



Enhanced Durability of Linker-Containing Carbon Nanotube Functionalized via Diazonium Reaction



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ABSTRACT

We present the fabrication of highly durable catalysts with the functionalized carbon nanotube (CNT) via diazonium chemistry for polymer electrolyte membrane fuel cell (PEMFC). The functionalization of the CNT with the thiolphenyl groups by diazonium coupling reaction was shown to enhance the dispersion of Pt nanoparticles with narrow size distribution deposited on the CNT surfaces as well as their electrochemical stability. The electrochemical analysis demonstrates that the Pt/functionalized CNT show higher electrochemical durability and catalytic activity than the Pt/unmodified CNT. The enhanced electrochemical performance of the Pt/functionalized CNT is attributed to the uniform distribution of Pt nanoparticles with smaller size and the strong interaction between Pt and the functionalized CNT support through the formation of Pt-sulfur bonding. This study shows that this simple functionalization of CNT by the *in situ* grafting of the thiolphenyl groups as the linker onto the surface is an effective way to fabricate a highly durable Pt catalyst for PEMFC, thus providing a design guide of the functionalized CNT support catalyst with a great potential as a PEMFC catalyst.

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1. Introduction

Recently, there is significantly growing interests in polymer electrolyte membrane fuel cells (PEMFC) as promising alternative electric power generation systems for stationary and automotive applications due to high efficiency and power density, low operating temperature, and reduced release of environmental pollutants relative to conventional energy conversion devices [1]. To realize the commercialization of PEMFC, however, technological hurdles, including high cost of the components, performance loss, and poor durability with long-term cycle, remain a challenge. In particular, despite significant advances of PEMFC over the past decades, low durability still presents one of the key challenges for their widespread commercialization [2]. The long-term performance loss of PEMFC is mostly caused by the degradation of PEMFC catalysts and carbon supports, particularly for the cathode catalyst where the oxygen-reduction reaction (ORR) occurs [3]. The Pt/C

catalysts with highly dispersed Pt particles supported on high surface area carbon blacks have been used to date as the state-of-the-art commercial catalysts for PEMFCs. However, Pt particles on conventional carbon black supports agglomerate into larger particles and dissolve into the electrolytes because of their weak adhesion and carbon corrosion under PEMFC operating conditions [4]. The poor durability of Pt/C catalysts is manifested by significant loss of the electrochemical surface area (ECSA) of Pt catalyst over a long cycle due to the corrosion of carbon supports and the complex behavior of the aggregation, dissolution, and electrochemical ripening of Pt particles during the PEMFC operation [5]. Although several types of Pt-based catalysts with enhanced catalytic activity or durability have emerged, they are still in their infancy to be fully developed [6]. Therefore, there are considerable efforts being devoted to the development of the new types of catalysts with enhancing stability as well as sustaining catalytic activity under a wide range of reaction conditions.

The problem of carbon corrosion can be alleviated by using more corrosion-resistant catalyst supports like as the graphitized-carbon material [7–9]. Of these graphitized-carbon materials, CNTs have emerged as promising support materials for PEMFC catalysts because of their large surface area, high electrical conductivity and excellent electrochemical durability [10]. However, it is difficult to

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effectively distribute Pt nanoparticles on the graphitized carbon-based supports due to their chemical inertness and hydrophobicity, and consequently the Pt/CNT catalysts have poor dispersion of Pt nanoparticles with a large diameter and broad size distribution, especially at high Pt loading [11]. To overcome these drawbacks, it is necessary to activate the graphitic surface of CNTs prior to the deposition of Pt nanoparticles. Chemical treatment of CNTs has been commonly applied to modify their surfaces by refluxing in the concentrated acid mixture to generate functional groups on their surfaces [12]. This chemical oxidation method, however, often results in the introduction of a large number of defects on the CNT surfaces, which can reduce their conductivity and corrosion resistance [13]. The corrosion of the carbon supports is considered one of the critical factors causing the ECSA loss of Pt/C catalysts and the decreased durability during PEMFC operation [14]. In this regard, a number of efforts have been thus undertaken to develop a more effective functionalization method for introduction of high density and homogeneous functional groups without a structural damage of CNTs.

One of the facile approaches to mitigate the carbon corrosion is to dope hetero atoms to the carbon frameworks. The use of heteroatom-doping to carbon supports has been demonstrated to change the nucleation and growth behavior of the deposited catalyst particles, and the resulting catalyst particles and carbon supports interactions have been implicated in the enhanced electrochemical durability and activity observed in the modified systems [15–18]. It has been reported that the modification of a graphitized carbon with poly(vinyl pyrrolidone) introduces surface functional groups with high density and homogeneity as well as low damage to CNT [11]. In addition, the coating of polypyrrole on carbon blacks to polish their surfaces by blocking micro-/mesopores was helpful for extending the triple phase boundary, leading to high Pt utilization [19]. Chen et al. [20] reported that Pt nanoparticles can be more uniformly deposited on the nitrogen-doped CNT than on pristine CNT due to higher wettability and active surfaces created by nitrogen doping. It has been also reported that the nitrogen-doped carbons used as Pt supports have an enhanced durability and catalytic activity toward the ORR [20,21]. Higher Pt dispersion and electrochemical properties of hetero atom-doped carbon supports relative to the unmodified carbons are confirmed by the first-principles calculations indicating stronger adsorption of Pt particles on the hetero atom-doped carbon than unmodified one [22,23].

