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Platinum on pyridine-polybenzimidazole wrapped carbon nanotube supports for high temperature proton exchange membrane fuel cells

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ABSTRACT

We synthesize polybenzimidazole (PBI) and pyridine-modified PBIs (Py-m-PBIs) from 3,3'-diamino benzidine (DAB), isophthalic acid (IPA), and 2,6-pyridinedicarboxylic acid (PyDA). Six polymers are obtained, in which the molar ratios of [PyDA]/[IPA] are 1/0, 8/2, 6/4, 5/5, 4/6, 0/1 and the molar ratio of [DAB]/([PyPA] + [IPA]) is fixed at 1/1. These modified PBIs are used to wrap the multiwall carbon nanotubes (MWCNTs) as supports for depositing Pt nano-particles. Pt on CNTs wrapped with Py-m-PBIs (i.e., Pt-Py-m-PBI/CNTs) are used as cathode catalysts for PBI/H₃PO₄ based membrane electrode assemblies, on which fuel cell tests are conducted at 160 °C with non-humidified H₂/O₂. We show that Pt-Py-m-PBI/CNTs give better fuel cell performance than Pt/C (Pt on XC-72 carbon support) catalyst and the performance increases with the increase in the [PyDA]/[IPA] molar ratio of the Py-m-PBIs wrapped on CNTs.

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Introduction

Polybenzimidazole (PBI; synthesized from 3,3'-diamino benzidine (DAB) and isophthalic acid (IPA) monomers) and pyridine-PBI (PyPBI; synthesized from DAB and 2,6-pyridine dicarboxylic acid (PyDA) monomers) doped with H₃PO₄ are two of the most promising proton exchange membranes (PEMs) for high temperature proton exchange membrane fuel cells (HT-PEMFCs; operating temperature 120 °C–200 °C) [1–3]. Compared to Nafion-based high humidity low temperature PEMFCs (LT-PEMFCs; temp < 100 °C), HT-PEMFCs possess few advantages such as having higher rapid electrode kinetics,

greater tolerance to CO impurities in the fuel gas, and simpler heat and water management [4–6].

Most of the current PEMFC catalysts are Pt-immobilized on porous conductive support materials with a high specific surface area. The durability of the catalysts depends highly on the support materials. A suitable support material for metal catalysts should possess the following properties: high electrical and thermal conductivities, good compatibility with metal catalyst, high specific surface area, high chemical and corrosion resistances, good electrochemical stability, and easy recovery of the metal catalyst [7,8]. Among various support materials, Vulcan XC-72 carbon based powder is most widely used in PEMFCs. However, several studies report that Vulcan

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XC-72 powder undergoes electrochemical corrosion at the cathode of PEMFCs after a long-term fuel cell operation [9–11].

The characteristic features of carbon nanotubes (CNTs), such as high specific surface area, good electric and thermal conductivity, high mechanical strength, and good chemical and thermal stability, lead them to be widely used as metal catalyst supports for PEMFCs [12]. However, the CNT surface is inert and not compatible with metal nano-particles (NPs). Therefore, it is necessary to modify CNTs in order to provide sufficient surface active sites to enable the deposition of metal catalyst NPs. There are two main categories for CNT modifications, viz., covalent and non-covalent functionalization [13]. The covalent surface modification of CNT leads to a permanent change in the CNT chemical structure due to the formation of a chemical covalent bond between the CNTs and the Lewis basic functional groups, such as $-\text{NH}_2$, $-\text{OH}$, $-\text{SH}_2$, etc. [13,14]. The non-covalent surface modification is usually a wrapping of a Lewis basic functional polymer film, such as PBI [15], PyPBI [16–18], polyaniline (PANI) [19], polypyrrole (PPy) [20], upon the CNT surfaces via van der Waals forces, electrostatic forces, hydrogen bonding, or other attractive forces [21]. These Lewis basic functional groups (i.e., $>\text{N}$ -, $-\text{NH}_2$, $-\text{NH}$, $-\text{OH}$, $-\text{SH}$ etc.) on the CNT surfaces provide binding sites for Pt^{4+} ion immobilization via Lewis acid–base coordination, and the subsequent reduction of Pt^{4+} ion to Pt-NPs.

The PBI and PyPBI polymers are highly compatible with CNTs because of their inter π – π interactions, and therefore have a great potential for wrapping CNTs [15,22]. Several studies have investigated CNT wrapped with PBI and PyPBI thin films. For instance, Okamoto et al. have reported the fabrication of PBI wrapped multi-wall CNT (PBI/MWCNT) supports, followed by the deposition of Pt-NPs onto the surfaces of PBI/MWCNTs to form Pt-PBI/MWCNTs. They have reported that the Pt-NPs deposited on PBI/MWCNT surfaces have larger electrochemical utilization efficiency than those deposited on pristine-MWCNT surfaces [15]. Fujigaya et al. have demonstrated using a high-resolution transmission electron microscope (HRTEM) that the immobilized Pt-NPs on the surfaces of PyPBI-wrapped MWCNTs (PyPBI/CNTs) are in close contact with the surfaces of MWCNTs and the Pt surfaces are partially exposed from the wrapped PyPBI film layer, which form a good triple-phase boundary structure for catalysis [16]. Berber et al. have reported that the Pt-NPs deposited on the PyPBI/CNT surfaces have a higher durability than those deposited on the PyPBI/CB (i.e., carbon black powder wrapped with PyPBI) surfaces [17].

