Deposition of platinum nanoparticles on organic functionalized carbon nanotubes grown *in situ* on carbon paper for fuel cells

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Deposition of platinum nanoparticles on organic functionalized carbon nanotubes grown *in situ* on carbon paper for fuel cells

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Abstract
Deposition of small Pt nanoparticles of the order of 2–2.5 nm on carbon
nanotubes (CNTs) grown directly on carbon paper is demonstrated in this
work. Sulfonic acid functionalization of CNTs is used as a means to
facilitate the uniform deposition of Pt on the CNT surface. The organic
molecules attached covalently to the CNT surface via electrochemical
reduction of corresponding diazonium salts are treated with concentrated
sulfuric acid and the sulfonic acid sites thus attached are used as molecular
sites for Pt ion adsorption, which are subsequently reduced to yield the small
Pt nanoparticles. Cyclic voltammograms reveal that, after removal of the
organic groups during high temperature reduction, these Pt nanoparticles are
in electrical contact with the carbon paper backing. A typical Pt loading of
0.09 mg cm^{-2} is achieved, that shows higher specific surface area of Pt than
an E-TEK electrode with Pt loading of 0.075 mg cm^{-2}. A membrane and
electrode assembly (MEA) is prepared with a Pt/CNT electrode as cathode
and an E-TEK electrode as anode, and it offers better performance than a
conventional E-TEK MEA.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotubes (CNTs) have been at the forefront of
novel nanoscale investigations due to their unique structure
dependent electronic and mechanical properties. They are
expected to have a wide range of practical applications
such as catalyst supports in heterogeneous catalysis, field
emitters, sensors, gas-storage media and molecular wires
for next generation electronic devices [1, 2]. Our interest
in CNTs is to use them as catalyst supports for Pt in a
proton exchange membrane fuel cell (PEMFC). There have
been several studies of deposition of Pt or other catalysts on
carbon nanotubes through impregnation or the electrochemical
deposition method [3–6]. These studies show that the pristine
surface of carbon nanotubes is inert and hence it is difficult

to attach metal deposits to it. Chemical modification of the
carbon nanotube surface is found to be necessary to obtain
a good adhesion and dispersion of metal particles on the
carbon nanotube surface. Oxidation is an often-attempted
method for functionalization where several oxidants such as
H_2SO_4–HNO_3, HNO_3, $K_2Cr_2O_7$ and $KMnO_4$ [7–9] have been
used to date. Still it is found to be difficult to control the particle
size and dispersion of Pt particles on carbon nanotube surface.

The unique approach adopted in our group is to
deposit multiwalled carbon nanotubes (MWNTs) directly on
carbon paper by chemical vapour deposition (CVD) using
electrodeposited Co/Ni catalyst, followed by Pt deposition.
This ensures that all the deposited Pt particles are in electrical
contact with the external electrical circuit. As demonstrated
in our previous work [10, 11], such a design gives an
improved Pt utilization and could potentially decrease Pt

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1. Electrochemical reduction of aryl diazonium salt on CNT surface
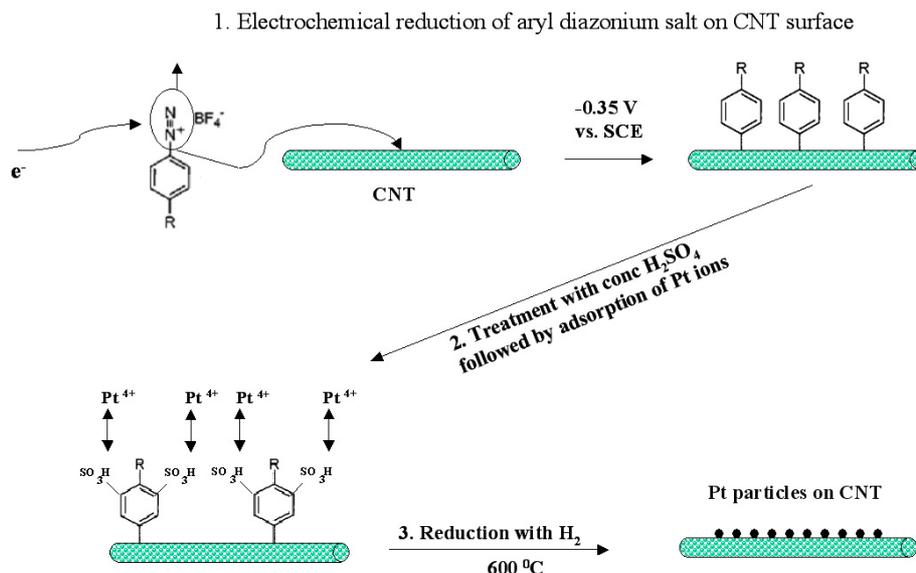
Figure 1. Scheme for Pt deposition on CNTs on carbon paper.

