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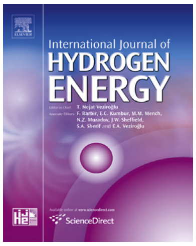

Graphene supported Pt–Ni nanoparticles for oxygen reduction reaction in acidic electrolyte

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ABSTRACT

The design of high performance oxygen reduction reaction (ORR) electrocatalysts play an important role in the commercialization of polymer electrolyte membrane fuel cells. The morphology, structure, and composition of the support material significantly affect the catalytic activity of the fuel cell catalyst. In this work, we report a systematic and comparative study of the effects of the support morphology for Pt–Ni nanoparticles for the ORR. The effect of the support morphology on the electrocatalytic oxygen reduction reaction was investigated. Pt–Ni alloy catalysts were characterized using various physico-chemical techniques, such as scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. Pt–Ni alloy nanoparticles were deposited uniformly on a graphene support and their oxygen reduction activities were evaluated in an acid electrolyte. The ORR activity of Pt–Ni supported on graphene was also compared with Pt–Ni supported on Vulcan carbon XC-72 and carbon nanotubes. The electrocatalytic activity and stability of Pt–Ni alloy catalysts were studied using cyclic voltammetry, linear sweep voltammetry, rotating disk electrode, and rotating ring disk electrode techniques. The results demonstrate that the graphene supported Pt–Ni catalyst showed the highest ORR activity among the three evaluated catalysts.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are one of the most promising energy conversion devices due to their higher energy efficiency than the conventional internal combustion engine. However, for successful commercialization of PEMFC technology, because costly platinum has been used as a catalyst at both the anode and cathode of fuel cells [1], it is necessary to decrease the amounts of Pt that are used. The electrochemical oxidation of hydrogen at the Pt anode is a facile reaction compared to the sluggish oxygen reduction reaction (ORR) at the cathode [2,3]. High Pt loadings are necessary to overcome the sluggish oxygen reduction kinetics in the cathode. Cost reduction and improvement of ORR activities are thus two major problems impeding the

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commercialization of fuel cells. At the cathode, the oxygen reduces to H_2O with a 4-electron reaction and peroxide can be involved as an intermediate [4]. However, the formation of hydrogen peroxide at the 4-electron pathway can be either extremely low or does not take place at all in the electrolyte [5]. It is known that intermediates such as O, OH, and OOH species are adsorbed on the Pt surface when the ORR is carried out [6,7]. Moreover, a mixed potential occurs through the formation of a Pt surface oxide such as Pt–O and Pt–OOH [8]. High adsorption of OH species on the Pt surface leads to a decrease in the active sites for O_2 adsorption, which causes a decline of ORR activities [9]. The adsorption of OH on the Pt/Pd surface can be reduced by alloying Pt with secondary transition metals such as Fe, Co, and Ni [10,11]. Essentially Pt has high binding energy between its surface and oxygen from oxygenated species such as O_2, O, OH, and OOH. The D-band center of a pure Pt surface is placed at a higher Fermi-level compared to that of the Pt–M (M = secondary transition metals such as Fe, Co, and Ni) alloy catalyst [12]. When a Pt–M alloy is formed, electron transfer takes place from the transition metal to Pt. As a result, the band width broadens and the d-band center of the Pt downshifts relative to the Fermi-level [13,14].

To further enhance the electrocatalytic activity of alloy catalysts, various carbon support materials such as carbon black and carbon nanotubes have been applied [15]. An ideal support for PEMFC electrocatalysts should have reasonable electrical conductivity, good metal–carbon interaction, high surface area, and high inertness in harsh chemical and electrochemical conditions [16].

Graphene has recently received considerable interest in many research fields due to its exceptional physical and chemical properties [17]. Graphene is a single nanosheet of graphite that consists of only carbon. One layer of graphene can be separated from graphite using chemical functionalization [18], thermal exfoliation [19], or mechanical cleavage [20]. Naturally, carbon has 2*s* and 2*p* orbitals and each orbital includes 2 electrons. These four electrons in carbon make different kinds of sp-hybridized orbitals. Every carbon atom in graphene is bound with the three neighboring carbon atoms as sp^2 hybridization [21]. Because of these extraordinary features, graphene has been investigated in relation to many applications, such as batteries [22] and fuel cells [23,24]. It can be utilized as a fuel cell electrode material, based on its unique and extraordinary features such as extensive nanostructure, high surface area [25], superior thermal conductivity [26] and electronic conductivity [27], and mechanical strength [28].

