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Carbon nanotubes as support for cathode catalyst of a direct methanol fuel cell

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Carbon nanotubes (CNTs) have attracted great interest from both a fundamental and an applied point of view since their discovery [1], and large-scale syntheses have been explored, owing to their high mechanical and unique electrical properties [2,3]. These materials are also considered to be potential supports for heterogeneous catalysts, especially for catalysts to be employed in liquid-phase reactions [4]. A number of studies relating to the synthesis of CNT-supported catalysts and their application in heterogeneous catalysis have been reported [5–9]. Direct Methanol Fuel Cells (DMFCs) have recently attracted much attention for their future potential as clean and mobile power sources [10–15]. However, a serious problem for polymer electrolyte fuel cells, including DMFCs, is the slow reaction rate of the cathode oxygen reduction reaction (ORR) [10–12,16]. One solution is to explore novel nanocarbon materials as supports for platinum catalysts of high activity towards ORR. Current investigations are focusing on template-synthesis methods for carbon tubule membranes [17] and highly ordered nanoporous arrays of carbon [18]. These nanoparticle platinum catalysts, supported on new carbon materials, showed better electrical activities of ORR in a half-cell configuration. GNF (graphite nanofiber) has also been considered as a potential support for electrocatalysts. Electrocatalysts of platinum particles supported on GNF were prepared by Bessel et al. [19], and better activities of

electrochemical oxidation of methanol were obtained in a cyclic voltammetry study. Recently, Lukehart's group [20,21] also prepared a Pt–Ru/herringbone GNF nanocomposite using a single-source molecular precursor as the metal source, and the performance of the DMFC with this nanocomposite as the anode catalyst was enhanced by 50% relative to that recorded by an unsupported Pt–Ru colloid anode catalyst. All these investigations suggest the possible applications of new carbon materials as catalyst supports in the electrodes of fuel cells.

We report on a highly dispersed platinum nanoparticle catalyst supported on carbon nanotubes, which was employed as the cathode catalyst of a DMFC. Higher activity of the oxygen reduction reaction and better performance of the DMFC, as compared to the catalysts supported on commercial carbons, was achieved.

The CNTs used in these experiments were produced from high-purity graphite by a classical arc-discharge evaporation method [1]. The diameters of the CNTs were in the range of 4 to 50 nm. The BET surface area of the CNT samples, determined by N_2 physisorption at 77 K, was about 42 m^2/g. The CNTs in these experiments were purified by ultrasonic treatment for 10 min, and then refluxed in 70% HNO_3 at 120 °C for 4 h. Surface oxidation of the CNTs was accomplished with a 4.0 N H_2SO_4–HNO_3 mixture for 4 h under refluxing conditions. The catalyst was prepared according to the following procedures. A 6-h reflux with chloroplatinic acid in ethylene glycol (250 mg CNTs in 70 ml solvent) at 140 °C was carried out to deposit platinum on the CNTs, then the solid was washed and dried in air at 70 °C, and the final

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Pt/CNTs catalyst with a metal loading of 10 wt.% was obtained. The synthesis method was partly adopted from Lordi's work on SWNTs [9], however we modified the concentration of the ethylene glycol solvent to decrease the ratio of the solvent to CNTs and we increased the temperature of reduction, and these conditions were found to be critical for the attachment of Pt to the surface-oxidized CNTs and for the Pt particle size distribution. For comparison, commercial XC-72 carbon (Vulcan XC-72, Johnson Matthey, BET surface area 267 m^2/g) was also used as the support to prepare Pt/XC-72 catalysts with the same metal loading by the same procedure.

Transmission electron microscopy (TEM) investigations were carried out using a JEOL JEM-2000EX microscope operating at 100 kV. Fairly clean CNTs and the agglomeration of few carbonaceous impurities in the bulk can be observed after purification treatment and surface oxidation processes (Fig. 1a). As shown in Fig. 1b, high and homogeneous dispersions of spherical Pt metal clusters with a narrow particles size distribution centered at 2–4 nm were obtained, and the average platinum particle size was about 2.6 nm. In the case of the XC-72 carbon supported catalyst, the resulting Pt particle distribution gave a mean diameter of 2.2 nm.

The electrochemical activities of these two Pt-based catalysts as cathode catalysts (metal loading 1.0 mg/cm^2) in DMFC were then examined. The anode catalysts were Pt–Ru/C (Johnson Matthey, 20 wt.% Pt, 10 wt.% Ru, and

2.0 mg/cm^2 metal loading), and Nafion-115 (Dupont) was used as the membrane. Preparation of the electrode was based on the procedure of Ref. [15]. The DMFC was assembled by mounting the MEA in a single cell with an active cross-sectional area of 4 cm^2. The single cell test fixture had a dynamic hydrogen reference (DHE) electrode, so that the cathode *I–V* curve could be obtained. The cathode and the single cell polarization curves were recorded after the operating conditions of the single cell had been stable for half an hour. A blank activity test conducted on the CNT support showed that it did not exhibit any activity for the oxygen reduction reaction.

