



Gas diffusion electrode based on electrospun Pani/CNF nanofibers hybrid for proton exchange membrane fuel cells (PEMFC) applications



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ABSTRACT

A novel hybrid system has been investigated based on polyaniline/carbon nanofiber (Pani/CNF) electrospun nanofibers for modification of gas diffusion electrode (GDE) in proton exchange membrane fuel cells (PEMFC). Pani/CNF hybrid nanofibers were synthesized directly on carbon paper by electrospinning method. For preparation of catalyst ink, 20 wt.% Pt/C electrocatalyst with a platinum loading of 0.4 mg cm^{-2} was prepared by polyol technique. SEM studies applied for morphological study of the modified GDE with hybrid nanofibers. This technique indicated that the electrospun nanofibers had a diameter of roughly 100 nm. XRD patterns also showed that the average size of Pt nanoparticles was about 2 nm. Subsequently, comparison of the hybrid electrode electrochemical behavior and 20 wt.% Pt/C commercial one was studied by cyclic voltammetry experiment. The electrochemical data indicated that the hybrid electrode exhibited higher current density (about 15 mA cm^{-2}) and ESA ($160 \text{ m}^2 \text{ gr}^{-1}$) than commercial Pt/C with amount of about 10 mA cm^{-2} and $114 \text{ m}^2 \text{ gr}^{-1}$, respectively. The results herein demonstrate that Pani/CNF nanofibers can be used as a good alternative electrode material for PEMFCs.

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1. Introduction

The proton exchange membrane fuel cells (PEMFCs) have been largely investigated as alternative future energy sources for electric power generation, vehicle application etc. Due to the strong dependence of the fuel cell efficiency to electrode components, catalysts-supporting strategies have been developed. Carbon blacks (e.g., Vulcan XC-72) are usually used as catalyst support because of their large surface area, which elevates metal dispersion and due to its pore structure, which facilitate the transport of reactant gases, and high electrical conductivity [1]. However, there are some disadvantages related to the use of carbon black such as attendance of high amount of micropores, that lead to the inaccessibility of the reactive species to the catalyst and also some other problems, is corrosion of carbon surface in the fuel cell environment that can be caused fuel cell performance losses. On this basis, various alternative catalysts supports such as nanostructured carbon materials and non-carbon materials (e.g., ceramics and conductive polymers) to improve the stability and catalytic activity of the catalyst have been studied [2–5]. Nanostructured carbon materials such as carbon nanofibers (CNF) [6] and carbon nanotubes (CNT) [7] have been investigated as catalyst support in comparison with carbon black in

many studies due to their excellent properties such as good electronic conductivity, high surface area and chemical stability and the results of these papers demonstrated that although these carbon nanomaterials enhanced the electrochemical activity of the catalyst but corrosion of carbon also is observed although the corrosion rate is reduced [8]. Moreover, the investigation of non-carbon catalyst supports such as conductive polymers (CPs) with suitable properties such as antipoisoning effect, high surface area and good porosity compared with carbon blacks in fuel cell conditions has shown that CPs (e.g., polyaniline and polypyrrole) although the active surface area of the catalyst increases but there are also some drawbacks such as the chemical degradation of the polymer [4]. Based on the cyclic voltammetry results, Kim and Park et al. [9] reported that catalyst supported on PtRu/Pani electrocatalyst has higher specific surface area than the same catalysts supported on carbon black. Hable and Wrighton [10] investigated the effect of polyaniline degradation on utility of platinum and showed that the catalytic efficiency is limited. Choi et al. [11] observed that the performance of PtRu/Pani as catalyst support was lower than of PtRu/C. Since the use of both carbon and non-carbon materials alone as catalyst supports has lead to failures in fuel cell conditions, therefore in recent studies, a hybrid of carbon and non-carbon materials as catalyst support have been studied [12]. These hybrid materials such as hybrid of conductive polymer-carbon can offer desirable properties as catalyst supports than their single components. Xu et al. [13] and Wu et al. [14] prepared a Pani-C hybrid support and observed that this hybrid support have higher electrochemical activity than

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Nomenclature

d	tip to collector distance (cm)
L	the average particle size (nm)
$[Pt]$	the loading of Pt (mg cm^{-2})
Q	flow rate of polymer solution (mL/h)
Q_H	the amount of charge transferred during electroadsorption of hydrogen (mC cm^{-2})
V	electrospinning voltage (kV)

Greek letters

β	the width of the peak at half height (rad)
λ	X-ray wavelength
θ_{max}	the angle of the maximum peak (rad)

