Platinum/multiwalled carbon nanotubes-platinum/carbon composites as electrocatalysts for oxygen reduction reaction in proton exchange membrane fuel cell

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Platinum/multiwalled carbon nanotubes-platinum/carbon composites as electrocatalysts for oxygen reduction reaction in proton exchange membrane fuel cell

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Pt-loaded multiwalled carbon nanotubes (Pt/MWCNTs) have been prepared by chemical reduction method using functionalized MWCNT synthesized by pyrolysis of acetylene over $MmNi_2$ (Mm denotes misch metal) hydride catalyst. Composites of Pt/MWCNT and commercial Pt-loaded carbon black (Pt/C) have been used as electrocatalysts for oxygen reduction reaction in proton exchange membrane fuel cell (PEMFC). Cathode catalyst with 50% Pt/MWCNT and 50% Pt/C showed best performance due to better dispersion and good accessibility of MWCNT support and Pt electrocatalysts for oxygen reduction reaction in PEMFC. A maximum performance of 540 mV at a current density of around 535 mA cm^{-2} has been obtained. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2214139]

Due to their high efficiency and low emissions, fuel cells have emerged as alternatives to combustion engines and will have an important role in future hydrogen fuel economy. Pt-based electrocatalysts are usually employed in proton exchange membrane fuel cell (PEMFC) as cathode electrocatalysts for oxygen reduction reactions. Electrocatalysts with small size and high dispersion result in high electrocatalytic activity.[1] Supporting materials with high surface area are essential to disperse catalyst particles, so as to reduce the catalyst loading and thereby improving the fuel cell performance. Multiwalled carbon nanotubes (MWCNTs) are attractive materials for catalyst support in PEMFC due to their morphology and interesting properties such as nanometer size, high accessible surface area, good electronic conductivity, and high stability. Several methods have been developed to decorate CNTs with catalytic metal nanoparticles.[2–4] However, it is important to develop techniques to improve adhesion through surface modification such as functionalization of CNTs before the decoration of metal nanoparticles. Yu *et al.*[5] have used mixed acids to produce surface functionalized CNTs. They observed low yield after pretreatment, due to excessive oxidation strength of the solution. Recently, it has been demonstrated that functionalization of CNTs leads to uniform dispersion of Pt particles with a narrow range, leading to higher performances of PEMFC.[6]

In this letter, we describe the preparation of nanocomposites of Pt-supported MWCNT (Pt/MWCNT) and commercial Pt-loaded carbon black (Pt/C) (Pt content of 20 wt %) as electrodes for the oxygen reduction reaction in PEMFC. The performance of the PEMFC with different compositions of Pt/MWCNT and Pt/C is systematically studied in order to investigate the optimum composition of Pt/MWCNT for better performance of PEMFC.

MWCNTs were grown by catalytic decomposition of acetylene over $MmNi_2$ (Mm denotes misch metal) hydride catalysts, using a single stage furnace thermal chemical-vapor deposition (CVD) apparatus.[7] These catalysts have been prepared through hydrogen decrepitation route by performing several cycles of hydrogenation/dehydrogenation of the alloy using a Seiverts apparatus.[8] The hydride powder with an average particle size of $5-10$ μm was directly used for the growth of MWCNTs. MWCNTs with a yield and purity of about 60% and 90%, respectively, were obtained after purification of these as-grown CNTs. Purification of MWCNTs were carried out by air oxidation at 350 °C for 2 h, followed by refluxing in concentrated HNO_3 for 24 h. Purified MWCNTs were functionalized by pretreatment with 70% HNO_3 in order to introduce surface oxides. Purified MWCNTs of 0.5 g were refluxed under constant stirring in 100 ml of 70% HNO_3 at 110 °C for 12 h. The solid phase was removed by centrifugation and washed with de-ionized water several times, and the recovered MWCNTs were dried at 80 °C for 2 h.