A comparison of DMFC galvanostatic cathode polarizations between Pt/CNTs and Pt/XC-72 catalysts under identical operating conditions is shown in Fig. 2a. At 700 mV (in the activation controlled region), the current density of DMFC for the Pt/CNTs catalyst was 14.7 mA/cm^2, while that for Pt/XC-72 was only 2.5 mA/cm^2. Thus the mass activity of Pt/CNTs is approximately six times higher than that of the Pt/XC-72 sample. The increase in ORR activity of the Pt/CNTs may be attributed to various factors, including: (a) the unique structure and electrical properties of CNTs, which can increase the conductivity of the CNTs, as compared to the commercial Vulcan carbon XC-72. Britto et al. [22] conducted ab initio density-functional-theory calculations and employed the molecular dynamics (MD) simulation method to study the adsorptive dissociation of oxygen on the CNT surface as well as the
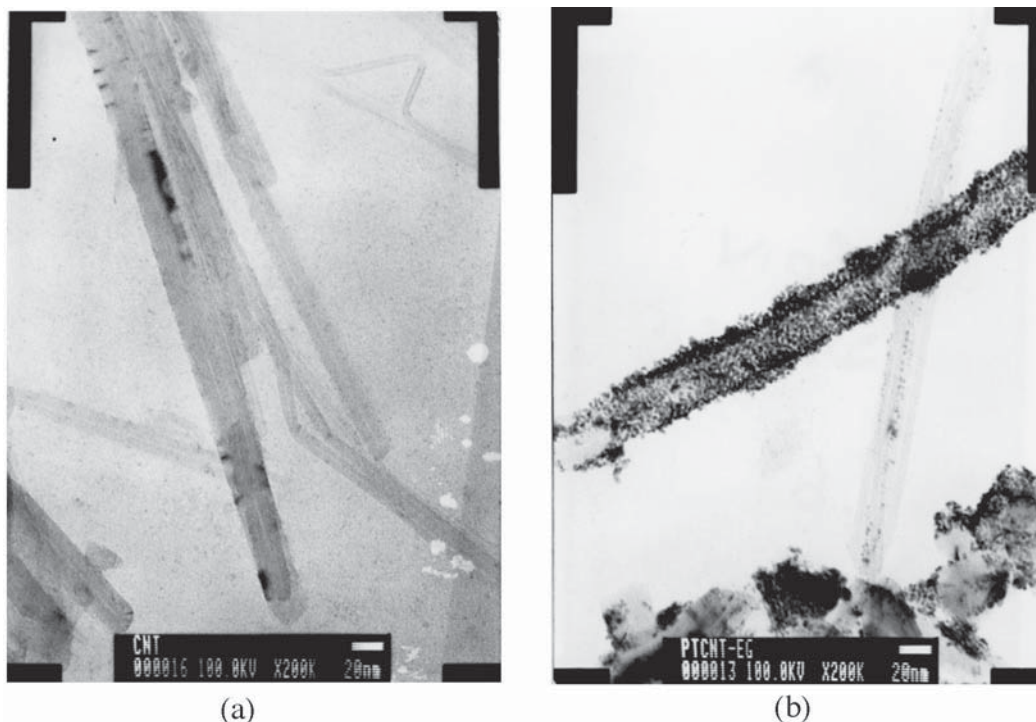

(a)   (b)

