Effect of the Number of Benzene-Ring, the Functional Groups and the Absorbent Material on the Performance of Pt Nanoparticles Supported on Modified Graphite Nanoplatelet

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ABSTRACT

A graphite nanoplatelet (GNP) modified with small organic molecules and inorganic element was prepared and subsequently used as an electrocatalyst for the electrooxidation of methanol. The Pt/modified-GNP composite catalyst was characterized by Raman spectrometer, X-ray diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy. The electrochemical properties and electrocatalytic activities of the Pt/modified-GNP hybrid were evaluated by cyclic voltammetry and chronoamperometry. The results indicate that the number of benzene-ring in the organic molecules and the identity of the inorganic elements can influence the dispersion of the Pt nanoparticles. Combine the inorganic elements with aminopyrene (amin) improved the activity of the resultant catalysts for methanol electrooxidation. The activity of the catalysts exhibits an order of Pt/Sn-amin-G < Pt/Ce-amin-G < Pt/Al-amin-G.

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1. Introduction

In the past several decades, direct methanol fuel cells (DMFCs) have attracted considerable attention due to their potential application as clean and mobile power sources because of their fast startup, easy transportation, low operating temperature (<100 °C), high energy efficiency with low exhaustion, and convenient fuel storage [1].

However, there is a large gap between the performance of DMFC and the commercial demand. The main problems with DMFC are that the electrochemical reaction rates for the anode and cathode are slow, using noble metal catalysts leads to high cost, and the liquid fuel penetrates through Nafion membrane [2–5]. Researchers have also found the following problems [6,7]: (1) the adsorption of intermediates can lead to poisoning of the anodic electrocatalyst and a decrease of the catalytic activity. Moreover, the Ru atoms in the Pt-Ru catalyst can dissolve and deposit on the cathodic electrocatalyst. This phenomenon can also lead to the loss of the electrocatalyst and a decrease in activity. (2) The Pt/C catalyst possesses good catalytic activity in the oxygen reduction reaction for the cathode. However in operation, the platinum

particle will congregate or dissolve and the carbon-support materials will also corrode. Those phenomena can decrease the performance of DMFCs. Currently, research on the prevention of fuel penetration, has included on the following areas [8–15]: the development of a new proton membrane, the improvement of the current membrane, the introduction of a fuel additive, the optimization of operation conditions, the design of a new electrode, and the use of methanol-tolerant catalysts.

Research on the improvement of the electrochemical reaction-rate, the stability of the electrocatalyst and the decrease of noble metal use, has investigate the application of new catalyst (such as, transition metal macrocyclic compound [16], platinum-base alloy [17,18], and nitrogen-containing compounds [19–23]) and the construction of new catalyst structures e.g., core-shell [24], and hollow structures [25,26].

Highly graphitized carbon materials, such as carbon nanotubes, carbon fibers, and graphene, exhibit advantages that include corrosion resistance, large specific area, and high electric and thermal conductivities. These carbon materials are ideal substitutes for the support of commercial Pt/C catalysts, because the support of commercial Pt/C is amorphous carbon black [27–29]. Depositing platinum nanoparticle on the surface of this sort of carbon material has thus been a priority in research.

The general characteristics of high-graphitized carbon materials are six-member rings of sp^2 hybridized carbon atoms and

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chemically-inert surfaces. Therefore, when nanoparticles of platinum are deposited on high-graphitized carbon, functional groups must be introduced on the surface of the carbon material. These functional groups can become nucleation sites for nanoparticles [30,31]. In general, carbon nanotube and carbon fibers are treated with concentrated acid. This method can introduce functional groups onto the surface of the carbon materials by grafting of oxygen-containing groups (carboxyl, carboxylic groups, and etc). However, on the surface of graphene, the functional groups include carboxyl and epoxy. Those groups are residual and thus not totally removed during the reduction of graphene oxide.

The introduction of oxygen-containing groups can destroy the graphitized support structure, and decrease the resistance to electrochemical corrosion. Meanwhile, the distribution uniformity of these introduced functional groups cannot be controlled. The lack of uniformity can influence the spatial distribution of platinum nanoparticles and can facilitate their aggregation.

The noncovalent functionalization of graphene with a polymer (e.g., polyaniline [32], polypyrrole [33]) or small organic molecule (e.g., benzylamine [34], and phthalocyanine [35,36].) can help avoid the above-mentioned problems, and can simplify the process of catalyst preparation.