usage. However, unlike conventional powder support catalyst preparation, where a much better mixing between CNTs and catalyst precursor can be achieved, the uniform deposition of Pt is a significant challenge for this configuration. In our previous work we deposited Pt on CNTs by electrodeposition and by the impregnation method. To reach the required loading (0.2 mg cm^{-2}), electrodeposition always gives a large Pt particle size of 25–30 nm [10]. Much smaller particles in the range 4–5 nm can be obtained with the impregnation method [11]. However, this particle size is still larger than the desired value of 2–3 nm as in conventional Pt/carbon black catalysts and the size distribution is quite broad, due to the inherent problems commonly associated with the direct impregnation method. In the present work we show that uniform deposition of Pt nanoparticles on these CNTs is possible by modifying the CNT surface with organic functional groups capable of adsorbing Pt ions. These organic molecules were introduced by electrochemical reduction of aryl diazonium salts. Besides serving as molecular templates for Pt ion adsorption; they also act as barriers for direct deposition of Pt precursor on the CNT surface. All these lead to a better Pt deposition on the CNT surface. Furthermore, we show that, after the removal of the organic groups during the high temperature reduction, these Pt particles are in electrical contact with the carbon paper and hence the carbon paper/CNT/Pt composite can be effectively used as an electrode in a PEMFC.

The scheme for Pt deposition on functionalized CNTs is as shown in figure 1. It has been well known that reduction of aryl diazonium salt on carbon surfaces gives strong covalent attachment of corresponding aryl groups to the carbon surface [12–14]. This has been demonstrated on CNT surfaces with successful sidewall functionalization [15–17]. Briefly, in our approach we first functionalize the CNT surface with aryl groups (methoxyphenyl in the study) by electrochemical reduction of the corresponding aryl diazonium salt. The aryl functional groups are then sulfonated by treatment with

concentrated H$_2$SO$_4$ to introduce sulfonic acid groups, which are subsequently used to adsorb Pt ions. The adsorbed Pt ions are then reduced to Pt(0) by heating in H$_2$ atmosphere at high temperature to give Pt nanoparticles on the CNT surface. The organic groups are removed during the high temperature reduction process, leaving Pt particles in direct contact with the CNT surface.

2. Experimental details

2.1. CNT synthesis

MWNTs are deposited directly on carbon paper by CVD using electrodeposited Co/Ni alloy catalyst as discussed in previous studies [10, 11]. The CVD is performed at 800 °C with acetylene as the carbon precursor. The unique advantage of electrodeposited catalyst here is that the CNTs are grown at electrically active sites on carbon paper so that all the CNTs are in electrical contact with the carbon paper backing.

2.2. Functionalization of CNTs and Pt deposition

All the chemicals, 4-methoxyphenyldiazonium tetrafluoroborate, tetrabutylammonium tetrafluoroborate and acetonitrile were obtained from Sigma Aldrich and used as received. 0.217 g of 4-methoxyphenyldiazonium tetrafluoroborate and 3.2 g of tetrabutylammonium tetrafluoroborate are dissolved in 100 ml acetonitrile to prepare an electrolytic solution of 10 mM 4-methoxyphenyldiazonium tetrafluoroborate in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile. Electrochemical reduction in a three-electrode assembly was then carried out for 30 min at −0.35 V versus an Ag/AgCl reference electrode with CNT/carbon paper as the working electrode and Pt wire as a counter-electrode. After electrochemical modification, the CNT/carbon paper samples were washed with acetonitrile and immersed in acetonitrile for 8 h. They were then ultrasonicated in acetonitrile for 1 min, washed with ethanol,

