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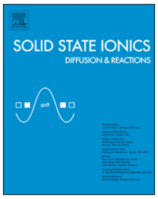

The influence of sulfonation level on the electrochemical characteristics of Pt/rSGO as electrocatalyst for proton exchange membrane fuels cells

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ABSTRACT

The influences of sulfonation level on the electrochemical characteristics of reduced-sulfonated graphene oxide (rSGO) as catalyst support in proton exchange membrane fuel cells (PEMFCs) was investigated. SGO samples were synthesized by mild heating of an aqueous mixture of GO and sulfanilic acid. The sulfonation level of SGOs was varied by changing the weight percentage of sulfanilic acid. The SGO sample with the optimized electrochemical characteristics was converted to rSGO through a chemical reduction route. The morphological, physicochemical and electrochemical characteristics of the prepared SGO and rSGO samples were compared. Pt-decorated rSGO samples (Pt/rSGO) were prepared by electroless reduction of an aqueous mixture of SGO and Pt$(NH_3)_4Cl_2$ using $NaBH_4$ as a reducing agent. SEM analysis revealed that the prepared SGOs possess a more folded morphology compared to GO and that the sulfonated groups prevent the agglomeration of Pt nanoparticles (PtNPs) during the reduction process. The electrochemical characteristics of SGOs and the corresponding rSGO samples were improved by increasing the sulfonation level from 0 to 50 wt% and afterward a reverse trend was observed. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements revealed that Pt/rSGO samples comprising of 50 wt% sulfonated groups exhibit higher catalytic activity towards hydrogen adsorption/desorption (HAD) reactions compared to Pt/rGO. This was attributed to more uniform distribution of PtNPs and the enhanced triple phase boundaries in Pt/rSGOs.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered as promising candidates for green power generation due to their remarkable features including; high power density, high efficiency, low operation temperature, fast startup and zero air pollution [1–4]. However, the widespread application of PEMFCs is limited by their relatively high cost and inappropriate cell durability [1,2,5,6]. Membrane electrode assembly (MEA) which is the heart of PEMFCs is comprised of a proton exchange membrane, catalyst and gas diffusion layers (GDL). MEAs are sandwiched between two flow field bipolar plates, and to generate greater voltages they can be stacked alternately [7]. The structure and composition of the catalyst layer can be adjusted to achieve a high density of catalyst active sites and efficient proton and electron conductivities. The catalyst layer in PEMFCs usually consists of three components; a noble metallic element (such as Pt, Pd) as catalyst, a nano-structured carbon-based support and an ionomer which acts as a binder and facilitates ion transfer processes between polymer membrane and catalyst particles [8,9]. A suspension of perfluorosulfonic acid polymers such as Nafion® is usually used as ionomer in fabrication of catalyst layer, which increases the fabrication cost of PEMFCs [9]. Nafion acts as a proton conductor and a binder in the catalyst layer and improves the reaction interface for proton conductivity [10]. Nafion content has a strong impact on the microstructure of the catalyst layer, the Pt electrocatalyst utilization and PEMFC performance [11]. It has been established that the optimized loading of Nafion could change in the range of 20 to 50 wt%, depending on the Pt loading and MEA fabricating process [11–14].

The catalyst supports usually are made of carbon materials because of their low cost, good electrical conductivity, high chemical resistance against harsh conditions of PEMFC medium and good formability [4,15]. Typically, the catalyst layer is deposited on one side of GDL or on both faces of Nafion membrane using spraying and brushing methods. Carbon black is widely used as catalyst support in fabrication of PEMFCs. Other carbon nanostructures including carbon nanotubes (CNTs), graphene and their derivatives have also been applied as catalyst support [16]. It has been established that graphene can effectively improve the performance of PEMFCs and reduce the use of Pt catalyst

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[17,18]. Graphene is a single atom thick layer of graphite which can be produced via mechanical and chemical methods [19]. Graphene possesses interesting characteristics such as high surface area, high electrical conductivity and relatively low manufacturing cost, which are prerequisites for suitable catalyst supports in PEMFCs [18,20]. Hummers method is regarded as a common method to synthesize graphene oxide (GO) from graphite [19]. GO nanosheet consists of a hexagonal ring-based carbon network possessing both sp^2- and sp^3-hybridized carbon atoms and a great number of oxygen-containing functional groups covalently bonded to graphene basal plane and edges. These functional groups enable GO to be easily functionalized and strongly interact with other materials [19,21,22]. GO can be converted to reduced-GO (rGO) using chemical or thermal treatments. Most of the oxygen-containing functional groups are removed through these processes and the restoration of conjugated system leads to the formation of highly conductive rGO nanosheets [22]. The remaining oxygenated functional groups in rGOs could facilitate anchoring of PtNPs on the graphene nanosheets [23]. Therefore, the electrochemical activity of graphene can be tuned to achieve a balance between the conductivity and the content of oxygen-containing functional groups. Researchers have shown that the presence of oxygen-containing functional groups in GO play multifunctional roles in facilitating the dispersion of metallic clusters, ionic diffusion and charge transfer [17,23]. Despite the efforts made to replace Pt with other catalysts, this noble metal is still the best choice for fabrication of PEMFCs. For example, iron has been coordinated to pyridinic nitrogen in N-doped graphene nanoflakes to decrease the production costs. However, the catalytic activity of the proposed compound was not at a desirable level to be considered as an effective substitution for Pt [24]. Pd-deposited GO could also be considered as a good substitute for Pt as the catalyst in PEMFCs, due to its relatively good catalytic activity and low activation energy [17].

