

Metallized Carbon Nanofiber Fabrication For Fuel Cell Applications

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Abstract

Carbon nanofibers (CNFs) with Platinum (Pt) and Palladium (Pd) nanoparticles were produced from poly(acrylonitrile) PAN solution by electrospinning and subsequent pyrolysis in the tube furnace with controlled atmosphere. Electrospinning is a novel technique for fiber formation and offers obtaining submicron diameter of polymeric fibers, and therefore, high surface area to volume ratio. Nanometer size zero-valent Pt and Pd atoms were precipitated selectively on nanofibers from PdCl_2 and H_2PtCl_6 solution in the presence of hydrazine, by using electroless plating techniques at ambient conditions. The surface area of resulting material was characterized by the Brunauer, Emmet, Teller (BET) method and found in the order of $200\text{m}^2/\text{g}$. The diameter of carbon nanofibers found at 200-800 nanometers and Pt and Pd nanoparticles formed on carbon nanofibers were measured 30-60 nanometers by using of scanning electron microscope (SEM). The results indicated that the materials produced were suitable for hydrogen adsorption and catalytic purposes.

Keywords: carbon nanofibers, Pt and Pd nanoparticles, catalyst electrode, electrospinning

Introduction

Carbon nanofibers (CNFs) are very promising materials that cause a major change in several fields of material science and open a way into the nanotechnology. They have taken the attention of researchers worldwide with their unique structural, electrical, mechanical, electromechanical, and chemical properties. Due to CNFs' high strength, chemical purity and inertness, they are suitable for their use as catalyst support, especially in hydrogenations [1]. This property causes them to be encouraging for fuel cell applications, especially in proton exchange membrane fuel cells (PEMFC) or with the other name polymer electrolyte fuel cell (PEFC).

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electrical energy. Through all types of fuel cell, proton exchange membrane fuel cells (PEMFCs) give the highest power density, which offers low weight, cost, and volume. Besides, PEMFCs operate at low temperature, allowing for faster startups and immediate response to changes in the demand for power. Because of these reasons, PEMFCs have a wider application area.

In PEMFCs, at the anode the hydrogen molecules give up electrons and form hydrogen ions, a process which is made possible by the platinum catalyst. The proton exchange membrane allows protons to flow through, but stops electrons from passing through it. As a result, while the electrons flow through an external circuit, the hydrogen ions flow directly through the proton exchange membrane to the cathode, where they combine with oxygen molecules and the electrons to form water.

The catalyst is a special material that is usually made of platinum or palladium and their powder very thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen. The most common carbon supports for Pt catalysts are furnace black and acetylene black. Carbon fibers for furnace blacks are manufactured from aromatic residue oils from petroleum refineries, while carbon fibers for acetylene blacks are made by thermal decomposition of acetylene. These carbon supports have poor structural, electrical and thermal properties compared to PAN-precursor carbon fibers.

To produce high performance carbon fiber, PAN fibers are known as the most important and striking precursor. When compared with other polymeric precursors, PAN fibers have higher degree of molecular orientation, higher melting point ($T_m = 317\text{ }^\circ\text{C}$) and greater yield of the carbon fiber. They are thermally stable and their molecular structure do not significantly disrupted when subjected to higher temperatures during carbonization, which provides them good mechanical property.

Metal nanoparticles are gaining desirable interest in science with their high surface area to volume ratio and quantum size effects. Electrical, optical and photonic properties of nanoparticles are obviously different than the bulk material [2]. While working with nanoparticles, primary undesirable property is their agglomeration [3]. In this study, we eliminate the agglomeration of nanoparticles by direct deposition of particles on electrospun fibers of PAN from solutions. These fibers form the precursor of our carbon fibers.

Transition metal particles have found large application area in catalysis, solar energy adsorption and magnetic materials. Platinum and palladium are known with their selective corrosion resistance, which provides extensive usage in plating onto activation components, turbine blades, electrodes, electronic components and jewellery. [4] It is a desirable material for important industrial processes. However, the main limit for use in many applications is its high cost. In order to decrease the cost, it is preferable to use it in highly dispersed form on supports like carbon, graphite, titanium, etc. Dispersed electrodes are useful in fuel cells and metal-air batteries [5].

This work combines three different steps of electrospinning, reduction of metal salts in hydrazine solution, and pyrolysis of fiber mat that produces large surface area CNFs with well-separated nanosized particles. Nanoparticles of platinum and palladium on PAN fibers were produced by direct reduction of H_2PtCl_6 and PdCl_2 respectively in aqueous hydrazine media.

Experimental Section

Polymerization reaction was accomplished by polymerization of AN with 0.001 wt% AIBN initiator in DMF at 80°C for 7h. The polymer was separated by precipitated in methanol. The solid product was dried under vacuum yielding the desired polymer. Dried polymer and metal salts (H_2PtCl_6 and PdCl_2) were dissolved in DMF at 4 wt% (PAN) and 0.5 wt% (salt) respectively. The solution was prepared at room temperature by stirring to provide dissolving of metal salts and PAN. The solutions were subjected to electrospinning and the details of electrospinning process were explained elsewhere [6]. Spinning process had continued for nearly 6 hours to obtain thick mat, which can be removed easily from the grounded aluminum sheet. An electrical field of 1.5kV/cm was applied to the solution. The electrospun fiber mat immersed into the dilute hydrazine water solution, in the ratio of 1:100 ($V_{\text{hydrazine}}: V_{\text{water}}$). The reducing agent, hydrazine, is miscible with water which is a non-solvent for both metal salts and PAN. Metallic Pt and Pd occur by reducing of their anions such as chloroplatinate (PtCl_6^{2-}) to Pt^0 or Pd^{2-} to Pd^0

metal particles. The indication of this reduction reaction was the color change of mat turning to dark gray after 4 hours.

