



A Simple Diazonium Coupling Reaction Enhances Durability of Modified Graphitic Carbons Used as Catalyst Supports for Polymer Electrolyte Membrane Fuel Cell



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ABSTRACT

We present the functionalization of graphitized carbons via simple diazonium reaction as a method for preparation of highly durable Pt catalyst supports for polymer electrolyte membrane fuel cells (PEMFCs). The functionalization of the graphitized carbon supports with the trifluoromethylphenyl groups via diazonium coupling reaction was shown to improve the dispersion of Pt nanoparticles and to reduce the Pt sintering phenomena, resulting in high stability and activity of the Pt/functionalized carbon. This approach also holds a potential for enhancing the dispersion of Pt nanoparticles on the surfaces of graphitized carbons without any deterioration of their intrinsic properties. Electrochemical analysis demonstrates that the Pt/functionalized carbon show improved electrochemical durability than the Pt/graphitized carbon and commercial Pt/C catalyst. The functionalized surfaces of the graphitized carbons not only increases the resistance against carbon corrosion but also offers better attachment of Pt nanoparticles to the carbon surfaces, resulting in the improved durability of the Pt/functionalized carbon. This study shows that this simple functionalization of graphitized carbons by the *in situ* grafting of functional groups onto their surfaces is an effective way to fabricate highly durable catalysts for PEMFCs, thereby providing a design guide of the functionalized carbon supports catalysts with a great potential as PEMFC catalysts.

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1. Introduction

With the increasing environmental concerns and depletion of fossil fuel-based resources, there is significantly growing interests in polymer electrolyte membrane fuel cells (PEMFCs) as a promising alternative electric power generation system for vehicle applications and backup power systems because of their advantages such as high efficiency and power density, low operating temperature, and reduced release of environmental pollutants relative to conventional energy conversion devices [1,2]. The PEMFCs, which directly convert chemical energy stored in fuel molecules into electric energy, are efficient and environmentally-friendly and serve as an electrical power generator on the basis of the oxidation

of hydrogen and the reduction of oxygen [3]. For these reasons, they have been developed as clean and efficient energy sources at a range of scale for automotive and portable power applications.

To realize the commercialization of PEMFCs, however, technological hurdles, including high cost of the components, performance loss, and poor durability with long-term cycle, remain a challenge [4–6]. In particular, despite significant advances of PEMFCs over the past decades, the low durability still presents one of the key challenges for their widespread commercialization [7]. The main contributor to the long-term performance loss of PEMFC is the degradation of PEMFC catalysts and carbon supports, particularly for the cathode catalyst where the oxygen-reduction reaction (ORR) occurs [8]. The Pt/C catalysts with highly dispersed Pt nanoparticles supported on high surface area carbon blacks have been used to date as the state-of-the-art commercial catalysts for PEMFC [9]. On the conventional carbon black supports, however, Pt nanoparticles agglomerate into larger particles and dissolve into the electrolytes due to their weak adhesion and carbon corrosion under PEMFC conditions [9]. The poor durability of Pt/C catalysts is manifested

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by significant loss of the electrochemical surface area (ECSA) of Pt nanoparticles over a long cycle due to the corrosion of carbon supports and the Pt dissolution/Ostwald ripening/aggregation during the PEMFCs operation [10–12]. 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 [13]. Thus, 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.

Currently, graphitized carbons are commonly used to fabricate Pt catalyst supports for PEMFCs due to their unique graphitic properties, high electronic and thermal conductivities, and good electrochemical stability and corrosion resistance [14–19]. However, it is difficult to effectively deposit Pt nanoparticles on the surfaces of graphitic carbons because they are chemically inert and their hydrophobic surfaces tend to prevent uniform dispersion of Pt nanoparticles. To overcome these drawbacks of commercial carbon supports, it is necessary to activate the graphitic carbon surfaces prior to the deposition of Pt nanoparticles [20–23]. Chemical treatments of carbons have been commonly applied to modify the surfaces of graphitic carbons by refluxing in the concentrated acid mixtures to generate functional groups on their surfaces. This chemical oxidation method, however, often results in the introduction of a large number of defects on graphitic carbons, leading to the reduced conductivity and corrosion resistance [24–26]. The corrosion of the carbon supports is considered one of the critical factors causing the ECSA loss of the Pt/C catalysts and the decreased durability during PEMFC operation [27]. 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 graphitic carbon materials.