Besides being highly compatible with CNTs, PBI and pyridine modified PBIs (Py-m-PBIs; which were polymerized from DAB and two dicarboxylic acid monomers, i.e., PyDA and IPA, with various [PyDA]/[IPA] molar ratios) are also compatible with H_3PO_4 . They are used as PEMs and catalyst electrolyte binders in the catalyst layers (CLs) of the membrane electrode assemblies (MEAs), and are proton conductors while doping with H_3PO_4 [23,24]. Therefore, we are interested in using PBI and Py-m-PBIs as CNT wrapping polymers for Pt^{4+} ion deposition and their applications in HT-PEMFCs. In this study, we have investigated the influence of the Lewis basic –N: group content in the polymers wrapped on CNT surfaces on the immobilization of Pt^{4+} ions; the reduced Pt particle sizes and Pt loadings on CNT surfaces; H_3PO_4 doping content and Pt

electrochemical surface area (Pt-ECSA) of the CLs fabricated using these Pt on polymer wrapped CNT (Pt-polymer/CNT) catalysts and PBI binders for HT-PEMFCs.

In a previous study, Py-m-PBI (i.e., 64PyPBI, in which [PyDA]/[IPA] = 6/4 and [DAB]/([PyDA] + [IPA]) = 1/1 by mole) was used to wrap MWCNT surfaces and immobilize Pt NPs to prepare Pt-64PyPBI/CNT catalysts for PBI/ H_3PO_4 based HT-PEMFCs [25]. We have investigated the influence of the wrapped 64PyPBI film thickness on the Pt-loading and Pt-particle size on the 64PyPBI/CNT supports (64PyPBI film thickness was varied from 1.0 to 2.4 nm) and the Pt electrochemical surface area (Pt-ECSA) and HT-PEMFC performance of the gas diffusion electrodes (GDEs) fabricated using these Pt-64PyPBI/CNT catalysts. We demonstrated that the Pt-64PyPBI/CNT catalyst composed of a 64PyPBI film thickness of ~1.6 nm (which was around half of the Pt particle size) wrapped on the CNT surface, having a Pt loading of ~44 wt.% and a Pt particle size of ~3.3 nm had the best HT-PEMFC performance.

The electron donating Lewis base –N: functional groups of PBI and Py-m-PBIs play an important role in the coordination with Pt^{4+} ion and immobilization of Pt NPs on the surfaces of PBI/CNT and Py-m-PBI/CNTs. In this study, five Py-m-PBIs with and a PBI composed of six [PyDA]/[IPA] with molar ratios of 1/0, 8/2, 6/4, 5/5, 4/6, and 0/1 and a fixed [DAB]/([PyDA] + [IPA]) with a molar ratio of 1/1 were used for wrapping and immobilizing Pt-NPs on the CNT surfaces. The wrapped Py-m-PBI and PBI films on the CNT surfaces, according to our earlier study [25], were controlled to a fixed thickness of around 1.6 nm. We demonstrated that under a fixed thickness of the wrapped film, the Pt loading increase, Pt particle size decrease, and the Pt-ECSA of GDEs fabricated using the present Pt-m-PyPBI/CNT and Pt-PBI/CNT catalysts increases with increasing the Lewis base –N: concentration of the wrapping polymer. The GDEs were doped with an aqueous solution of phosphoric acid and used to prepare PBI/ H_3PO_4 based membrane electrode assemblies (MEAs) and perform HT-PEMFC test at 160 °C with non-humidified H_2/O_2 fuel gases. We showed that both the H_3PO_4 loading of the GDE and the fuel cell performance of the MEA increased with increasing the Lewis base –N: group content of the polymer wrapped over the CNT surface.

Experimental

Syntheses of low molecular weight (LMW) PBI and Py-m-PBIs for CNT wrapping

LMW PBI and Py-m-PBIs were synthesized from DAB (Aldrich Chem. Co.), IPA (Aldrich Chem. Co.), and PyDA (Aldrich Chem. Co.) monomers using polyphosphoric acid (PPA, Aldrich Chemical Co.) as a solvent. Table 1 lists the fed monomer compositions for each polymerization synthesis in a 500 g PPA solvent. In each polymerization, the fed tetramine and dicarboxylic acid monomers were controlled at a fixed molar ratio of [DAB]/([PyDA] + [IPA]) = 1/1. However, the fed [PyDA]/[IPA] molar ratio was different in each polymer. Thus the Lewis base –N: concentration in each polymer was different. The detailed PBI and Py-m-PBI polymerization procedures were

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