The mats were then washed with water and dried. Dried mats were pyrolyzed in an inert atmosphere of Argon gas in the tube furnace as shown in Fig.1. To prevent oxidation of fibers, the inert gas was purged into the system before the pyrolysis process. The metallized PAN membrane was heated to 600-800 °C and maintained at that temperature for 30 m. The heating rate was 5 °C/min. and argon gas flow rate was 110 cm³/min [7]. The cooling process was also performed in an inert atmosphere.

Fig.1. Argon gas pyrolysis system

Characterization of metal containing carbon nanofibers made by field emission scanning electron microscope with energy dispersive spectroscopy function (FE SEM-EDS/Leo Supra 35VP). The precise diameter measurements of particles and fibers were performed on 60 test particles. The specific surface areas of the samples were calculated from nitrogen adsorption isotherms by the Brunauer, Emmet, Teller (BET) method mainly for comparative purposes.

Results

Figure 2 shows the SEM image of carbon nanofibers before and after the pyrolysis process. Images of fiber surface can be viewed clearly. The diameters of fibers and particles are estimated by processing these images. The fibers have uniform diameter in the range of 400-500 nm for PAN-Pt samples and 800 nm for PAN-Pd samples and a well-defined shape, Figure 2a,b. During pyrolysis process the morphology of fibers at some points are disrupted as seen in Fig.2c,d. At some points fibers break and attach each other losing their boundaries. Figure 2e,f. shows that the Pt and Pd particles are spherical and well distributed on the nanofibers. The normalized distribution of particle sizes is given in Figure 3, which can be concluded as monodisperse.

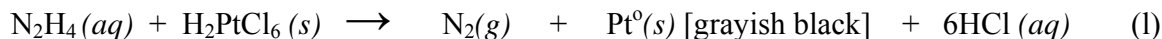
(a) PAN-Pt before pyrolysis	(b) PAN-Pd before pyrolysis
(c) PAN-Pt after pyrolysis	(d) PAN-Pd after pyrolysis
(e) Pt particles on carbonized PAN	(f) Pd particles on carbonized PAN

Fig. 2. Electron microscope images Polyacrylonitrile nanofibers and their metallized

Fig.3. Diameter distribution of Pd and Pt particles

EDS attached to SEM was employed to identify Pt and Pd metal particles. Pt and Pd particles were produced inside the electrospun mats by reducing H₂PtCl₆ and PdCl₂ with hydrazine hydrate.

The redox reaction of H_2PtCl_6 and PdCl_2 in hydrazine solution are illustrated as follows:



The oxidation-reduction reaction proceeds with the appearances of bubbles on the electrospun fibers. These bubbles are the N_2 gas according to eq. 1 and 2. The energy-dispersive spectra collected from a region of carbonized mat approve the presence of Pt and Pd particles showing peaks around 2.04 keV and 9.44 keV for Pt and the appearance of dominant peak at around 0.2 keV and small peak around 3 keV approves the presence of Pd particles.

Results of the BET measurements of PAN-Pt show that the specific surface area of films is on the order of 200 m^2/g of carbon fibers Table 1. For a textural characterization of any porous solid, the concept of surface area does not give a visual picture of it. Pore size and pore size distributions are necessary if the material is to be fully characterized. The pore size distribution in the mesopore region was obtained by applying the method of BJH [8] to the desorption brunch of the isotherms of nitrogen at 77 K, assuming the pores to be cylindrical in shape. PAN-Pt samples prepared at different temperatures have mesopores of which diameters are around 22 Å.

Sample PAN-Pt	BET surface area, m^2/g	BJH method cumulative desorption pore volume, cc/g	BJH method desorption pore diameter, Å
600°C	279.3	0.2006	22.09
700°C	113.4	0.1318	22.02
800°C	200.4	0.1618	22.06

Table 1. Specific surface area, gas desorption volume and pore diameters of carbonized PAN-Pt Samples, prepared at 600°C, 700°C, 800°C.

Conclusion

In this study, we successfully prepared Pd and Pt nanoparticles containing carbon fibers webs for possible catalytic uses. We investigated the production of CNFs from Pt and Pd containing PAN fiber mats. Zerovalent nanoparticles and their dimensions were characterized by EDS analysis. Fiber diameters are measured by SEM and surface area were calculated by BET method. Their catalytic activities are under investigation. For future work, we plan to increase the effective surface area of electrospun film by obtaining thinner nanofibers by changing spinning viscosity or polymer molecular weight and moreover, Pt and Pd particle sizes will be controlled by introducing a polar co-monomer on the PAN backbone to obtain smaller and more uniform size metal particles [3].

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