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Composite electrodes made of Pt nanoparticles deposited on carbon nanotubes grown on fuel cell backings

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Abstract

Multiwalled carbon nanotubes (MWCNTs), with typical lengths of 20 μ m and diameters of 40 nm, have been grown directly on carbon paper backing. A sulfonic acid–silicate intermediate was used to deposit Pt particles on the MWCNTs in order to obtain an electrode that could be used in electrocatalysis. The electrical path between the Pt nanoparticles (1.2±0.3 nm in size) and the carbon paper, through the MWCNTs, was demonstrated by cyclic voltammetry. The Pt surface density of a typical MWCNT composite electrode is estimated to be about 25% of that of an ELAT electrode from E-TEK, containing 0.4 mg Pt/cm².

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1. Introduction

Carbon nanotubes are of significant interest, due to their unique structure, properties and potential applications [1–3]. If the attention today is mainly focused on the synthesis, purification, functionalization and possible applications of single walled carbon nanotubes (SWCNTs), multiwalled carbon nanotubes (MWCNTs) are certainly closer to commercial applications. For instance, the use of MWCNTs in composite materials [4], or as electrical field emitters [5], is well established. Our interest in MWCNTs is to use them as electrocatalyst supports in polymer electrolyte membrane (PEM) and in direct methanol fuel cells. Indeed, the use of carbon nanostructures as metal supports in electrochemistry and fuel cells has been reported by several authors [6–11]. However, in these reports, the catalysts were deposited onto loose nanotubes, or nanohorns, just as on carbon black. Our strategy for the electrode fabrication in this work is different.

We recently developed a unique CVD procedure permitting us to grow MWCNTs on the carbon fibers of a fuel cell backing. In the present work, we will show that it is possible to deposit Pt particles on these MWCNTs and, therefore, to obtain a composite electrode for which an electrical path exists between the Pt catalyst and the

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carbon backing. The deposition of Pt on MWCNTs has been chosen because Pt and its alloys are currently the most extensively used catalysts in PEM and direct methanol fuel cells [12–14].

Carbon nanotubes are hydrophobic materials, rendering difficult the adhesion of metal deposits. It has been reported that carbon nanotubes cannot be wet by liquids with surface tension higher than 100–200 mN/m [15], indicating that most metals would not adhere to them. In order to improve metal deposition onto nanotubes, two main approaches were previously developed: (i) surface modification and (ii) sensitization activation. The former is associated with the oxidation of the nanotube surface, in order to create functional groups and increase metal nucleation [16,17]. The latter involves the generation of small nuclei (e.g., of Pd–Sn) to further promote metal deposits on carbon nanotubes [18,19].

In our previous studies on the growth of MWCNTs [20,21], we successfully used a sulfonic acid–silicate intermediate to disperse Co–Ni particles, used in the catalytic decomposition of ethylene, to promote the growth of nanotubes on the carbon backing (see Fig. 1). In this work, we ex-



Fig. 1. Schematic reaction of the silane derivative, which hydrolyzes and polymerizes to become a sulfonic acid-silicate layer able to exchange protons with Ni and Co ions, as a first step in the production of catalytic sites on carbon paper. The surface polarity of this support may be modified by methanol pretreatment. The same procedure may be used with Pt ions to obtain a Pt sulfonate-silicate, which is the precursor of the Pt particles.

ploit the same idea to deposit Pt particles onto MWCNTs grown on carbon paper. The present work demonstrates that it is possible to obtain very small Pt particles deposited onto MWCNTs and that these metal particles are in electrical contact, through the MWCNT, with the carbon backing, enabling the composite structure to be used as an electrode.

2. Experimental

MWCNTs were synthesized by heating Co-Ni particles deposited on the fibers of a carbon paper in a specifically designed CVD reactor [22]. This reactor takes advantage of the fact that the carbon fuel cell backing (E-TEK, Division of DeNora with 81% porosity) is the most resistive part of the electrical circuit. It can therefore be heated by Joule effect, up to 800 °C, a temperature high enough to decompose ethylene and grow nanotubes. Prior to Co-Ni deposition, the carbon backings were pretreated with methanol for 30 min, in order to improve the homogeneity of the Co-Ni particle sizes and their distributions on the carbon fibers of the backing. Details of Co-Ni particle deposition have been described previously [20,21] but the important step in their fabrication is the use of a commercially available silane derivative (2(4-chlorosulfonylphenyl) ethyl trichlorosilane, from United Chemical Technologies) which, upon hydrolysis, forms a sulfonic acid-silicate, permitting the exchange of H⁺ for Co²⁺ and Ni²⁺ ions (see Fig. 1). The latter ions are the precursors of the Co-Ni particles. Pt deposition was carried out using the same silane derivative but, this time, using Pt²⁺ ions as Pt particle precursors. The deposition of Pt particles was carried out by immersing the MWCNT/carbon paper composite structure in a solution containing 0.04 M PtCl₂, 1 vol% of silane derivative and 6 vol% of water in ethanol. The composite structure was then dried at room temperature and reduced in a flow of $H_2 + Ar$, at 580 °C for 15 min. The methanol treatment, which was used with success to improve the distribution of Co-Ni particles on the carbon paper, was also applied to the nanotubes before adsorbing the Pt sulfonated-silicate (see Fig. 1).