A high level of activities have been made to develop simple and flexible approaches for inducing various functional groups with the desired properties onto the surfaces of carbon materials with the benefit of advanced surface chemistry [24]. As Pinson and co-workers reported the electrochemical reduction of aryl diazonium salt at the carbon surfaces, resulting in the formation of a covalent carbon-carbon bond with the surfaces [25], the diazonium chemistry has attracted great interests in the fields ranging from the basic science to the industrial applications. A number of studies on the spontaneous modification of carbonaceous materials in the presence of diazonium salts suggest that diazonium ions can be considered an excellent reagent for the functionalization of carbon surfaces through both electrochemical and chemical methods [26–28]. The simple and fast reaction of diazonium chemistry as

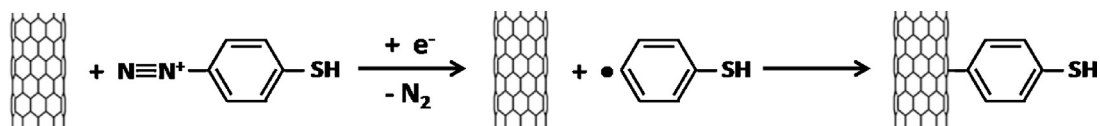
well as the formation of a covalent bond of diazonium ions at carbon surfaces makes them promising modifiers for the functionalization of various types of carbon materials [27–29].

Herein, we demonstrate the modified CNT support by the introduction of sulfur-containing functional groups on the CNT surfaces via simple diazonium reaction. The modified CNT has been synthesized by *in situ* grafting of the thiolphenyl groups to the CNT surfaces through the reduction of the corresponding diazonium cations. The modified CNT has a large number of the thiolphenyl groups on their surface for achieving high Pt dispersion and hydrophobic surfaces. For the modified CNT, moreover, the functional groups directly connect to the main π -conjugated body of CNTs which can minimize the contact resistance between Pt nanoparticle and carbons. In particular, the sulfur-containing functional groups introduced on the CNT surfaces can act as binding sites for anchoring Pt nanoparticles, leading to strong interaction between Pt and CNT support as well as uniform Pt dispersion, which are helpful for preventing the Pt sintering phenomena. As a consequence, the resulting Pt/modified CNT shows higher electrochemical durability than the Pt/unmodified CNT. Our study suggests that the electrochemical durability of the Pt/modified CNT depends on uniform Pt distribution as well as strong interaction between Pt and CNT, which can be enhanced by surface functionalization of CNT, providing a design guide of a highly durable catalyst support with a great potential for a PEMFC electrocatalyst.

2. Experimental

2.1. Surface functionalization of CNT.

The nanotube used in this study was multi-walled CNTs (degree of purity > 95%, Iljin Nanotech) synthesized by a thermal chemical vapor deposition process. According to the supplier, the diameter and length of CNTs were in the range of 10–30 nm and 10–50 μm , respectively, indicating the aspect ratio reaches 1,000. The CNT was modified with the thiolphenyl groups in aqueous medium by spontaneous reduction of the *in situ* generated diazonium cations as shown in Scheme 1 [30–32]. Typically, the functionalization of CNTs was conducted by dispersing 1 g of CNT in 100 mL of the deionized water with the benefit of the ultrasonication for 30 min, to which the desired amount of 4-aminobenzothiol (> 97%, TCI Co.) and the controlled addition of sodium nitrate (NaNO_2 , > 97%, Sigma-Aldrich) upto a concentration twice that of 4-aminobenzothiol for ensuring the total transformation of the amine into diazonium, and followed by the addition of concentrated HCl. The resulting solution was stirred at ambient temperature for 12 h, vacuum-filtered, washed with deionized water sufficiently, and finally dried in a vacuum oven at 70 °C overnight. For comparison, the CNT was oxidized in the mixture of concentrated H_2SO_4 and HNO_3 with the volumetric ratio of 3:1 at 80 °C for 4 h to create the carboxylic acid groups on the CNT surfaces. The Pt nanoparticles (Pt 45 wt.%) were deposited onto the functionalized CNT using the polyol process according to procedures described elsewhere [33]. The functionalized CNT was mixed with a desired amount of Pt precursor (H_2PtCl_6) and sodium hydroxide in the mixture of ethylene glycol/water with the molar ratio of 0.25. The reaction solution was filtered, washed with



Scheme 1. Schematic drawing of the surface modification of CNTs with the diazonium salts. The *in situ* grafting of a substituted thiolphenyl groups onto the CNT surfaces was achieved by reduction of the corresponding diazonium cations through simple diazonium reaction.

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