrich), sodium nitrate (Sigma–Aldrich), perchloric acid (Sigma–Aldrich), potassium permanganate (J. T. Baker), ethylene glycol (J. T. Baker), acetone (Mallinckrodt Baker), and chloroplatinic acid hexahydrate (Alfa Aesar) were of ACS reagent grade and utilized as received. The nonionic surfactant Tergitol 15-S-12 (Dow Chemicals), Nafion® perfluorinated resin solution (5 wt% copolymer resin, DuPont), and commercial platinum catalyst (nominally 20%) on carbon black (HiSPEC™ 3000, Alfa Aesar) were used as received. Graphite used in the preparation of the graphene oxide and the reduced graphene oxide nanosheet was purchased from Bay Carbon Inc. (Bay City, MI). Deionized water from the Millipore Milli-Q ultra-purification system having resistivity greater than 18.2 MΩ·cm was used in the sample preparation.

2.2. Preparation of the Pt/r-GO catalysts

The platinum catalysts supported on the reduced graphene oxide nanosheets, denoted as the Pt/r-GO catalysts, were prepared by using the polyol reduction process. In brief, the catalyst support, r-GO, can be readily obtained from natural graphite with procedures described as follows.

Firstly, GO (graphene oxide) was prepared from natural graphite according to Hummers method [35]. Typically, 0.5 g GO and *ca.* 0.2 g $H_2PtCl_6 \cdot 6H_2O$ were added to 100 mL EG (ethylene glycol) containing 20 ppm Tergitol 15-S-12 surfactant, followed by sonication for 30 min. The pH value of the precursor solution was adjusted to the predetermined values, e.g. 2, 5, 7, 9 and 12, with a dropwise addition of the NaOH/EG solution. Subsequently, the precursor was placed into a three-necked round-bottom flask for the polyol process, in which the reducing temperature was set at 130, 150 or 170 °C. After two hours from the onset of the polyol reduction process, the reacting mixture was cooled down to room temperature, centrifuged, and washed thoroughly with DI water thrice and acetone once. The solid product, namely the Pt/r-GO catalyst, was harvested and dried in the oven for 24 h. Meanwhile, the graphene oxide without chelation of any Pt precursor was undergone with the same polyol reduction process to give the reduced graphene oxide nanosheets without Pt nanoparticles deposited. These r-GO nanosheets without Pt nanoparticles deposited were employed in the electrochemical tests to provide

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