A Hitachi-9000 NAR high-resolution transmission electron microscope (HRTEM), with energy dispersive X-ray spectroscopy (EDX), operated at 300 kV, and a Hitachi S-4700 fieldemission scanning electron microscope (FE-SEM), operated at 15 kV, were employed to characterize the structure, composition and morphology of the carbon nanotubes and Pt particles.

The electrochemical properties of the electrode materials were investigated by cyclic voltammetry in a standard three-electrode cell. A Pt foil served as counter electrode, and a saturated calomel electrode (SCE) was used as reference electrode. All working electrodes had the same 1 cm² of geometrical surface. Cyclic voltammetry measurements were carried out using a 273A EGG Potentiostat with a 10 mV/s sweep rate. $Fe(CN)_6^{3-/4-}$ were used as the oxydo-reduction couple (as a 10 mM solution of K_3 Fe(CN)₆ in 0.5 M K₂SO₄) for the bare carbon paper and for the MWCNT/carbon paper electrodes. A H₂SO₄ solution, at, pH 1, purged with Ar, was used to perform the voltammetry of Pt particles deposited on MWCNT/carbon paper. For all those experiments, the voltammograms were recorded after cycling the working electrode at least 20 times, at 50 mV/s, in the same potential range as that used to record the voltammetry. The amount of Pt in contact with the electrolyte was measured by integration of the charge related to the H-adsoption in the cyclic voltammogram recorded at 10 mV/s. In order to be sure that the electrolyte wets the electrodes, they are soaked under stirring during 15 min in methanol, then in H₂SO₄ at, pH 1, before being placed in the cell under Ar atmosphere.

3. Results and discussion

A typical SEM micrograph of MWCNTs, grown on the fibers of a carbon paper, is shown in Fig. 2a. Fig. 2b displays a TEM close-up of the same MWCNTs. A high density of tubes, firmly anchored on the carbon paper, resulted from the methanol pretreatment of the carbon paper before adsorbtion of the Co–Ni sulfonate–silicate. The latter is used as precursor of the Co–Ni particles, which are the catalysts used for the growth of the



Fig. 2. (a) Scanning electron micrograph and (b) transmission electron micrograph of the MWCNTs on a carbon fiber. Inset: high resolution micrograph of the wall of a typical nanotube.

nanotubes [20,21]. These tubes are about 20 μ m in length and are characterized by a diameter of 30–50 nm. They are tip-grown, as indicated by the presence of the Co–Ni alloy particles at the tip of the tubes (Fig. 2b). These particles are completely enclosed in the nanotube and are therefore protected from dissolution when the MWCNT/carbon paper electrode is immersed in an acid solution. A closer observation of the walls of a typical tube is shown in the inset of Fig. 2b. The high resolution TEM micrograph reveals that the tube is composed of 22 well organized concentric carbon layers, separated by 0.34 nm.

It is possible to deposit Pt particles on these nanotubes by simply adsorbing the Pt salt on methanol pretreated MWCNT/carbon paper. This procedure yields large (~4–10 nm) Pt particles after heat-treatment in a reducing atmosphere, as shown in Fig. 3a. However, much smaller Pt particles (Fig. 3b) are obtained when Pt ions are dispersed on MWCNT/carbon paper using the silane derivative procedure (Fig. 1) to adsorb Pt ions onto the nanotubes. A magnified view of the homogeneous dispersion of the small Pt particles is presented in Fig. 3c, which also displays the graphitic structure of the nanotube walls, comprising 15 concentric graphene sheets. This tube has an outer diameter of nearly 35 nm with a hollow center of about 25 nm. The size of about 100 Pt particles was measured on a high resolution TEM micrography and an average Pt particle size of 1.2 ± 0.3 nm was determined. The EDX compositional analysis of several Pt nanoparticles confirms the presence of Pt, along with a small amount of Co and Ni, which have their origin in the metals used as catalysts for the nanotube growth. An



Fig. 3. Transmission electron micrographs of Pt nanoparticles deposited on MWCNTs. (a) In the absence of the silane precursor; (b) in the presence of the silane precursor; (c) higher magnification TEM of (b).

important point to stress is that neither S (a poison for Pt) nor Si signals were detected by EDX, with the Pt signal. It should also be noted that all Pt particles are located on the external surface of the tubes because the tubes were not opened. The density of the Pt particles, based on averaging the measurements performed from HRTEM micrographies on five tubes, is nearly one particle/ 100 nm². Accordingly, if one typical nanotube is 20 μ m long and 40 nm in diameter, it will be decorated with 2.5×10^4 Pt particles on its outer wall.