In this work, platinum–nickel alloy electrocatalyst supported on different carbon materials (Vulcan XC-72, CNTs, and graphene) have been investigated in order to reduce the amount of platinum loading and improve the oxygen reduction reaction activity. Other fundamental properties of various Pt–Ni alloy electrocatalysts, such as stability and methanol tolerance in an acidic solution, were carried out. The ORR electrocatalytic activity and stability of Pt–Ni alloy catalysts were evaluated using cyclic voltammetry (CV), linear sweep voltammetry (LSV), rotating disk electrode (RDE), and rotating ring disk electrode (RRDE) techniques. The results demonstrate that the graphene supported Pt–Ni catalyst showed the highest ORR activity among the three evaluated catalysts.

Experimental section

Preparation of graphene oxide

Graphene oxide was prepared based on the Hummers method [18]. One gram of graphite powder was ground with 50 g of sodium chloride (NaCl) until it became a fine powder. The gray powder was washed with distilled water several times and washed with ethanol finally. Filtrated graphite was dried at 80 °C in an oven and the remains were collected. The graphite powder was refluxed at 80 °C in an oil bath with sulfuric acid (H_2SO_4, 4 mL), potassium persulfate ($K_2S_2O_8$, 0.84 g), and phosphorus pentoxide powder (P_2O_5, 0.84 g) for 4.5 h. It was then cooled to room temperature for 10–20 min. Subsequently, 167 mL of distilled water was added and the solution was stirred overnight at ambient temperature. The solution was then filtrated and the remaining black powder was washed with distilled water several times. The product was dried at 80 °C in an oven. After drying, the product was stirred with 40 mL of H_2SO_4 and potassium permanganate ($KMnO_4$, 5 g) was added slowly in an ice bath. Subsequently, 84 mL of distilled water was mixed and the solution was stirred at 35 °C in an oil bath for 2 h. Then, 167 mL of distilled water and hydrogen peroxide (H_2O_2, 10 mL) was added and the solution was stirred for 0.5 h in ice bath. The color of the solvent changed rapidly from black to dark yellow. Finally, the solvent was removed by centrifugation, performed several times at 12000 rpm for 20 min until the pH was adjusted to 7. The centrifuged solid was dried overnight at 80 °C in an oven.

Chemical reduction of graphene oxide to reduced graphene

One gram of graphene oxide was dispersed in 375 mL of acetic acid (99.7%). After sonication, the solvent was stirred until the solution became clear. Then, 20 mL of hydroiodic acid (HI) was added and the mixture was stirred continuously at 40 °C for40 h. The solution was then filtrated with 250 mL of saturated sodium bicarbonate ($NaHCO_3$) and 10 mL of acetone. Finally, it was dried at 30 °C for 7 h in a vacuum oven.

Preparation of supported Pt–Ni (1:1) alloy catalysts

Three different carbon materials (Vulcan XC-72, CNTs, and graphene) were used as supports of a Pt–Ni alloy catalyst and the synthesis procedure was the same except for the use of carbon supports. In this section a typical synthesis of Pt–Ni supported on graphene is discussed. A similar procedure was used to prepare the other catalysts. One hundred milligrams of graphene was dispersed in 20 mL of anhydrous ethanol and the solution was sonicated for 1 h. Chloroplatinic acid (H_2PtCl_6 $6H_2O$, 0.0265 g) and nickel chloride ($NiCl_2$ $6H_2O$, 0.04 g) as a metal precursor were dissolved in distilled water. The resultant solution was then added drop wise to graphene dispersed ethanol under sonication. Sodium hydroxide (1 M, 400 μL) was added to adjust the pH to around 13. Sodium borohydride ($NaBH_4$, 0.5 g) as a reducing agent was also added slowly. The solution was stirred for 1 h at room temperature under a N_2 atmosphere. It was finally centrifuged using water at 12000 rpm for 20 min several times to obtain a pH 7 solution.