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 [28,29]. 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 [30], the diazonium chemistry has attracted great interests in the fields ranging from the basic science to the industrial applications. Tour and co-workers demonstrated that sidewall functionalization of single wall CNT causing the permutation of sp^2 carbon atom to sp^3 hybridization, which was reversible upon heat treatment [31–34]. A number of studies also reported the spontaneous modification of carbonaceous materials in the presence of diazonium salts [35–39], where the diazonium ions can be considered an excellent reagent for the functionalization of carbon surfaces through both electrochemical and chemical methods [40–42]. The simple and fast reaction of diazonium chemistry as well as the formation of a covalent bond of diazonium ions at carbon surfaces make them promising modifiers for the functionalization of various typed of carbon materials [40–43].

Herein we present the fabrication of functionalized carbon supports for PEMFC catalysts with enhanced durability and activity. The graphitized carbon supports were functionalized by the *in situ* grafting of trifluoromethylphenyl groups onto the carbon surfaces via simple diazonium reaction. The functionalized surfaces may not only increase the resistance against the corrosion of carbon support but also offer better attachment of Pt nanoparticles to the surfaces of the functionalized carbons. For the functionalized carbons, the functional groups directly connect to the main π -conjugated body of carbons, which can significantly minimize the contact resistance between Pt nanoparticles and carbons in the Pt/functionalized carbon catalysts. The prepared Pt/functionalized carbons also exhibit

significantly much better durability with enhanced catalytic activity than the Pt/graphitized carbon and commercial Pt/C catalysts. Our study demonstrates that the durability of the Pt catalyst depends on the uniformity of Pt nanoparticles dispersion and the capability of preventing their coarsening, which can be enhanced by surface functionalization of graphitic carbons, providing a design guide of highly durable Pt catalyst supports with a great potential for PEMFCs.

2. Experimental

2.1. Surface functionalization of carbon supports

The carbon supports used in this study are amorphous carbon blacks (Ketjen Black ECP 300J) and they are heat-treated at 2250 °C under nitrogen/argon atmosphere to form the graphitic layer structures. The graphitized carbons were modified with a trifluoromethylphenyl grafted layer in aqueous medium by spontaneous reduction of *in situ* generated diazonium cations. Typically, the functionalization of graphitized carbons was conducted by dispersing 1 g of carbon powders in 100 mL of the deionized water with the benefit of ultrasonication for 30 min, to which the desired amount (2, 4, 8, 16, and 32 mM) of 4-aminobenzotrifluoride ($C_7H_6F_3N$, >98%, Tokyo Chemical Industry Co.) and the controlled addition of sodium nitrite ($NaNO_2$, >97%, Sigma-Aldrich Co.) upto a concentration twice that of 4-aminobenzotrifluoride for ensuring the total transformation of the amine into diazonium, and followed by the addition of concentrated HCl. The mixture 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. The surface coverage of the functionalized carbons can be controlled by adjusting the concentration of reactants in the synthesis medium. Pt nanoparticles were deposited onto the functionalized carbons using the polyol process according to procedures described elsewhere [44]. The functionalized carbons were mixed with a desired amount of Pt precursor (H_2PtCl_6) and sodium hydroxide (NaOH) in the mixture of ethylene glycol and water with the molar ratio of 0.25. The reaction solution was filtered, washed with ultrapure water, and then dried in a vacuum oven at 120 °C overnight.

2.2. Characterization

X-ray photoelectron spectroscopy (XPS) spectra were obtained on a VG ESCALAB 220-I system using an Mg K α radiation as the excitation source with the pass energy of 1253.6 eV. XPS analysis was performed under high vacuum conditions (10^{-9} Torr). All binding energies were calibrated with respect to the C1s neutral carbon peak at 284.6 eV. X-ray diffraction (XRD) patterns were obtained using a Philips Xpert X-ray diffractometer with Ni-filtered Cu K α radiation ($\lambda = 0.1542$ nm). Raman spectra were acquired using a JASCO NRS-3100 Raman spectrometer equipped with a 532 nm diode laser, and the laser beam with a nominal power of 30 mW was focused to a spot size of 5 μ m diameter. The high-resolution field emission transmission electron microscopy (HR-FETEM) was used to observe the surface morphology and the dispersion of Pt nanoparticles of the Pt/functionalized carbons. HR-TEM micrographs were obtained using a JEOL TEM-2100-F operated at an accelerating voltage of 200 kV. The ultrahigh resolution field emission scanning electron microscopy (UHR-FESEM) was used to the surface morphology of the functionalized carbons. UHR-FESEM micrographs were obtained using a Hitachi S-5500 by applying beams at low accelerating voltage of 1~2 kV.

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