Pt-supported MWCNT (Pt/MWCNT) electrocatalysts were prepared by a chemical reduction method using a Pt salt and pretreated MWCNTs. About 0.2 g of pretreated MWCNTs were ultrasonicated in 20 ml of acetone for 1 h and then magnetically stirred for 24 h after adding 1% hexachloroplatinic acid solution. The Pt salt was reduced by slowly adding a reducing solution, which is a mixture of 0.1M $NaBH_4$ and 1M $NaOH$. Once the reaction was complete, the solution was washed with de-ionized water and filtered and dried by vacuum filtration. The recovered Pt/MWCNT was dried at 80 °C for 3 h. The pretreated MWCNTs and Pt/MWCNT electrocatalysts have been characterized by powder x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive x-ray analysis (EDAX). The MWCNTs were of diameters in the range of $20-30$ nm and several micrometers in length. MWCNTs functionalized with carboxylic groups, produced by pretreatment with concen-

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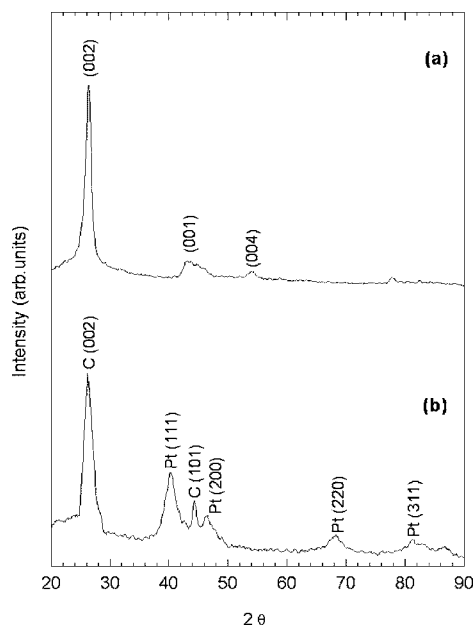
FIG. 1. Powder x-ray diffractograms of (a) purified MWCNTs prepared by pyrolysis of acetylene over $MmNi_2$ hydride catalyst and (b) Pt-loaded MWCNTs.

trated HNO_3, have been characterized by x-ray photoemission spetroscopy (XPS) measurements. Figure 1 shows the powder XRD patterns (Cu $K\alpha$ radiation) of pretreated MWCNTs and Pt/MWCNT electrocatalysts. The broader diffraction peaks for the Pt reflect its smaller average particle size. X-ray diffraction from the CNT support was similar to the hexagonal reflections from graphitic carbon. TEM images of purified MWCNTs and Pt/MWCNT are shown in Figs. 2(a) and 2(b) respectively. A uniform and high dispersion of Pt nanoparticles is seen on the MWCNT surface with a particle size distribution of 5–8 nm. EDAX measurements
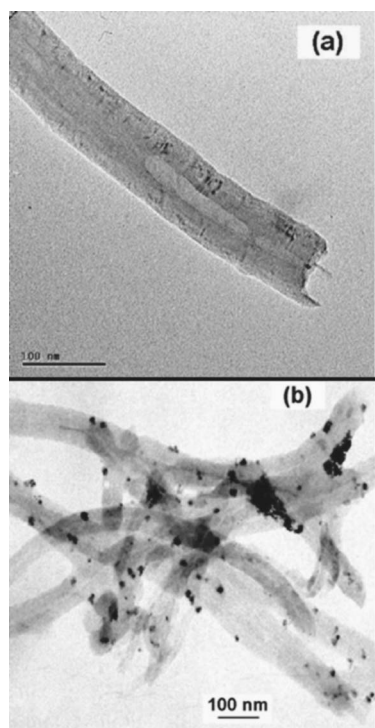

FIG. 2. TEM images of (a) purified MWCNTs prepared by pyrolysis of acetylene over $MmNi_2$ hydride catalyst and (b) Pt-loaded MWCNTs.

showed a Pt content of 19.6 wt % in Pt/MWCNT. Chemical functional groups such as –COOH and –OH derived from acid oxidation processes act as anchoring sites for metal nanoparticles. Thus the particle size of Pt may be correlated with the oxidation of MWCNTs, as efficient deposition of Pt nanoparticles results from a strong interaction between the metal salt precursor and the graphene edges of MWCNT.[4]

