



Carboxylated carbonized polyaniline nanofibers as Pt-catalyst conducting support for proton exchange membrane fuel cell



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ABSTRACT

Polyaniline based nanofibers (PANF) prepared via emulsion polymerization without auxiliary organic solvent are carbonized to become a 1D and nitrogen-containing electrocatalyst support for proton exchange membrane fuel cell. The carbonization can significantly increase the conductivity of PANF but also create hydrophobic surface, causing much less Pt-loading reduced by ethylene glycol. Carboxylic acid groups are subsequently grafted to the surface by refluxing in sulfuric and nitric acids, which allow carbonized PANF to be dispersed in the aqueous solution and profoundly increase the Pt-loading.

Carboxylated carbonized PANF electrocatalyst support demonstrates better electrochemical activity that prepared from carbon black (Vulcan XC-72) in the cyclic voltaic and ORR testing. The single-cell performance illustrates a higher power and max current density for MEA made of carboxylated carbonized PANF than that of carbon black. Besides, the MEA experiences neither a serious power density loss at high current density (in the cathode) nor the accumulation of water product in the cathode of MEA.

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1. Introduction

The long-standing prospective advantages of replacing fossil fuels with hydrogen fuel can substantially reduce greenhouse gas emissions and smog pollution [1–3]. Therefore, hydrogen fuel cell technologies have been applied in many areas for possible solutions to these problems [4].

Attention has recently been paid on hydrogen and oxygen system of proton exchange membrane fuel cells (PEMFCs) under the considerations of both transportation and emergency electric power sources owing to its friendly by-products, high power density, low noise, and low operating temperatures. However, one of the main problems to commercialize PEMFCs is how to produce low-cost Pt-catalysts with high catalytic efficiency and lasting durability under the working or harsh conditions [5]. The performance of the PEMFCs depends on the properties of the gas flow characteristics in the membrane electrode assembly (MEA) [6] in which interfacial areas between the reactant, electrolyte and catalyst itself, the so-called triple-phase boundary, play important roles on efficiency of PEMFCs. To make a good use of the catalyst, the boundaries between these different phases in the MEAs need to find good ionic and electronic conducting media to create lots

of connected pathways for the protons to pass through the electrolyte and for the electrons to transport through the three-phase electrodes to the outer circuit. Consequently, connected catalyst supports with high porosity and conductivity need to be prepared to accommodate more reactants (fuel gases) to react and allow the produced electrons protons, and water to transport in shorter time. Therefore, we need conducting catalyst supports with nanoscaled pores to accept and effectively disperse the reduced Pt on them [7]. At present, catalyst material for MEA is prepared by loading nanoscale platinum (Pt) particles on the surface of conducting/nanostructure carbon black (CB) support in PEMFC. However, adopting CB as the fuel cell catalyst support still has some disadvantages. For example, the particulate CB can significantly interrupt the passing of electrons to the outer circuit since some of the CB particles do not touch with each other. Meanwhile, carbon support in the cathode is subjected to severe corrosion in the presence of water and produces carbon dioxide at high performing temperature [8–10]. This effect deteriorates the performance of the catalysts and shortens the lifetime of PEMFCs. Eventually, Pt/C catalyst is still provided with a high price, which has already delayed the commercialization of PEMFC. Therefore, cheaper Pt-catalyst supporting material which can resist water corrosion at the working temperature is urgently needed to replace CB, and conducting metal oxides and conducting polymers are some of the candidates [7,11,12].

In the past decades, conducting polymers have been under wide researches for lots of applications in the fields of corrosion

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protection, electrochemical displays, energy conversions, interconnection technology, microelectronics, and sensors [13–17]. Among the conducting polymers, cheap polyaniline and its derivatives [18,19] are qualified candidates because of their high surface area and porosity when prepared on the electrode substrate via simple electrochemical polymerization in acidic media [20].

Another approach to obtain polyanilines with conducting and stable three-dimensional nanostructure is to chemically prepare conducting polyaniline with nanofibrous morphology (PANF) as the support for fuel cell catalysts. Michel et al. [7] introduced a functionalized Pt/PANF composite and demonstrated its high fuel cell performance and high Pt utilization. Wolz et al. [21] reported using polyol reducing method to deposit Pt nanoparticles on PANF and single-walled carbon nanotubes (SWCNTs) to build up alternating layers of PANI supported catalyst, it results in high power densities. Huang et al. [22] investigated the morphology-dependent electrochemical properties of polyaniline micro/nanostructures as catalyst supporters in DMFC applications. Qu et al. [23] prepared core-shell polyaniline/Vulcan Carbon composite structures by in situ chemical polymerization, followed by the deposition of Pt particles to improve the CO anti-poisoning ability and catalytic efficiency of the Pt-catalyst. Yli-Rantala et al. [24] prepared PtNPs/C-PANI/graphitized-CNFs as a highly efficient catalyst with superior thermal stability and corrosion resistance for PEMFC. In comparison with a conventional PtNPs/C catalyst, PtNPs supported on C-PANI materials, modified by a chemical treatment with NaOH, H₂O₂, or HNO₃ at room temperature, provided up to 34% higher power density in PEMFC [25].