single Pani or single Vulcan XC-72. They reported that the presence of Pani or Carbon together in the form of hybrid support can improve the conductivity and durability of catalyst support. Gharibi et al. [15] prepared Pani-C hybrid support and found that stability, electrochemical active surface area (EAS), and activity for fuel oxidation of Pt/Pani-C electrocatalyst were higher than Pt/C. They indicated that presence of Pani in hybrid support improved conductivity of both protons and electrons. Shi et al. [16] prepared a hybrid of Pani-CNT and they observed that porosity and electrical conductivity of Pani changes by the introduction of CNT, also they reported that the electrocatalytic activity of Pt/Pani-CNT was higher than Pt/Pani electrocatalyst. Suk oh et al. [17] used hybrid of polypyrrol-CNT as support and found that Pt nanoparticles have better distribution on this hybrid support and also observed that catalytic performance has been higher than Pt/CNT. Rajesh et al. [18] investigated morphological characteristics of conductive polymer as catalyst support. They used nanotubules of polyaniline as platinum support and found that the catalytic activity of platinum based on this nanostructured electrode was higher than Pt/C electrocatalyst and another one that prepared by conventional synthesized polyaniline. On this basis, one-dimensional nanomaterials such as nanofibers and nanotubes, because of their high aspect ratio can be enhanced the catalyst dispersion, conductivity and also charge transport between electrode and electrolyte [19,20]. Among the polyaniline nanostructures, polyaniline nanofibers that have been prepared by electrospinning method, with unique functionality such as good mechanical properties, high porosity and high specific surface area without loss of conductivity have been reported as a good candidate for electronic devices such as fuel cell electrode, sensors and etc [21–23]. Michel et al. [24] and Zhu et al. [25] synthesized polyaniline nanofibers through different methods as catalyst support and indicated that the nanostructured of Pani exhibited a significantly higher catalytic activity than the conventional Pani. Chen et al. [26] prepared polyaniline nanofibers (PaniNFs) as catalyst support and observed that the Pt/PaniNFs support had higher electrochemical active surface area than Pt/C. In many studies electrospinning of conductive polymers with nanoparticles or carbon nanotubes as additives have been reported [27–29], but till now, no studies about preparation of Pani/CNF electrospun nanofibers reported. In addition, many studies on CNT and CNF that were grown on carbon paper by in situ methods (e.g., CVD method) [30–33] for modification of the gas diffusion electrode (GDE) have been carried out. To the best of our knowledge, no study about in situ growth of conductive polymers/CNF electrospun nanofibers as modification of GDE has been reported yet.

In the present study, a new electrode based on a hybrid of carbon-polymer in the form of Pani/CNF electrospun nanofibers as both catalyst support and modification of GDE to improve their

properties are investigated. First, Pani/CNF hybrid nanofibers synthesize via electrospinning method directly on carbon paper. Also, the electrospinning process parameters were investigated for the preparation of uniform and thin nanofibers. Then, Pt/C electrocatalyst are prepared by polyol method, and subsequently the prepared catalyst ink is pipetted on the surface of modified carbon paper with hybrid nanofibers. The physical characterization and electrochemical measurements of the modified GDE with hybrid nanofibers are examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and cyclic voltammetry test, respectively. In order to justify the practical application of this noble hybrid support, the electrochemical results of the hybrid nanofibers are compared with carbon black as catalyst support.

2. Experimental

2.1. Electrocatalyst preparation

Electrocatalyst was prepared by reduction of Pt precursor via the conventional polyol method [34]. The required amount of Pt salt precursor, $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ (Merck) was first dissolved in 25 mL ethylene glycol, and then pH adjustment to above 10 was performed by aqueous NaOH solution. To oxidation of ethylene glycol and production of required electrons to reduce Pt ions, the resulting solution was refluxed in oil bath at 433 K for about 3 h. Afterward, the resulting dark solution was permitted to cool. 0.04 g of Vulcan XC-72R carbon was added to the previous solution under magnetic stirring for 12 h at room temperature. Finally the resulting solution filtered and washed several times with water and acetone. Subsequently, it was dried in vacuum oven at 80 °C and a black powder of the 20 wt.% Pt/C was achieved.

2.2. Pani/CNF hybrid nanofibers preparation

2.2.1. Preparation of Pani/CNF polymer solution

To prepare the Pani/CNF blend solution, 0.03 g of commercially emeraldine base polyaniline (from Sigma Aldrich Grade, Conductivity: 30 S/cm) was mixed in 3 mL of N-methyl pyrrolidone (NMP, 98%, Merck) by stirring for a period of 1 h at 50 °C and then filtered. Also, in another container polyvinyl alcohol (PVA, $M_w = 720,000 \text{ g mol}^{-1}$, Merck) powder was dissolved as spinning agent in distilled water under magnetic stirring for at least 1 h at 70 °C until a viscose solution was achieved. 0.001 g carbon nanofibers (from Sigma-Aldrich, platelet type) were dispersed in 1 mL ethanol using an ultrasonic bath for 30 min. The resulting dispersions was added to the filtered Pani solution, under stirring for 30 min. PVA solution mixed with the previous dark solution and resulted mixture was stirred for 30 min at 50 °C and then filtered to remove particles until a homogenous solution was yielded.

2.2.2. Electrospinning

Electrospinning system was set up and the prepared polymer solution was loaded to a plastic syringe with a tip around 0.5 mm in diameter. Flow rate of the polymer solution was adjusted by a syringe pump. A piece of aluminum foil was positioned below the tip of the needle to collect the hybrid nanofibers. A high voltage was applied between needle and aluminum foil by high-voltage power supply set. Finally, electrospinning method was carried out for the preparation of uniform and thin nanofibers and the value of applied parameters have been listed in Table 1.

The spinning voltage, distance from tip to collector and flow rate of spinning solution, have changed according to data presented in Table 1. Then, the Pani/CNF hybrid nanofibers were collected directly on carbon paper that was placed on the aluminum foil.

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