and dried under vacuum. The functionalized CNT/carbon paper sample was then transferred to 98 wt% H_2SO_4 and heated to 80 °C to attach sulfonic acid groups to the methoxyphenyl group. This CNTs/carbon paper sample was then dipped in 100 mM aqueous H_2PtCl_6 solution for adsorption of Pt ions at the sulfonic acid groups. Pt(IV) ions thus adsorbed were reduced to Pt(0) in H_2/Ar (1:4) mixture at 600 °C for 30 min. The Pt loading was determined to be 0.09 mg cm^{-2} by measuring the weight difference.

2.3. Preparation of electrodes and membrane electrode assembly (MEA)

2.3.1. Pt/CNT electrode.
To facilitate water repelling and mass transport, a gas diffusion ink was prepared by ultrasonicating polytetrafluoroethylene (PTFE) and carbon black in 1:3 weight ratio in isopropanol. The gas diffusion ink was applied on the backside of a Pt/CNT/carbon paper electrode (opposite side of the CNT deposited face of carbon paper). The loadings of carbon black and PTFE were 4 and 1.33 mg cm^{-2} respectively. The gas diffusion layer was annealed at 340 °C for 1 h. A 2.5 wt% Nafion ink was then prepared in isopropanol and sprayed on the CNTs side with a Nafion loading of 2 mg cm^{-2}. The electrode was then annealed at 140 °C for 1 h.

2.3.2. Conventional electrodes.
A conventional electrode was prepared with E-TEK Pt/Vulcan XC-72 as catalyst. Carbon paper backings were hydrophobically treated with PTFE to reach a PTFE loading of 10 wt% and then annealed at 340 °C in air. A gas diffusion layer was then applied with the same loadings of PTFE and carbon black as in the Pt/CNT electrode and annealed at 340 °C for 1 h. A catalyst layer was applied on the gas diffusion layer with a Nafion loading of 2 mg cm^{-2} and Pt loading of 0.2 mg cm^{-2} for the anode and 0.075 mg cm^{-2} for the cathode. The electrode was then annealed at 140 °C for 1 h.

An MEA was prepared by hot pressing a Nafion 117 membrane between a Pt/CNT cathode and a conventional E-TEK anode with 0.2 mg cm^{-2} Pt loading at 140 °C and 140 atm pressure for 90 s. This MEA is termed the Pt/CNT MEA. For comparison purposes, another MEA was made by hot pressing Nafion 117 membrane between the two E-TEK electrodes (with 0.075 and 0.2 mg cm^{-2} Pt loadings for cathode and anode respectively). This MEA is termed the conventional E-TEK MEA.

2.4. Characterization

The MWNTs prepared directly on carbon paper were characterized by scanning electron microscopy (SEM, Philips XL 30 FEG) and transmission electron microscopy (TEM, Philips CM 300). The functionalized MWNTs were characterized by attenuated total reflectance Fourier transform infrared (ATR FTIR, Bruker Equinox 55 FTIR) spectroscopy. Pt deposited MWNTs were characterized by TEM.

The electrochemical properties of the as prepared MWNTs and the functionalized MWNTs were characterized by cyclic voltammetry in 5 mM $K_3Fe(CN)_6$ aqueous solution in 0.5 M K_2SO_4 in a standard three-electrode cell. The
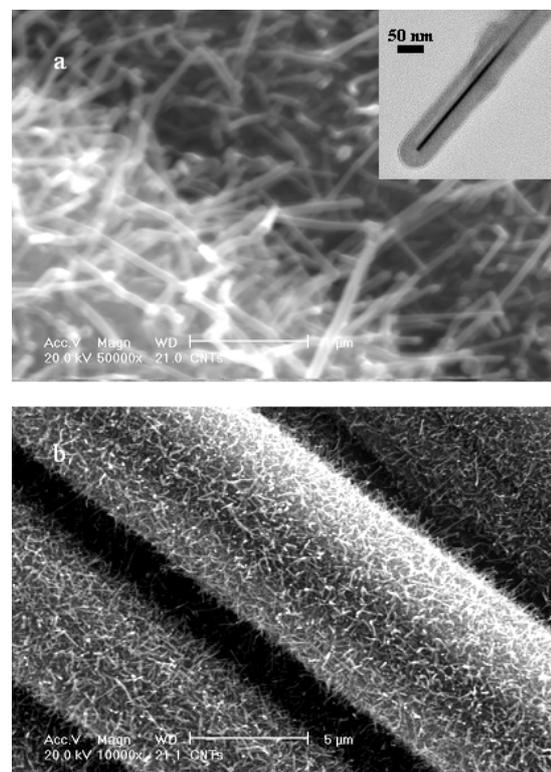