It has been established that the sulfonated graphene oxide (SGO) possesses potential to enhance the proton conductivity, water uptake, mechanical characteristics and electrochemical performance of proton exchange membranes such as Nafion [25], poly(vinyl alcohol) [26], polyether ether ketone [27]. Researchers have shown that grafting sulfonic acid groups onto the surface of Pt/CNT via thermal decomposition or in situ radical polymerization could decrease Pt consumption in PEMFCs. It was also found that the sulfonation of CNTs could increase the active triple phase boundaries (TPB) and improve the performance of Pt/CNT-based electrodes [1]. A lyophilization-assisted approach has also been used to synthesis sulfonated reduced GO (S-rGO) as catalyst support and also size-controller of PtNPs in fabrication of PEMFCs. The electrochemical performance of Pt/S-rGO catalyst was improved by enhancing the TPB and hydrophilic affinity. In addition, the metal binding sites promoted the formation of PtNPs with a narrow size distribution on S-rGO [6].

Herein, we demonstrate how the level of sulfonation affects the ion exchange capacity and the hydrophilicity of reduced sulfonated GO (rSGO) as catalyst support and also the particle size distribution of PtNPs. These parameters, in turn, influence the TPB and the electrochemical performances of catalyst layer. To this end, SGO was synthesized by mild heating of an aqueous mixture of GO and sulfanilic acid (SA). The sulfonation level was varied by changing the weight percentage of SA. The SGO sample possessing the best electrochemical characteristics was converted to rSGO using a chemical reduction process. PtNP-decorated rSGO (Pt/rSGO) was prepared by electroless reduction of an aqueous mixture of SGO and $Pt(NH_3)_4Cl_2$, using $NaBH_4$ as a reducing agent. The morphological, physicochemical and electrochemical characteristics of the prepared samples were compared.

2. Experimental section

2.1. Materials

Graphite powder, sodium nitrate ($NaNO_3$), sulfuric acid (H_2SO_4, 98%), sulfanilic acid (SA, $C_6H_7NO_3S$), nitric acid (HNO_3), hydrochloric acid (HCl) and absolute ethanol were purchased from Merck (Germany). Potassium permanganate ($KMnO_4$, 99%) and sodium borohydride ($NaBH_4$) were supplied by Scharlau (Spain). Hydrated tetraammineplatinum (II) chloride, $[Pt(NH_3)_4Cl_2 \cdot H_2O]$ was purchased from Alfa Aesar (USA). Hydrogen peroxide (H_2O_2) was purchased from Dr. Mojallali (Iran). Nafion 117 solution (5 wt% in a mixture of lower aliphatic alcohols and water) was supplied by Sigma Aldrich (USA). Deionized water (DIW) was used throughout all experiments. All chemicals used in this work were of analytical grade and used without further treatment.

2.2. Preparation of GO and SGO samples

GO was prepared using a modified Hummers method, according to our previous work [21]. Briefly, graphite powder (1 g) and $NaNO_3$ (1 g) were added to H_2SO_4 (150 mL) in a flask and stirred for an hour in an ice water bath. $KMnO_4$ (3 g) was gradually added over 2 h into the flask and the mixture was stirred at 40 °C for 3 h. In 30 min, 30 mL of DIW was added to the flask and the mixture was further diluted by adding 40 mL of DIW. In order to eliminate the metal ions formed through the reaction, H_2O_2 (31%, 2 mL) was added to the flask and the mixture was centrifuged for 30 min at 6000 rpm. The resulting brown residue (GO) was repeatedly centrifuged and washed with DIW and HCl (5% (v/v)) solution. The purified GO solution was then transferred into a clean petri dish and left at room temperature to dry. The obtained GO powder was stored in a container.

Four types of SGO samples with different sulfonation level were prepared as follows: 50 mg of GO powder was dispersed in 25 mL DIW with the aid of mild sonication. Then, a pre-calculated amount of SA powder (25, 50, 75 and 100 wt% versus GO) was added gradually to the GO dispersion while the mixture was stirring at 70 °C for 4 h. The SGO product was centrifuged and washed repeatedly with DIW and then transferred to a petri dish, dried in ambient conditions and stored as powder. Hereafter, these samples are referred to as SGO25, SGO50, SGO75 and SGO100 to represent the weight percentage of the applied SA through the synthesis process. Table 1 shows the naming system and the detailed processing information of the SGO samples.

2.3. Preparation of reduced-SGO (rSGO) samples

To synthesis the reduced-SGO (rSGO) samples, 10 mg of the prepared SGO samples (see Table 1) was homogenously dispersed in 20 mL of DIW using an ultrasonic bath. Then, 25 mL of a freshly prepared $NaBH_4$ solution (0.5 M) was added dropwise into the mixture over 4 h while vigorously stirring at 70 °C. The resulting rSGO samples were centrifuged and washed three times with DIW and then transferred into a clean petri dish, left to dry at ambient conditions and stored as powder in a closed container. The reduced samples were named as rSGO25, rSGO50, rSGO75 and rSGO100, respectively.

2.4. Preparation of Pt/rGO and Pt/rSGO

The method used to prepare Pt/rGO and Pr/rSGO samples is described as follows; 10 mg of SGO50 (or GO) and 3.61 mg Pt

Table 1
Shows the naming system and the detailed processing information of the SGO samples.

Sample	GO (mg)	SA (mg)	SA/GO ratio (wt%)	Sulfonation time (h)
SGO25	50	12.5	25	4
SGO50	50	25	50	4
SGO75	50	37.5	75	4
SGO100	50	50	100	4