Membrane electrode assembly (MEA) was obtained by sandwiching a pretreated Nafion 1135 membrane between the anode and the cathode. Both the anode and cathode layers consisted of a backing layer, a gas diffusion layer, and a catalyst layer. To prepare the catalyst layer, the required amount of catalyst was suspended in de-ionized water and ultrasonicated by adding 5 wt % Nafion solution. The suspension was spread uniformly over a carbon fabric (SGL Carbon). The electrodes were of 11.56 cm^2 area. The electrodes were sandwiched by hot pressing at 130 °C and 70 bars for 2 min. The anode was a 3.4×3.4 cm^2 Pt/C (Pt content of 20 wt %) electrode (E-TEk), with a platinum loading of 0.25 mg cm^{-2}. The cathode was prepared from a suspension containing mixture of Pt/MWCNT (Pt content of 19.6 wt %) and Pt/C (Pt content of 20 wt %), with a platinum loading of 0.5 mg cm^{-2}. A single PEMFC was assembled using the MEA, two graphite plates with gas channels machined with a serpentine geometry, two Teflon gaskets, and two aluminum end plates. The performance of the PEMFC was studied at 60 °C using an indigenously fabricated fuel cell test station and a dc electronic load box. Since hydration of the electrolyte membrane is important for attaining maximum performance of the PEMFC, reactant gases were humidified with water. The polarization curves were obtained from the single cell PEMFC using the same type of anode. To study the electrocatalytic activity of Pt/MWCNT on the performance of PEMFC, active material of composition of x wt% Pt/MWCNT and y wt% Pt/C, with $x+y=100$, where $x=0$, 25, 40, 50, 60, 75, and 100, was taken as cathode catalyst. Prior to polarization studies, the electrodes were activated between open-circuit potential and high current densities. The activation cycle is necessary to activate the catalyst for the oxygen reduction reaction. The performance of Pt/MWCNT electrocatalysts, prepared using pretreated MWCNTs grown over $MmNi_2$ hydride catalysts, mixed with varying amounts of commercial Pt/C as cathode catalyst in PEMFC, under an operating pressure of 1 bar is shown in Fig. 3(a). In the low current density region, the voltage drop in the potential-current curve, generally known as activation polarization, reflects the sluggish kinetics intrinsic to the oxygen reduction reaction at the cathode surface. The voltage drop in the middle to high current density range, or Ohmic polarization, arises from limitations in proton transport through the electrolyte membrane from anode to cathode and/or limitations in electron flow in the electrode materials. Better performance of PEMFC was observed for cathode catalysts with Pt/MWCNT content compared to those containing commercial Pt/C, which could be attributed to the higher catalytic reactivity of smaller Pt particles with uniform sizes decorated on the MWCNTs. The higher performance of the Pt/MWCNT electrodes compared to the Pt/C electrodes [Fig. 3(a)] could be ascribed to the networks and interiors of CNTs consisting of spaces for gas diffusion and the high electric conductivity of MWCNTs.

TEM analysis [Fig. 2(b)] shows a homogeneous distribution of smaller Pt particles on the MWCNT surface, which
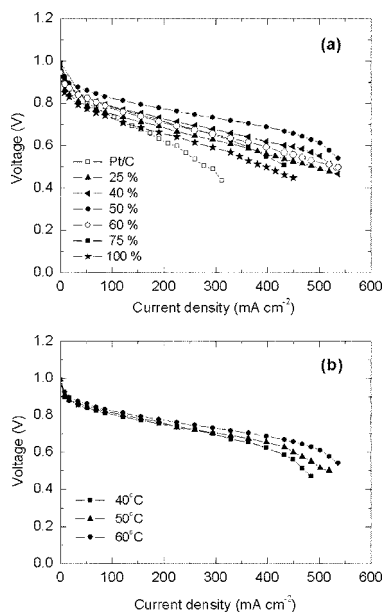
FIG. 3. (a) Polarization curves of PEMFC at 60 °C with cathode catalyst containing nanocomposite of Pt/MWCNT and Pt/C electrocatalysts in equal weight percentage. (b) Polarization curves of PEMFC at different temperatures with Pt/MWCNT and Pt/C electrocatalysts in equal weight percentage as cathode catalyst.