Figure 2. (a), (b) SEM images of CNTs deposited directly on carbon paper by chemical vapour deposition method; inset of (a) the TEM image of a typical CNT.

measurements were carried out with an SI 1287 potentiostat (Solartron) with a saturated calomel electrode (SCE) as the reference electrode. A sweep rate of 50 mV s^{-1} was used.

The MEAs were characterized in a single-fuel-cell test station (Electrochem Inc., USA). The Pt/CNT electrode was used as cathode and the E-TEK electrode as anode during the characterization of Pt/CNT MEA. For the conventional E-TEK MEA the electrode with 0.075 mg cm^{-2} Pt loading was used as cathode. Pure H_2 and O_2 were prehumidified at 80 and 70 °C and fed to the anode and cathode respectively. The fuel cell performance was examined at 70 °C and 20 psig pressure. *In situ* cyclic voltammetry was conducted to measure the electrochemically active surface area of Pt/CNT electrode. For this purpose, N_2 was supplied to the cathode and H_2 was supplied to the anode which also served as the reference electrode.

3. Results and discussion

Figure 2 shows the SEM images of MWNTs grown on carbon paper by CVD. The inset of figure 2(a) shows the TEM image of a typical CNT. It shows the catalyst encapsulated at the tip in a cylindrical shape, which suggests that the catalyst is in molten state during the CNT formation. From the SEM and TEM observations the length of the MWNTs is typically 2–5 μm and the diameters are in the range of 30–60 nm. The CNTs are densely packed on the carbon paper and the loading of CNTs obtained by weight difference measurement is around 0.3 mg cm^{-2} for a Co/Ni loading of 1 C cm^{-2}.
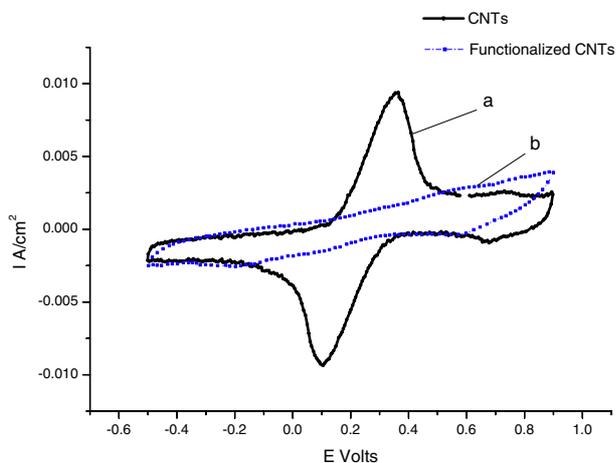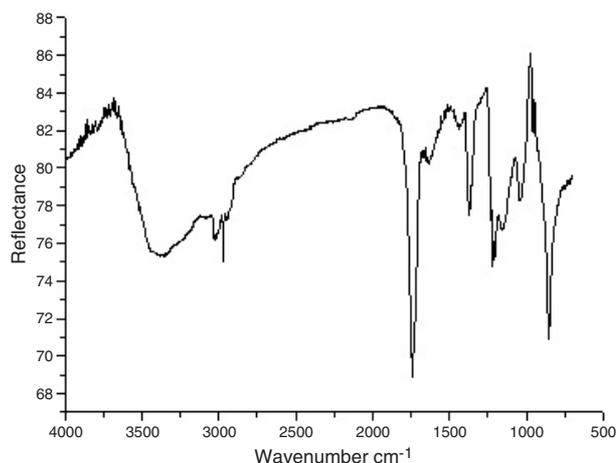
Figure 3. Cyclic voltammograms of (a) as-prepared CNTs and (b) functionalized CNTs in 5 mM $K_3Fe(CN)_6$ and 0.5 M K_2SO_4.

