Electrochemistry Communications 11 (2009) 438–441

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

# 3-D composite electrodes for high performance PEM fuel cells composed of Pt supported on nitrogen-doped carbon nanotubes grown on carbon paper

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ARTICLE INFO

*Article history:*
Received 14 November 2008
Received in revised form 2 December 2008
Accepted 4 December 2008
Available online 13 December 2008

*Keywords:*
Pt nanoparticles
Carbon nanotubes
Nitrogen-doped carbon nanotubes
Electrocatalysis
Proton exchange membrane fuel cells

ABSTRACT

The 3-D composite electrodes consisting of Pt nanoparticles supported on nitrogen-doped carbon nanotubes ($CN_x$) grown directly on carbon paper were successfully prepared. The effect of the nitrogen atom incorporation in carbon nanotubes (CNTs) on the Pt nanoparticle dispersion and catalytic activities for the oxygen reduction reaction has been investigated. Compared to regular CNTs, highly dispersed Pt nanoparticles with smaller size (2–3 nm) and higher electrochemical Pt surface area as well as higher fuel cell performance were obtained for $CN_x$.

## 1. Introduction

Proton exchange membrane fuel cells (PEMFC) are receiving widespread attention as an alternative power source due to their low pollution, high power density at low temperatures (55–95 °C), and compact design [1]. Despite the advantages, there are some barriers still existing, such as low catalytic activity, durability, and cost issues that have to be overcome before it can become economically viable [2,3]. The catalytic activity of Pt-based catalysts depends on many factors, among which the carbon-supported material plays an important role, since it is used as support for the catalysts [4]. Carbon black (Vulcan XC-72) has been widely used as the support of the Pt catalysts in the state of the art PEMFC [4,5]. In spite of their high surface area, the presence of micropores limits its use as catalyst support because the metallic particles get trapped in the micropore and become electrochemically inaccessible.

Recently, carbon nanotubes (CNTs) have been proposed as promising support materials for PEMFC catalysts because of their high aspect ratio, good electronic conductivity and high surface area [6–8]. However, the effective attachment of Pt nanoparticles uniformly dispersed onto CNTs remains a formidable challenge because of the inertness of the CNT surface [9]. Therefore, CNTs surfaces need to be functionalized by chemical oxidation in order to obtain reactive sites for the adhesion of Pt metal particles [10]. However, it is difficult to deposit Pt nanoparticles on the surface of CNTs with uniform size and good dispersion because Pt particles are spontaneously formed at the defect sites on the surface of CNTs. Furthermore, these acid treatments reduce considerably the mechanical and electronic performance, as well as (electro) chemical stability, of the tubes due to the introduction of large numbers of defects and surface functional groups. The doping of CNTs with other elements (e.g., nitrogen) could be a particularly interesting way to modify their electronic and mechanical properties [11]. Recently, nitrogen-doped CNTs ($CN_x$) were reported as support materials in fuel cell catalysts, especially in terms of well dispersion of Pt nanoparticles [12–14]. $CN_x$ contain nitrogenated sites (substitutional and pyridinic nitrogen) that are chemically active. Therefore, it should be possible to avoid functionalization processes that use strong acid treatments, and attach Pt nanoparticles onto the $CN_x$. In addition, $CN_x$ as the catalyst support is expected to improve the durability due to the strong electron donor behavior of nitrogen and the enhanced $\pi$-bonding [3,15].

In this paper, the deposition of Pt nanoparticles on both of CNTs and $CN_x$ directly grown on the carbon paper is investigated. The unique advantage of the growth of nanotubes directly on carbon paper is that all the deposited Pt particles are in electrical contact with the external electrical circuit and much improved Pt utilization has been achieved [8,16]. The influence of the nitrogen incorporation in CNTs on the dispersion of Pt nanoparticles and fuel cell performance is discussed.

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doi:10.1016/j.elecom.2008.12.013