Those polymers and small organic molecules contain two bonds or aromatic ring. On the basal plane of graphene, the sp^2 hybridization of carbon not only leads to strong covalent bonding, but also to the delocalization of π electrons [37]. The interaction of the basal plane with the two bonds or aromatic rings of the guest molecules leads to π–π conjugation. Therefore, the polymer or small organic molecule can be loaded onto the basal plane of graphene through charge-transfer adsorption. Furthermore the functional groups of those materials can provide some anchoring sites for the landing platinum nanoparticles. Therefore, the noncovalent modification of graphene will decrease the size of platinum nanoparticles, and improve the spatial distribution of the catalyst. Moreover, the specific area of the electrocatalyst is increased and the support stability is maintained. However, the size and spatial distribution of the platinum nanoparticles varies with the different electrocatalyst modifiers. In addition, the

influence factor and action mechanism on the modifier-assisted deposition of platinum is not still clear.

This paper describes the use of graphite nanoplates (GNPs) as the support structures after modification with organic small molecules and inorganic ions. Pt/GNPs catalysts were prepared by soft chemical methods. Next, we studied the catalysts' potential application in DMFCs. The physical chemistry characteristics of the Pt/GNPs catalyst were also investigated.

2. Experimental

2.1. Synthesis of electrocatalysts

All chemicals used in this experiment were analytical pure. The graphite nanoplatelets (carbon content >99.5%, specific surface area >90 m^2/g, ACS Material. Com) has a thickness of 1–5 nm and a width of 0.5–20 μm. A solution-blending method was employed for the preparation of modified GNP. In a typical procedure, 100 mg of GNP was homogenously dispersed in 100 ml deionized water and sonicated for 2 h. The solid was filtered, washed with deionized water, dispersed in 100 ml of ethylene glycol (EG) and sonicated again for 1 h at room temperature. The small organic molecule was added into 100 ml ethylene glycol to obtain a dispersed solution. The two solutions were mixed and mechanically stirred for 0.5 h. Deionized water was added to mixed solution and stirred for 12 h ~ 24 h. Next, 0.01 mol/L H$_2$PtCl$_6$ in EG solution was added into the above-mentioned solution and mechanically stirred at 120 °C for 4 h. The solid was filtered, washed with deionized water, and dried in an oven at 60 °C for 12 h. In this study, we used the following small organic molecule: 1,10-phenantholine (phen, 3 rings), aminopyene (amin, 4 rings), perylene (pery, 7 rings) and perylene-3,4,9,10-tetracarboxylic di-imide (PTCDI, 7 rings). Their structures are shown in Fig. 1. We found that the pery forms a carboxylic acid in water and alcohol, so we consider it to have 5 rings, that the phenomenon will not happen with PTCDI, which means that its ring content is 7. As a reference, we prepare the Pt/G catalyst without the small organic molecules. When the GNP was modified by inorganic ions, some details of the
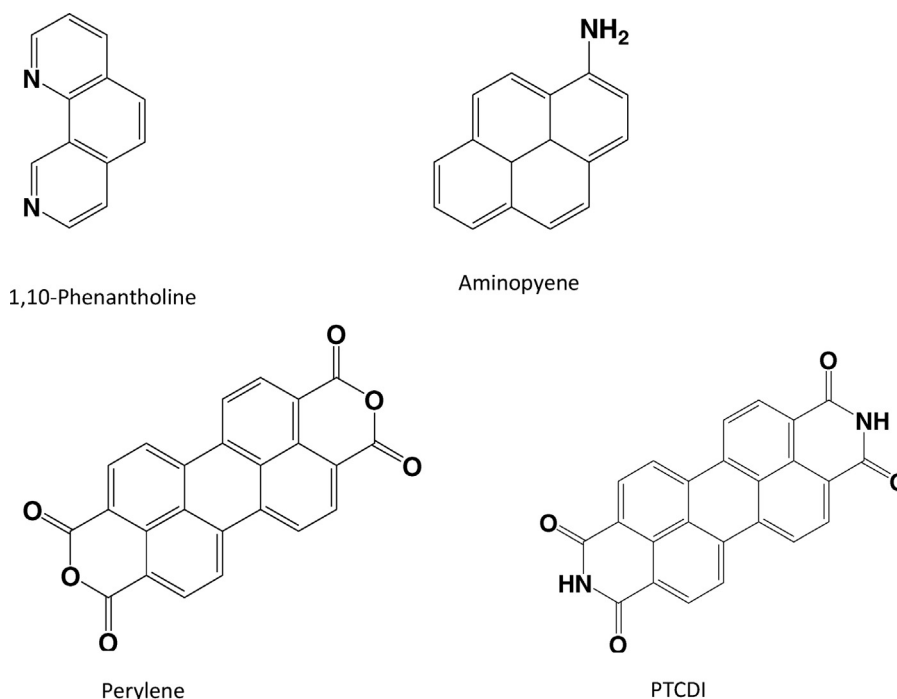

1,10-Phenantholine

Aminopyene

Perylene

PTCDI

Fig. 1. A schematic representation of the structure of the small organic melocule.