Figure 4. ATR IR spectra of functionalized CNTs after concentrated H_2SO_4 treatment.

Figure 5. A blow-up of ATR IR spectra of functionalized CNTs after concentrated H_2SO_4 treatment for the sulfonic acid peak in the ATR IR spectra in figure 4.

Subsequent electrochemical modification with the 4-methoxyphenyl diazonium tetrafluoroborate attaches the methoxyphenyl groups to the CNT sidewalls. Diazonium salts have been widely used to functionalize the CNT sidewall surface. The attachment of the functional group to CNT is covalent in nature as discussed in the literature. Also it gives a very compact layer of the aryl functional groups on the carbon surfaces. Desilets *et al* [18] have functionalized the CNTs grown on carbon paper with a silane derivative with the sulfonic acid functional group for Pt ion exchange. They used the dipping method to functionalize their CNTs. Our electrochemical route for functionalization of CNTs with diazonium salts is particularly useful for this case since the carbon nanotubes are already anchored to the carbon paper support.
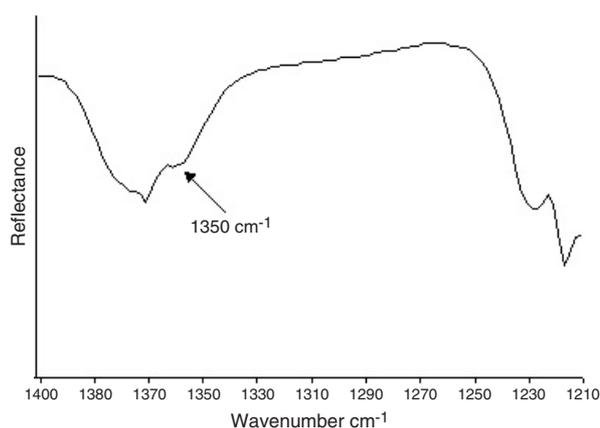
The cyclic voltammetry plots for as-prepared CNTs and functionalized CNTs on carbon paper in $K_3Fe(CN)_6$ are shown in figure 3. It is evident from the plots that the 4-methoxyphenyl groups grafted on the CNTs reduce the electrochemical response. This is due to the electrical as well as physical hindrance provided by the methoxyphenyl groups to the incoming electroactive species. This behaviour is usually observed in the case of aryl chain grafted electrodes, which further illustrates that these grafted layers can act as barriers for the direct Pt salt adsorption on CNT electrodes.

The attenuated total reflection infrared spectrum of the functionalized CNTs after concentrated H_2SO_4 treatment is shown in figure 4. The presence of sulfonic acid groups is evident from the peak at 1352 cm^{-1} shown in the blown-up spectrum in figure 5. Methoxy-group presence is confirmed from 1040 and 1215 cm^{-1} peaks. The 1440 cm^{-1} peak represents the –OCH$_3$ symmetrical bending vibrations. The spectrum also shows the presence of alcoholic, sulfate and carboxylic groups, which suggests that some H_2SO_4 reaches the pristine CNT surface through the grafted aryl layers and adds these hydrophilic groups to the surface.