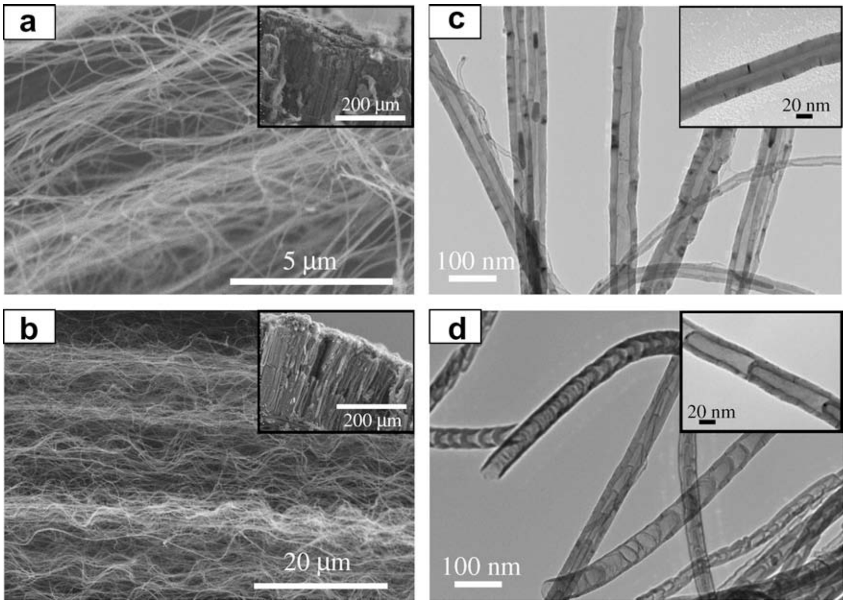

**Fig. 1.** (a,b) SEM images of (a) regular CNTs and (b) $CN_x$ grown on carbon paper by the AA-CVD method. Insets: cross-sectional views. (c,d) TEM images of regular CNTs and (b) $CN_x$. Insets: single nanotube.

## 2. Experimental

The CNTs and $CN_x$ were grown directly on the fibers of carbon paper (E-TEK, a division of BASF Fuel Cells, Somerset, NJ) by using aerosol-assisted chemical vapor deposition (AA-CVD) method. The typical nanotube carpets were obtained from pyrolysis of a solution of 5 wt.% ferrocene dissolved in m-xylene with sonication at 850 °C during 1 h time period. Argon (99.999%) was introduced into the heating system at a flow rate of 600 sccm and $H_2$ as the reaction gas was introduced at a flow rate of 200 sccm with Ar flow rate of 200 sccm. For the growth of $CN_x$, the metal catalyst precursor, 1.1 mM [Fe(III)(acetylacetonate)$_3$], is dissolved in a mixture of acetonitrile and tetrahydrofuran with atomic C/N ratio about 6. Other parameters were kept the same as for CNTs above.

The Pt nanoparticles were deposited on CNTs and $CN_x$ by the impregnation method described in the literature [10]. The Pt loading in the Pt/CNTs and Pt/$CN_x$ composites were determined to be 0.11 and 0.12 mg/cm$^2$, respectively, by inductively coupled plasma–optical emission spectroscopy (ICP–OES). The morphologies were examined using a scanning electron microscope (SEM) (Hitachi S-2600 N) and transmission electron microscopy (TEM) (Philips CM10).

The electrochemical measurements were carried out using an Autolab potentiostat/galvanostat (Model, PGSTAT-30, Ecochemie, Brinkman Instruments) in a three-electrode, two-compartment configuration cell. A Pt wire served as the counter electrode and a reversible hydrogen electrode (RHE) were used as the reference electrode.

The detailed procedure for cell assembly and electrode preparation are described elsewhere [17]. The cathode was a Pt/CNTs or Pt/$CN_x$ electrode and the anodes were commercially available 30 wt.% Pt/C. The electrode area was 1.0 cm$^2$ and typical loading of Nafion ionomer in all electrodes was in the ranges of 0.5–0.8 mg/cm$^2$.

## 3. Results and discussion

Fig. 1 shows SEM and TEM images of CNTs and $CN_x$ directly grown on the fibers of carbon paper by the AA-CVD method. As shown in Fig. 1a and b, highly dense CNTs and $CN_x$ of 15 µm length completely cover the surface of the carbon fibers. Furthermore, the surface of $CN_x$ was not as smooth as that of non-doped CNTs. TEM showed that CNTs have smooth surfaces while $CN_x$ exhibited a bamboo-like structure [18].

Fig. 2 shows the TEM images of Pt nanoparticles supported on CNTs and $CN_x$ and the corresponding particle size distribution histograms. The histograms of Pt particle size distribution are obtained based on measurements of over 300 Pt particles. As can be seen in Fig. 2a, the surface of CNTs was covered with Pt nanoparticles exhibiting diameters ranging from 3 to 7 nm. In addition, these particles were inhomogeneously dispersed on the surfaces of CNTs with large agglomerates of Pt nanoparticles. In the case of $CN_x$, the Pt nanoparticle have been homogeneously dispersed on the nanotubes and particle sizes were found to be around 2–3 nm (Fig. 2b). It is evident that a narrower particle size distribution with average particle size of 2.63 nm is achieved for $CN_x$. In comparison, the mean particle size of Pt on the CNT support is higher (5.89 nm) and the particle size distribution is wider. The better dispersion of Pt nanoparticles on the $CN_x$ might be due to the substitutional N site in $CN_x$ which favors the Pt deposition [13].

