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Platinum on boron doped graphene as cathode electrocatalyst for proton exchange membrane fuel cells

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ABSTRACT

Boron doped graphene (BG) has been prepared using a facile technique and platinum (Pt) nanoparticles has been deposited on BG using different methods like sodium borohydride, polyol and modified polyol reduction method and used as oxygen reduction reaction (ORR) electrocatalyst in hydrogen fuel cell. The identification of crystal phases through X-ray diffraction (XRD) and the dispersion of the electrocatalyst by the Transmission Electronic Microscopy (TEM) have been studied. The electrochemically active surface area has been investigated by Cyclic Voltammetry (CV). The ORR activity has been evaluated by polarization studies using fuel cell fixture. Stability test also conducted in fuel cell mode for 50 h. This study revealed the superior ORR activity and stability of platinum nanoparticles decorated BG, which is synthesized by modified polyol reduction technique. Hence it can be considered as the alternative electrocatalyst for replacing contemporary electrocatalysts.

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Introduction

Fuel cell is an attractive energy device that directly converts chemical energy into electricity through chemical reaction. Hence it has drawn great attention in terms of both fundamentals and applications. Particularly hydrogen based polymer electrolyte membrane fuel cells (PEMFCs), are projected to become ideal source of energy, due to its high efficiency, high power density and low operating temperature. However, due to low operating temperature and acidic environment in PEMFCs, it is necessary to use Pt as electrocatalysts for anode and cathode electrodes. Owing to the high degree of

irreversibility of the cathodic reaction (oxygen reduction reaction) even under open-circuit conditions, the over-potential of PEMFC is about 0.2 V. In fuel cells, oxygen reduction reaction (ORR) is very interesting and challenging due to its complicated pathway resulting in five orders of magnitude slower kinetics on Pt compared to that of the hydrogen oxidation reaction [1]. The ORR electrocatalyst has to fulfill several requirements, such as high intrinsic activities, structural stability towards oxygen adsorption and desorption, stability in electrolyte medium, efficient breaking of oxygen bonds, ability to decompose hydrogen peroxide, good conductivity to realize maximum efficiency of the PEMFC. Usually Pt [2–11] and Pt related are materials [5,12–23] used as

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cathode electrocatalysts in fuel cell applications. Not only the electrocatalyst, but electrocatalyst support material also plays crucial role to improve the rate of reaction in fuel cells. The support modification with metal oxides, bi or tri-metallic dispersion, metallic core shell structures and with metal carbides can enhance the catalytic activity [24–29]. The efficient utilization of electrocatalysts can be achieved by dispersing it on the support material. Suitable support materials are highly sought after and require good electric conductivity, high surface area and strong chemical and thermal stability. Usually, the electrocatalyst is supported onto a porous carbon support in order to increase its contact area with the reactants [30]. Since both the electrons and protons are involved in the electrochemical reactions, the porous electrocatalyst layer must conduct both of these species [31].

Graphene has been the material of interest for various applications because of its distinct electronic and mechanical properties and enormously high surface area. Particularly, this two-dimensional (2D) one atom-thick material has been demonstrated to be promising for use in fuel cells as electrocatalyst support. Graphene itself is an attractive potential electrocatalytic support. Heteroatom (such as N and B) doped graphene [32–35] may afford further benefits i.e. the Fermi level of doped graphene can be shifted, up or down, to increase the density of state (DOS) by hole – or electron doping, which has been predicted to modify the band structures [36–39]. In the doped materials the electrocatalytic activity depends on the doping precursor [35].

Introduction of boron (B) heteroatom into graphene can modify the electronic band structure of graphene [39–41] as the number of valence electrons in boron atom differs by one compared to carbon atoms. It is expected that the p-type doping can be accomplished by the incorporation of boron atoms into the graphene sheets by replacing the carbon atoms. The boron can act as an electron acceptor and induce a redistribution of the p-electrons between the layer planes, ultimately lowering the Fermi level. B-doped graphene (BG) is also a promising material in fuel-cell electrocatalysis, because the doping of B facilitates the oxygen capture on graphene surface and then supports high catalytic activity for ORR.