The deposition of Pt can thus take place through both the hydrophilic groups on the CNT surface and the sulfonic acid groups on the organic functional groups. However, the deposition of Pt salt ions on the CNT surface groups will be severely hindered by the presence of the compact layer of the bulky aryl groups. The deposition of Pt on CNT most likely takes place through ion exchange at the sulfonic acid functional groups on the organic molecules attached. This avoids the problems of aggregation and nonuniform size distribution associated with direct deposition of Pt on CNT surface. Although there is small probability of some Pt deposition on the CNT surface directly, in this case again the presence of bulky organic groups will act as barriers between the adsorbing Pt ions and hence avoid the aggregation of the Pt nanoparticles in the subsequent reduction step. In the case of the pristine CNT surface however the inertness of the surface for Pt deposition results in nonuniform Pt ion adsorption and hence produces Pt nanoparticle aggregates on the CNT surface. Figure 6 shows the TEM image of Pt deposited on CNTs functionalized with the diazonium salt. As expected, the particle size of Pt is found to be small, around 2–2.5 nm, and is very uniform. It was also found from TEM that the CNT tips are still closed, indicating that the treatment of concentrated H_2SO_4 is a mild surface treatment for the CNTs. The EDAX spectrum (figure 7) of the Pt/CNT composite electrode shows no presence of S, indicating the removal of the organic functional group during the final high
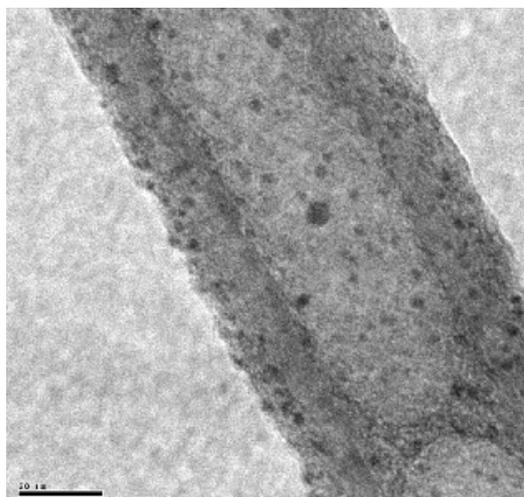
Figure 6. TEM image of Pt nanoparticles deposited on CNTs grown directly on carbon paper.
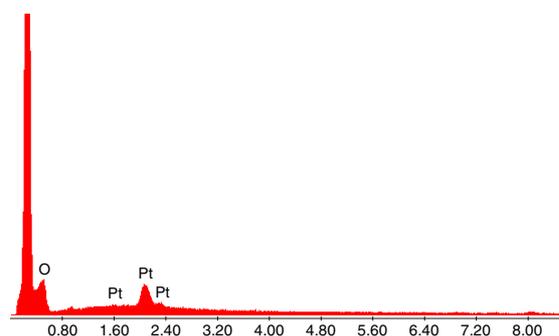

**Figure 7.** EDAX spectra of Pt/CNT composite electrode.

temperature reduction stage. The removal of organic groups confirms the electrical connectivity of the Pt nanoparticles to the CNT surface.

Finally, it is important to see the electrochemical activity of these Pt particles in the Pt/CNT electrode for PEMFC application. Figure 8 shows the *in situ* cyclic voltammogram of the Pt/CNT electrode. The loading of Pt from weight gain is about 0.09 mg cm^{-2}. For comparison, the *in situ* cyclic voltammogram of the E-TEK electrode (cathode) with Pt loading of 0.075 mg cm^{-2} is also presented. The electroactive specific surface area of the Pt/CNT electrode from the hydrogen desorption peak is 50 m^2 g^{-1}, while that for the E-TEK electrode is 34 m^2 g^{-1}. This proves that the Pt particles thus deposited show higher utilization and are in electrical contact with the carbon paper, which is essential in making a good MEA for a PEMFC.