Fig. 3 compares the cyclic voltammograms of Pt/CNT and Pt/$CN_x$ composites in Ar-saturated 0.5 M $H_2SO_4$ aqueous solution. The voltammetric features of both electrodes reveal the typical characteristics of Pt metal [19], with well-defined hydrogen adsorption–desorption peaks in the potential region 0.0 to 0.2 V. By using the charge passed for hydrogen adsorption and desorption ($Q_H$), the Pt electrochemical surface area is 55.6 m$^2$/g$_{Pt}$ for the Pt/$CN_x$ composite, which is about 36% higher than that for Pt/CNT. The high surface area for the Pt/$CN_x$ electrode is owing to the presence of narrow size and uniform distribution of the Pt nanoparticles as shown in the TEM images (Fig. 2).

Fig. 4a shows the single-cell performance for the MEA made with Pt/CNT or Pt/$CN_x$ composite as cathode and standard E-TEK GDE as anode. For comparison, the polarization curve of the conventional MEA made with Pt/C electrodes as cathode and anode is also shown here. It was observed that both Pt/CNT and Pt/$CN_x$ electrode showed better performance than the conventional Pt/C MEA, especially in the high current density region. The incorporation of N atoms into CNTs to produce $CN_x$ contributes to better cell polarization characteristics than regular CNTs. Based on cell

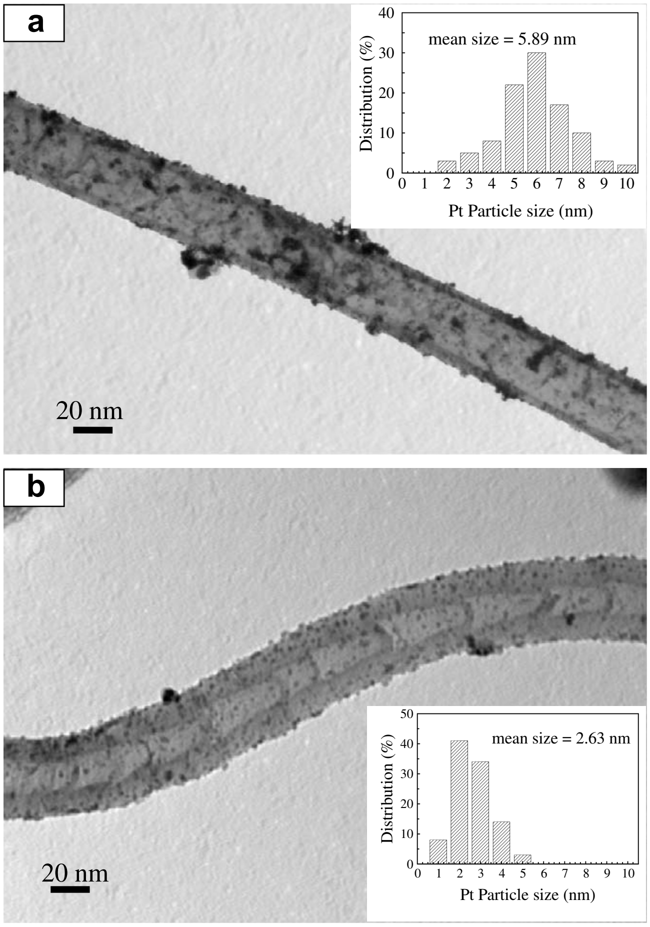

**Fig. 2.** TEM images of (a) regular CNTs and (b) $CN_x$ grown on carbon paper after deposition of Pt nanoparticles by the impregnation method. Insets: size distribution of Pt particles.