Only few reports mention the synthesis of boron doped graphene and used as ORR electrocatalyst for PEMFC. Acharya et al. reported that Pt supported on boron doped carbon lowers the corrosion of carbon support through cyclic voltammetry in acidic medium [41]. Bo et al. explained that boron doped graphene supported Pt shows higher methanol oxidation than graphene supported Pt in acidic medium [32]. Sheng et al. reported that boron doped graphene shows excellent catalytic activity and stability towards ORR in alkaline medium. It has good methanol and CO tolerances [42]. Xu et al. reported that boron doped and nitrogen doped graphene has excellent metal free ORR catalyst in alkaline medium through half cell studies [43]. To the best of our knowledge, only a few studies have been performed on boron doped graphene supported Pt and they do not report the as ORR electrocatalyst in acidic medium, in addition the fuel cell studies are also not performed.

In the present study, boron doped graphene (BG) has been prepared and Pt is deposited on BG using different reduction methods like sodium borohydride, polyol and modified polyol.

The prepared materials are characterized by X-ray diffraction (XRD) and the dispersion of the electrocatalyst is ascertained by the Transmission Electronic Microscopy (TEM). The electrochemically active surface area has been investigated by Cyclic Voltammetry (CV). The ORR activity has been evaluated by polarization studies using fuel cell fixture. Stability test also conducted in fuel cell mode for 50 h.

Experimental section

Materials

Graphite powder and Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma Aldrich. Boric acid (H_3BO_3) from Finar chemicals, Sodium hydroxide (NaOH), Sodium borohydride (NaBH_4) were from Sd fine chemicals, Ethylene glycol (EG) from Merck, Isopropyl alcohol from Rankem, Perchloric acid (HClO_4), (20 wt%) Pt/C from Aroramthey and high pure (18.2 M Ω) deionized (DI) water were used in all the experiments.

Synthesis of boron doped graphene

The graphite oxide (GO) was prepared from graphite through the modified Hummers method [44]. Boron doped graphene was synthesized through thermal annealing of GO in the presence of boric acid (H_3BO_3). GO and H_3BO_3 were taken in the ratio of 1:4 and mixed with DI water to get uniform mixture. Then the mixture was transferred to quartz boat. The mixture was heat treated at 250 °C for 40 min and then at 950 °C for 3 h under constant flow of hydrogen and argon gas (50 and 160 sccm) mixture using tubular furnace. Subsequently the sample was cooled to room temperature under argon atmosphere, yielding boron doped graphene (BG). To remove excess boron, the sample was refluxed in 3 M NaOH aqueous solution at 60 °C for 2 h [42]. Finally the solution was filtered and washed several times with DI water and then dried in vacuum oven at 60 °C for 7 h.

Synthesis of electrocatalysts

Pt on boron doped graphene (Pt/BG) prepared by various methods, namely Sodium borohydride reduction, polyol and modified polyol method is described as below.

In sodium borohydride (NaBH_4) reduction method to prepare Pt/BG 18 ml of 1 wt% of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was mixed with 150 ml of DI water and was added to well disperse aqueous BG under stirring condition. Alkaline NaBH_4 was added to the mixture drop by drop. The reaction mixture was heated at 80 °C under stirring for an hour to complete the reaction process, followed by cooling to room temperature. The mixture was filtered and washed with DI water and dried at 60 °C overnight under vacuum.

In Polyol method, the BG was dispersed in 50 ml of ethylene glycol through ultrasonication then 18 ml of 1 wt% of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was added. Subsequently, the reaction mixture was kept in microwave oven for 5 min and cooled to room temperature. Then the mixture was filtered with copious amount of water

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