The polarization curve for the same Pt/CNT MEA is shown in figure 9. The loading of Pt at the CNT electrode (cathode) was 0.09 mg cm^{-2} and that at the anode was 0.2 mg cm^{-2}. A maximum power density of 290 mW cm^{-2} was obtained. For comparison, the polarization curve of the conventional E-TEK MEA with 0.2 mg cm^{-2} Pt loading at the anode and 0.075 mg cm^{-2} Pt loading at the cathode is shown. The cathode specific activity of the Pt/CNT MEA and the conventional E-TEK MEA are presented in figure 10.
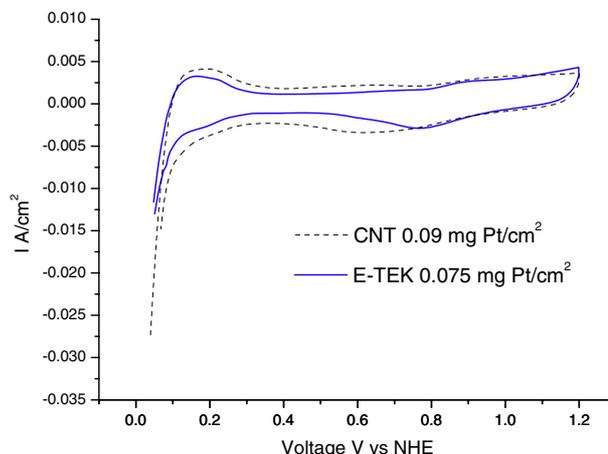
Figure 8. *In situ* cyclic voltammograms of (a) E-TEK electrode with 0.075 mg cm^{-2} Pt loading and (b) CNT on carbon paper electrode and Pt deposited CNT/carbon paper electrode with 0.09 mg cm^{-2} Pt loading.
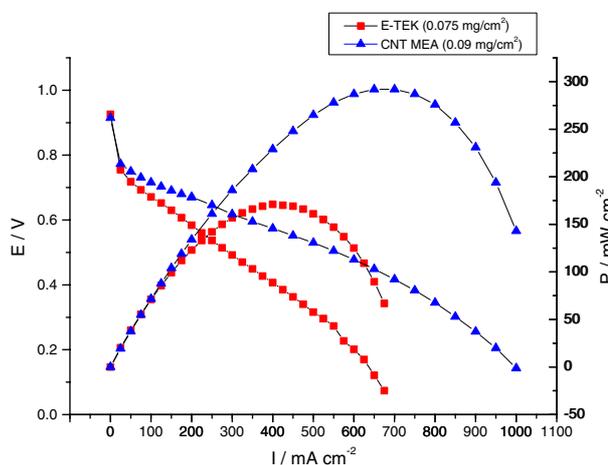

Figure 9. Polarization curves for Pt/CNT MEA (Pt/CNT electrode as cathode and E-TEK electrode as anode) and E-TEK MEA (anode and cathode both E-TEK electrodes) at 70 °C; 20 psig pressure at both anode and cathode; Nafion 117 membrane; 200 sccm H$_2$ and 100 sccm O$_2$ at anode and cathode respectively.

Clearly, the Pt/CNT MEA offers a better performance than the conventional E-TEK MEA of comparable Pt loading. These data underline our claim that the Pt utilization is better in the CNT based electrode. Particularly in the high current density region, the performance of the CNT based MEA is much better. This is attributed to the more open structure of the Pt/CNT electrode as discussed in our previous studies [11].

4. Conclusion

The deposition of small Pt nanoparticles 2–2.5 nm in size has been achieved on organically functionalized carbon nanotubes deposited *in situ* on carbon paper. The small size of Pt nanoparticles is attributed to the presence of bulky functional groups on CNTs which act as molecular sites for the Pt ion adsorption and also avoid nonuniform Pt deposition on the CNT surface. Cyclic voltammetry suggests that after removal of the organic functional groups these Pt particles
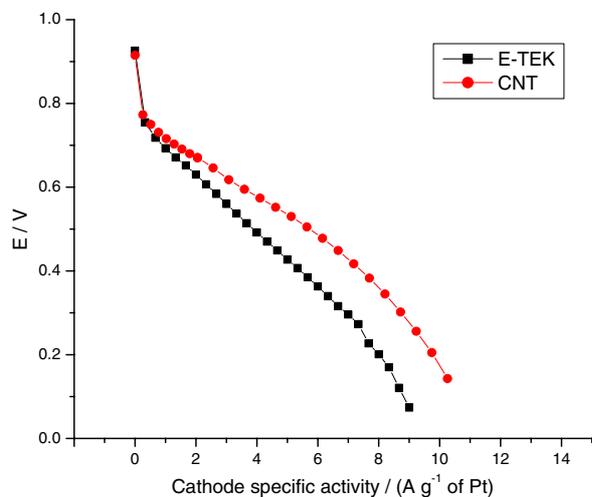
Figure 10. Cathode specific activity for the Pt/CNT electrode and E-TEK electrode.

are in electrical contact with the carbon paper backing layer. An MEA with Pt/CNT as cathode and a conventional E-TEK electrode as anode was prepared, which showed a better performance than a conventional E-TEK based MEA. Further work is ongoing in our laboratory on optimization of the CNT based MEA in terms of the electrode structure and Nafion loading.

Acknowledgments

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