It is of practical importance to demonstrate that this composite structure is really an electrode, i.e., that:

- (i) the MWCNTs are in electrical contact with the fuel cell backing,
- (ii) the Pt particles are in electrical contact with MWCNTs.

The electrical contact between MWCNTs and the carbon fibers of the fuel cell backing is demonstrated in Fig. 4. This figure shows the voltammetry of the $Fe(CN)_6^{3-/4-}$ couple on a bare carbon paper and on MWCNTs grown on the carbon paper. A typical voltammogram with graphite features [23] and a higher available electroactive surface is obtained on MWCNTs, strongly suggesting that these nanotubes are electrically con-



Fig. 4. Cyclic voltammograms in a $K_3Fe(CN)_6$ aqueous solution of: bare carbon paper substrate; MWCNTs deposited on the carbon paper. Geometrical area of both electrodes: 1 cm².

nected to the carbon backing. The electrical contact of Pt particles with MWCNTs is demonstrated in Fig. 5. Figs. 5a and b display the voltammograms obtained in an Ar purged H₂SO₄ solution at pH 1, for the carbon paper alone and for the MWCNTs on carbon paper, respectively. The full curve in Fig. 5c is the voltammogram occurring on Pt particles on MWCNTs in the same solution, while the dotted curve in Fig. 5c is the voltammogram occurring on Pt particles on carbon black in an ELAT electrode from E-TEK (0.4 mg Pt/cm²; 20 wt% Pt/C). The characteristic features of Pt surface electrochemistry [24], superimposed on a capacitive current, are seen in both voltammograms of Fig. 5c, suggesting that Pt particles are in electrical contact with MWCNTs in the composite electrode as they are with carbon black in the ELAT electrode.

It is of interest now to determine how many Pt atoms of the MWCNT and of the ELAT electrodes are in contact with the electrolyte. This may be evaluated by measuring the charge related to



Fig. 5. Cyclic voltammograms in H_2SO_4 (pH 1) of: (a) a bare carbon paper; (b) MWCNTs grown on carbon paper; (c) small Pt particles on MWCNTs and Pt on carbon black in ELAT electrode (0.4 mg Pt/cm²) from E-TEK. Geometrical area of all electrodes: 1 cm².

the H-adsorption in both cyclic voltammograms of Fig. 5c. A typical charge of 15.2 mC/cm² is detected for Pt on MWCNTs. For comparison, the charge measured for the E-TEK electrode is 66.4 mC/cm^2 . Therefore, the charge ratio: $Q_{\text{E-TEK}}/Q_{\text{MWCNT}} = 4.4$. Based on the findings that a smooth polycrystalline Pt surface shows a Hadsoprtion charge of 0.210 mC/cm² for 1.3×10^{15} Pt atoms/cm² [25,26], the Pt surface density is therefore 4.1×10^{17} Pt/cm² for ELAT, while it is 0.9×10^{17} Pt/cm² for the MWCNT composite electrode.

A short-time stability test for Pt particles on MWCNTs was performed by immersing the electrode in H_2SO_4 (pH 1) for 18 h. TEM observation of this electrode indicates that Pt particles are not removed by this treatment and that they maintain their small size. The MWCNTs remain also strongly bond to the carbon paper substrate.

4. Conclusions

It has been demonstrated that highly dispersed, and very small $(1.2 \pm 0.3 \text{ nm})$, Pt particles have been successfully deposited on the surface of MWCNTs grown on the fibers of carbon paper used as fuel cell backing. Cyclic voltammetry strongly suggests that there is an electrical contact through MWCNTs between the Pt particles and the carbon backing, enabling the use of these composite structures as electrodes. The Pt surface in contact with the electrolyte is estimated to be about 25% of that of a typical 0.4 mg Pt/cm² ELAT electrode from E-TEK. The silane derivative procedure used to obtain Pt (or Co-Ni) particles on MWCNTs (or on carbon paper [20,21]) is very versatile and may well be adapted to obtain any Pt alloy (e.g., Pt-Ru) at any composition, or to obtain electrodes with nanoparticles made of several other transition metals and alloys.

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