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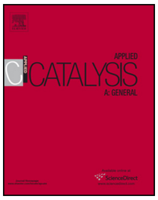

Review

An overview of the electrochemical performance of modified graphene used as an electrocatalyst and as a catalyst support in fuel cells

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ABSTRACT

Fuel cells have recent drawn particular attention from scientists because they are both environmental friendly and highly efficient energy devices. Nevertheless, the commercialization of fuel cells is restricted by the high cost of Pt and the low stability of carbon supports, which are susceptible to corrosion. Graphene is a carbon support that may be able to replace carbon black because it offers a larger active surface area and better resistance toward corrosion. In this paper, graphene-supported Pt-based materials and non-Pt metals are compared to the analogous systems supported on carbon black. The primary issues attributed to graphene are its poor dispersion in solvent and electrochemical inertness. These issues can be resolved by modifying the structure of graphene, obtaining the desired chemical and physical properties through heteroatom doping or chemical functionalization. The properties of the modified graphene include improved solubility in solvent, which is attributed to the presence of foreign atoms or molecules on the graphene sheet; this change leads to a modification of its hydrophilicity. The effects of these additional functional groups or substituted elements on the electrochemical performance of the graphene catalysts in a fuel cell system are discussed herein. In the later sections of this paper, the applications of modified graphene as a catalyst support and as an electrocatalyst for fuel cells are reviewed.

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1. Introduction

A fuel cell is an electrochemical device that converts the free energy of a chemical reaction to electrical energy. Fuel cells are divided into two main categories: high-temperature fuel cells and low-temperature fuel cells. Low-temperature fuel cells include several established types such as proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cell (DMFCs), alkaline fuel cells (AFCs) and microbial fuel cells (MFCs). In contrast, solid oxide fuel cells (SOFCs), molten carbonate fuel cells (MCFCs) and phosphoric acid fuel cells (PAFCs) are types of high-temperature fuel cells. A fuel cell consists of an anode, a cathode and an electrolyte that allows charge to move between the two sides of the fuel cell, which is where the redox reactions in the fuel cell occur to produce electricity. The anode reaction in fuel cells is either the direct oxidation of hydrogen or methanol oxidation via reforming for hydrocarbon fuels, whereas the cathode reaction is an oxygen reduction reaction from air [1]. The sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode and the methanol oxidation reaction (MOR) at the anode are major factors that affect the overall performance of fuel cells and hinder their application as efficient energy storage and conversion devices [2]. Therefore, an efficient catalyst is required to improve these reactions.

The catalyst is a key factor in determining the efficiency, activity and cost of fuel cell devices. An anodic electrocatalyst that produces high anodic current density and a highly negative onset potential toward the MOR is preferable for DMFCs, whereas a cathodic electrocatalyst that produces high cathodic current density and a highly positive onset potential toward the ORR is highly desirable in most fuel cells. Platinum and carbon black are the current state-of-the-art catalyst and catalyst support materials in fuel cells due to their high electrocatalytic activities during fuel cell reactions. Despite their significant catalytic activities, certain critical issues remain, such as low Pt utilization when supported on carbon black, the poisoning of Pt by CO and the degradation of the catalyst support through a support-corrosion mechanism [3]. To address these issues, efforts have been focused on loading a metal catalyst or Pt on carbon nanomaterials, which are more durable and stable and have a larger area available for metal deposition and a higher utilization efficiency of Pt compared to carbon black. Among the various carbon nanomaterials available, graphene is a promising support material due to its unique physical and chemical properties, such as its high electronic and thermal conductivity, large surface area, high chemical stability, high mechanical strength and ease of modification [4]. Graphene sheets can be produced by chemical vapour deposition (CVD) [5], hydrothermal reduction of graphene oxide by hydrazine or $NaBH_4$ [6], thermal annealing of graphene oxide [7], etc. Among these methods, thermal annealing and hydrothermal reduction of graphene oxides are widely employed in this research area due to their simple preparation procedures. The products are normally referred to as graphene or reduced graphene oxide (rGO) [8,9]. Previous studies have reported that Pt/graphene is a better ORR catalyst than Pt/C in terms of stability and durability [10,11].

However, several issues must be resolved before graphene can be used as a catalyst support: the severe aggregation of Pt nanoparticles on graphene surfaces and the restacking of graphene layers due to van der Waal forces. These issues affect the utilization efficiency of noble metal catalysts [12]. Because it is chemically inert and relatively insoluble in organic solvents or aqueous solutions, depositing metal on graphene surfaces has remained difficult.

Common strategies for mitigating these issues include modification of the physical and chemical properties of graphene, such as its solubility, to expand its potential for fuel cell applications. For instance, the assembly and dispersion of metal catalysts on a carbon surface can be improved by introducing suitable functional groups or molecules onto a graphene surface, such as nitrogen atoms [13], sulfonic groups [14], and metal-oxide groups [15]. These functional groups can serve as anchor sites during catalyst deposition. Recent studies have shown that functionalized graphene outperforms plain graphene electrochemically when used to support metal catalysts due to the better dispersion of the metal catalysts on the modified graphene surface [7,16]. In addition to being an excellent catalyst support, the potential of using modified graphene as a non-Pt electrocatalyst in fuel cells has also been demonstrated in some studies [17,18].

Recent developments in producing functionalized graphene catalysts or supports for fuel cell applications are discussed herein. This overview consists of two major sections: (1) the current progress regarding the electrochemical performance of graphene as a support for Pt and non-Pt metal catalysts and (2) the electrochemical performance of different types of modified graphene as catalysts and supports for fuel cell applications.

2. Electrochemical performance of graphene catalyst supports in fuel cells

Currently, carbon black is the state-of-the-art catalyst support material for fuel cell electrodes due to its high electrical conductivity. Nevertheless, some of its properties, such as its surface area and pore size distribution, prevent adequate performance from being achieved in fuel cell reactions [19]. The major drawbacks of carbon black supports include their poor stability during long-term operation and low utilization of the metal catalysts deposited on their surface. Consequently, many studies have been conducted to search for better supports for immobilizing metal particles and thereby maximizing the electrocatalytic activity and reducing the use of metals [20,21]. Due to the superior properties of graphene, such as its high specific surface area and high electrical conductivity [22], scientists have found that graphene can replace carbon black as a support material for metal electrocatalysts in fuel cells. The benefits of possessing a high specific surface area and electrical conductivity, respectively, are the provision of additional catalyst deposition sites per unit volume and the acceleration of electron transport.

2.1. Pt on a graphene support

The development of graphene as a catalyst support in fuel cells has been thoroughly explored recently because Pt/graphene exhibits better catalytic activity [23] and durability [24] toward fuel cell reactions than does Pt/C. Typically, Pt/graphene can be prepared through a chemical reduction route using hydrazine hydrate ($NaBH_4$) or ethylene glycol (EG) [25]. Han et al. [26] observed that Pt nanoparticles loaded on a graphene surface were smaller (2.83 nm) than those loaded on carbon black (4.21 nm) due to the wider surface area of the 2D graphene sheets available for metal loading [27]. In addition, the residual defects in the reduced graphene oxide