Fig. 1. TEM micrograph of the carbon nanotubes after purification and HNO$_3$–H$_2$SO$_4$ mixture oxidation (a) and the carbon nanotube supported platinum catalyst (magnification 2×10^5) (b).
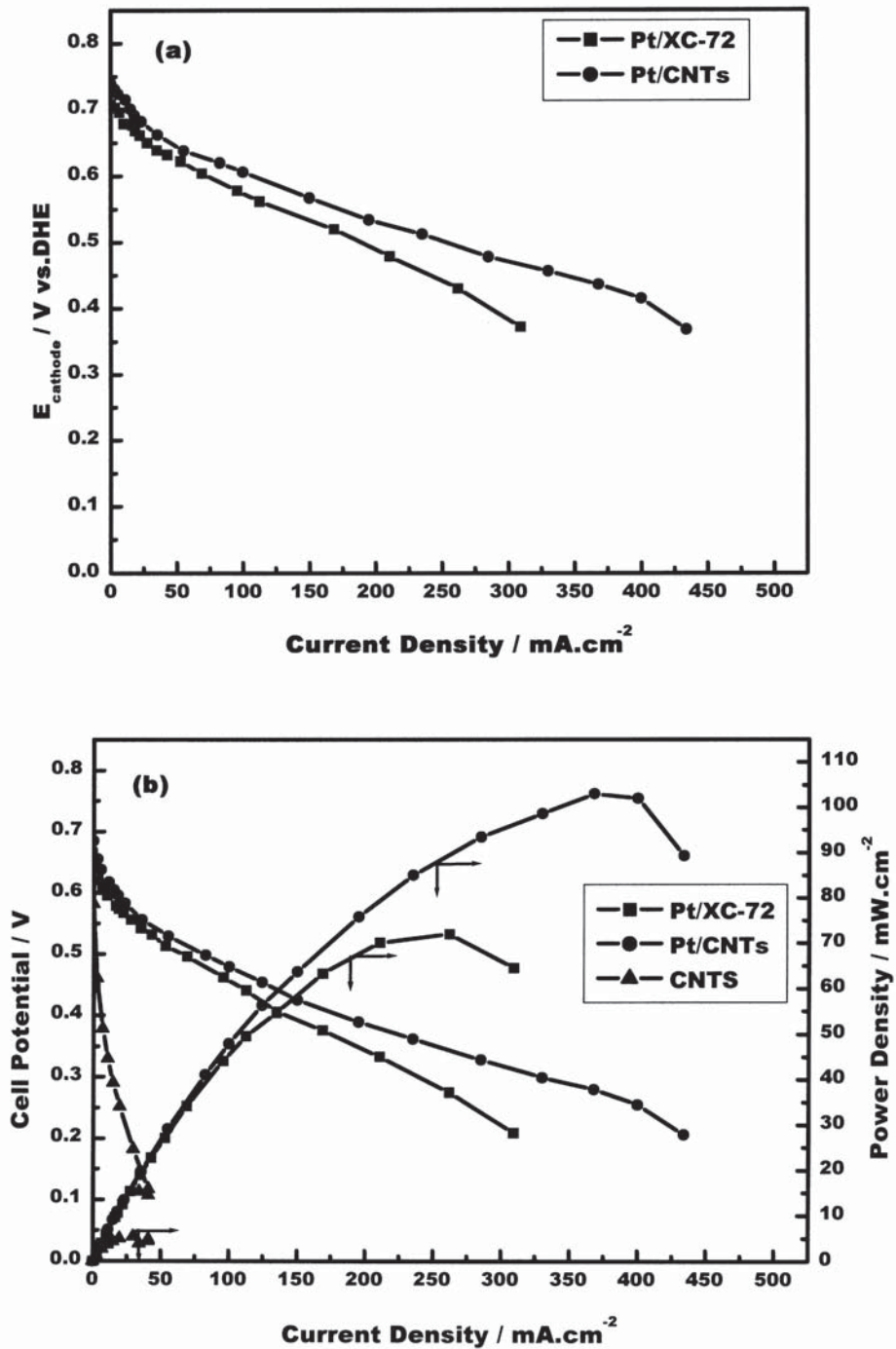
Fig. 2. (a) Comparison of the cathode polarization curve for the oxygen reduction reaction at 90 °C in the DMFC at Pt/XC-72 or Pt/CNTs cathode catalysts. (b) Comparison of polarization data for the DMFC in the presence of Pt/XC-72, Pt/CNTs or CNTs cathode catalysts at 90 °C. 1.0 M CH_3OH, 0.2 MPa O_2 feed. Anode, Pt–Ru/C (20 wt.% Pt, 10 wt.% Ru, JM; catalyst loading 2.0 mg Pt–Ru/cm^2); membrane, Nafion-115 (Dupont).

charge transfer process, and proposed a mechanism for improved electron transfer on CNTs. (b) CNTs have a very small amount of impurities, while the Vulcan carbon XC-72 contains significant quantities of organosulfur im-

purities, which can poison the Pt metal during ORR. On the contrary, CNTs have a rather low sulfur content since they are produced from sulfur-free processes.

A further enhancement in cell performance in the high

current density region was observed by using a Pt/CNTs cathode, as compared to the cathode with traditional XC-72 (Fig. 2b). Since the Pt loading was maintained at 1.0 mg/cm^2 and the density of CNTs was higher than that of XC-72, the catalyst layer of DMFC with the Pt/CNTs cathode was lower than that with the Pt/CNTs cathode, and a faster oxygen–water transport through the active cathode layer could be achieved. The maximum power density of a single cell with our Pt/CNTs sample was 103 mW/cm^2, while that with the Pt/XC-72 sample was only about 70 mW/cm^2.

In summary, the preliminary experimental results presented here show that using CNTs as supports for cathode catalysts in a direct methanol single cell produces better performance compared to XC-72 carbon. The high electro-catalytic activity may be attributed to the unique structure and better electric properties of the CNTs, as well as to the specific interaction between Pt and CNTs.

Acknowledgements

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Formation of nano-combi carbon fibers on a planar silicon substrate using (TiO)SO$_4$ as a catalyst precursor

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Catalytic chemical vapor deposition is a general method to fabricate vapor growth carbon fibers (VGCFs) and various forms, such as cylindrical and hollow-cored fibers,