TABLE I. Voltage (at a current density of 300 mA cm^{-2}) and current density (at 540 mV) of PEMFC with cathode catalyst containing a mixture of Pt/MWCNT and Pt/C electrocatalysts (prepared using purified MWCNT synthesized by pyrolysis of acetylene over MmNi$_2$ hydride catalyst).

Pt/MWCNT composition in the cathode catalyst (%)	Voltage (mV) at 300 mA cm^{-2}	Current density (mA cm^{-2}) at 540 mV
0 (E-Tek)	0.47	258
25	0.62	431
40	0.67	508
50	0.72	535
60	0.65	472
75	0.64	404
100	0.58	352

results in an enhanced interaction between the Pt and MWCNT, leading to higher performance. Furthermore, the pretreatment of MWCNTs with concentrated. HNO$_3$ results in functionalization of the MWCNT surface with carboxylic acid groups, which would act as additional anchoring sites for better adherence of Pt nanoparticles onto the MWCNT surface, thereby giving a better performance at higher current densities. The PEMFC performance also depends on the electrical conductivity of the MWCNT support and its ability to transport electrons to the current collector of MEA. In the present study, the performance of the PEMFC passes through a maximum for cathode catalyst with nanocomposite containing Pt/MWCNT and Pt/C in equal weight percentage ($x=y=50$). The performance of PEMFC with nanocomposite containing Pt/MWCNT and Pt/C in equal weight percentage as cathode electrocatalyst at various temperatures is shown in Fig. 3(b). The fuel cell performance is found to improve with cell temperature, under the same operating conditions (pressure and gas flow rates). At higher current densities, the cell voltage has been increased by about 30% with an increase in temperature of 20 °C. The lower performance at the mass transfer controlled region (high current density) is mainly due to flooding of the electrode and the resulting mass transport difficulty.

A comparison of the fuel cell performance with cathode catalyst containing mixture of different compositions of Pt/MWCNT, prepared using MWCNTs synthesized over MmNi$_2$ hydride catalyst, and commercial Pt/C is given in Table I. PEMFC with Pt/C as cathode catalyst shows a lesser performance with a potential of about 540 mV at a current density of 258 mA cm^{-2}. Under the same operating conditions, PEMFC with nanocomposite containing Pt/MWCNT and Pt/C in equal weight percentage as cathode catalyst shows the maximum performance, with a potential of 540 mV at a current density of around 535 mA cm^{-2}, and thus seems to be the optimal composition for better perfor-

mance of PEMFC under the present study. Thus the composition of Pt/MWCNT plays the key role in the overall performance of the PEMFC. Since the Pt loading is around 20% in both Pt/MWCNT and Pt/C, the loading of Pt in the mixture at different compositions remains the same. Therefore the present study indicates that the accessibility of MWCNTs and hence the Pt electrocatalysts in the mixture for the oxygen reduction reaction may be the determining factors in deciding the performance of the fuel cell. The uniform loading of well dispersed MWCNTs with nanoparticles of Pt ($5-8$ nm) results in more efficient Pt usage compared to the Pt/C electrodes, thereby increasing the available triple-phase boundaries[9] (gas-electrolyte-catalyst).

In summary, Pt/MWCNT electrocatalysts with Pt nanoparticles of around $5-8$ nm in diameter were prepared by a chemical reduction method using pretreated MWCNTs synthesized by pyrolysis of acetylene over MmNi$_2$ hydride catalyst. The performance of PEMFC with cathode catalyst containing different compositions of Pt/MWCNT and Pt/C were systematically studied. We have demonstrated that Pt/MWCNT have better electrocatalytic activity compared to Pt/C for the oxygen reduction reaction in PEMFC. Cathode catalyst containing nanocomposite of Pt/MWCNT and Pt/C in equal weight percentage showed higher performance, which could be attributed to the good accessibility of MWCNT support and more efficient Pt electrocatalysts usage in the nanocomposite mixture for the oxygen reduction reaction.

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