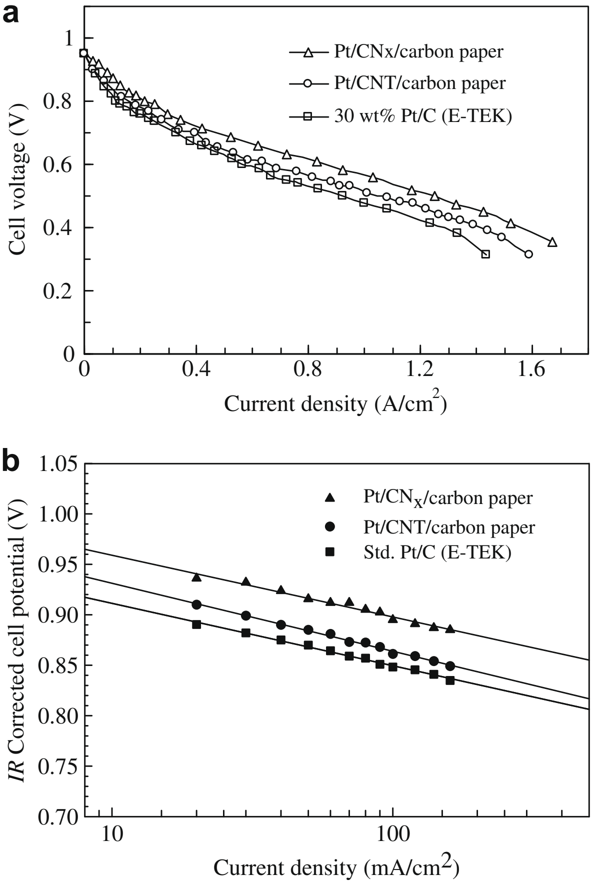

**Fig. 4.** (a) Comparison of cell performance with MEAs made of Pt/CNT, $Pt/CN_x$ and conventional Pt/C electrodes with $H_2/O_2$ at 80 °C, Nafion 112 membrane, 25/30 psig anode and cathode back pressure, respectively. Anodes were E-TEK electrodes with a Pt loading of 0.5 mg/cm$^2$. (b) *IR* corrected Tafel plots for comparison of kinetic parameters.

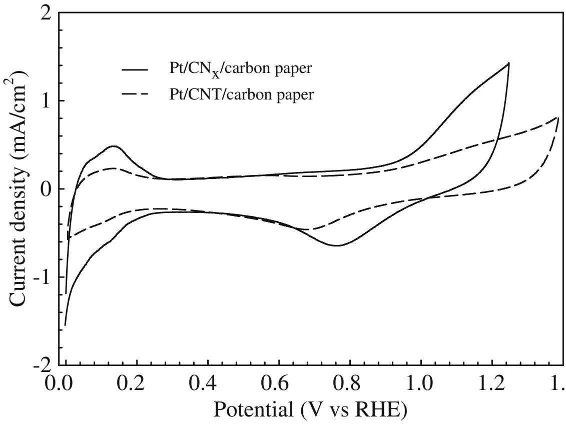

**Fig. 3.** Cyclic voltammograms in Ar-saturated 0.5 M $H_2SO_4$ for Pt/CNT and $Pt/CN_x$ electrodes. Potential scan rate: 50 mV/s.

polarization data shown in Fig. 4a, the kinetic parameters of the oxygen reduction reaction can be obtained using the semi-empirical equation proposed by Ticianelli et al. [20].

Comparison of the *iR*-free Tafel plots for oxygen reduction is presented in Fig. 4b. It can be seen that the Tafel slope is *ca.* 60 mV/dec for all of the electrodes which is common to most supported and unsupported Pt electrodes [21]. The current density at a potential of 900 mV ($i_{900\ \mathrm{mV}}$) for the CNT-based electrode (29.0 mA/cm$^2$) is higher than that for the conventional Pt/C electrode (15.2 mA/cm$^2$). As expected, $CN_x$ electrode shows a higher current density at 900 mV than CNT electrode. The high performance of $Pt/CN_x$ electrode is believed to be due to the superior dispersion of smaller Pt particles, an improved catalyst-support binding and a synergistic effect of $CN_x$ as catalyst support. The doping nitrogen atoms also change their electronic properties. The resulting $CN_x$ contain an extra electron, which is more easily donated to $O_2$, thus improving the catalytic activity [15].

## 4. Conclusions

Pt nanoparticles supported on CNTs and $CN_x$ grown directly on carbon paper were prepared by the impregnation method. The Pt nanoparticles, which were uniformly dispersed on the $CN_x$, had an average particle size of 2.63 nm and had a very narrow particle size distribution. The CNT supports, by comparison, had average Pt particles size about 5.89 nm, and a broad particle size distribution. The $Pt/CN_x$ electrodes have a greater electrochemical surface area than the Pt/CNT electrodes as well as higher single-cell performance in a $H_2/O_2$ fuel cell.

## Acknowledgements

This research was supported by Natural Sciences and Engineering Research Council of Canada (NSERC), Ballard Power System Inc., Canada Research Chair (CRC) Program and Ontario Early Researcher Award (ERA). We are in debt to David Tweddell for his kind help and fruitful discussions.

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