However, the poorer conductivity of polyaniline can cause the slow electron transportation during redox reaction and significantly reduce the power supply of PEMFC. Recently, carbonization of nanofibrous nitrogen-containing conducting polymers to increase its conductivity but retain some of the N-related composition after carbonization at high temperature has opened new perspectives for PANF to be a better catalyst support material than CB [26]. Conducting carbonized polyaniline nanotubes prepared by Mentus et al. [27], present a new nitrogen-containing material which is considered as a promising candidate for Pt support. Gavrilov et al. [28] prepared the nitrogen-containing carbonized nanotube/nanosheet polyaniline as a new carbonaceous support for Pt nanoparticles. High electrocatalytic activity of the PtNPs/Carbonized polyaniline electrocatalyst toward ORR in both acidic and alkaline media was clearly seen.

The commercial Pt/C catalyst is usually prepared by loading reduced Pt atoms onto the surface of a CB (Vulcan XC-72) whose pure carbon structure can be eroded during performing of FC and cause a significant concentration polarization of oxygen reduction in the cathode. In this study, we try to replace CB with PANF in the preparation of an MEA of PEMFC to avoid the degradation (corrosion) of the electrode materials and reduce the concentration polarization with the N-related groups of PANF [27,28]. Various properties such as, conductivity, surface area, surface pore diameters of the catalyst support, which have connections with the % and dispersibility of Pt-loading, and electrochemical activities including performance of the single cell of PEMFC will be studied as well.

2. Experimental

2.1. Materials

The aniline monomer (TOKYO KASEI KOGYO CO.) was distilled under vacuum before use. Ammonium persulfate (APS, Showa Chemicals Instrument Co.), *para*-phenolsulfonic acid hydrate (PSA, Tokyo Chemical Industry), hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O, Aldrich), ethylene glycol (EG, J.T.

Baker), hydrochloric acid (HCl, Riedel-de Haën (RDH)), Nitric acid (HNO₃, Riedel-de Haën (RDH)), Sulfuric acid (H₂SO₄, Riedel-de Haën (RDH)) were used without further purification.

2.2. Synthesis of PANF

PANF were prepared through an emulsion polymerization method, described in previous publications [29–32].

The only difference from the previous preparation of PANF was we replace *para*-phenolsulfonic acid hydrate with *n*-dodecylbenzene sulfonic acid as the doping protonic acid.

2.3. Carbonization and carboxylation on PANF electrocatalyst supports

2 g PANF powder prepared in 2.2 was carbonized in an oven at 1100 °C in a nitrogen atmosphere (CPANF) [26]. Then 0.5 g of CPANF was mixed with mixture of concentrated 200 mL 1 M HNO₃ and H₂SO₄ (3:1) and ultrasonicated at 0 °C water for 12 h under ultrasonication. Finally, the obtained acid treated polyaniline (CPANF-COOH) was washed with de-ionized water until the filtrate became neutral and the filter cakes were dried in an oven at 60 °C for 12 h.

2.4. Platinum deposited on various polyanilines

Pt containing polyaniline composites were prepared by reducing a 0.02 mol hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆·6H₂O) with 20 mL of ethylene glycol (EG) in the presence of 16 mg of suspended neat PANF (or CPANF, CPANF-COOH) powders and mixed under sonication for 20 min. The H₂PtCl₆ aqueous solution was drop wise added to the EG and electrocatalyst support (polyanilines) mixture which was under vigorous stirring for 1 h. Then some NaOH was introduced to adjust the pH of the EG solution to above 11. The solution was then heated to 170 °C and refluxing for 2 h. The obtained Pt composites named as Pt/PANF (or Pt/CPANF, Pt/CPANF-COOH) were isolated by filtration and washed with de-ionized water, dried at 60 °C overnight. Theoretically, 20 wt% (or 25 wt%) of Pt will be present in the obtained Pt/polyaniline composite if it is fully reduced by EG.

For comparison, Pt ions were reduced onto Vulcan XC-72 CB at the same H₂PtCl₆ acid concentration and conditions.

2.5. Materials characterization

2.5.1. FTIR spectroscopy

The functional groups of carbonized and carboxylated samples were characterized by FTIR spectroscopy. The FTIR spectra were recorded on an IFS3000 v/s Fourier-transform infrared spectrometer at room temperature.

2.5.2. Raman spectroscopy

The Raman spectra of neat and degraded samples were carried out by a Triax 550 spectroscopy with a green laser light source of 520 nm wavelength. The samples were pressed into tablets before exposing to Raman source.

2.5.3. Electron spectroscopy for chemical analysis (ESCA)

The different binding energy spectra of C_{1s} of various, which were used to estimate the percentage of carbon, carboxylic groups, were analyzed by an ESCA instrument of Fison (VG)-Escalab 210 using Al K α X-ray source at 1486.6 eV. The pressure in the chamber was maintained under 10⁻⁶ Pa or lower during the measurement. A tablet sample was prepared by a stapler. The binding energies of the C_{1s} around 285 eV were recorded.

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