Single-Wall Carbon Nanotube-Based Proton Exchange Membrane Assembly for Hydrogen Fuel Cells

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A membrane electrode assembly (MEA) for hydrogen fuel cells has been fabricated using single-walled carbon nanotubes (SWCNTs) support and platinum catalyst. Films of SWCNTs and commercial platinum (Pt) black were sequentially cast on a carbon fiber electrode (CFE) using a simple electrophoretic deposition procedure. Scanning electron microscopy and Raman spectroscopy showed that the nanotubes and the platinum retained their nanostructure morphology on the carbon fiber surface. Electrochemical impedance spectroscopy (EIS) revealed that the carbon nanotube-based electrodes exhibited an order of magnitude lower charge-transfer reaction resistance ($R_{ct}$) for the hydrogen evolution reaction (HER) than did the commercial carbon black (CB)-based electrodes. The proton exchange membrane (PEM) assembly fabricated using the CFE/SWCNT/Pt electrodes was evaluated using a fuel cell testing unit operating with H2 and O2 as input fuels at 25 and 60 °C. The maximum power density obtained using CFE/SWCNT/Pt electrodes as both the anode and the cathode was ~20% better than that using the CFE/CB/Pt electrodes.

Introduction

High surface area carbon materials such as activated carbon, carbon nanofibers, and carbon nanotubes as new electrode materials have drawn significant interest in recent years for improving the performance of fuel cells.1–4 Unique electrical and electronic properties, wide electrochemical stability windows, and high surface area of single wall carbon nanotubes (SWCNTs) apart them from the rest.5–7 It is this expected improvement in conductivity and charge transfer at the electrode interfaces that has prompted a number of groups to use these carbon nanotubes as electrode materials for both oxidation and reduction reactions in fuel cells.8–11 The expectation is that the enhanced electrocatalytic properties of CNTs would reduce the amount of precious metal catalyst such as platinum (Pt) that would substantially increase the commercial viability of fuel cells.

Anchoring the carbon nanotubes on the conducting surface is the crucial step in constructing a robust electrode-catalyst assembly with low resistivity. Past efforts to employ SWCNTs as a nanostructured carbon support in proton exchange membrane fuel cells have involved either casting a film with a polymer binder or growing the carbon nanotubes directly onto the carbon paper or cloth.12–15 Although the use of binders provides a convenient method to cast SWCNT films, they often pose the problem of increased resistivity. Recently Wang and co-workers have grown multiwalled carbon nanotubes (MWCNTs) on carbon paper through chemical vapor deposition with Co as a catalyst support.16 Electrophoretic deposition is another effective and comparatively facile approach for assembling SWCNTs on the desired electrode surface. In our earlier work, we have made use of the asymmetric charging effects of SWCNTs in tetrahydrofuran (THF) suspensions to assemble them as linear bundles and deposit them on a conducting electrode surface.17,18 The electrodes cast on conducting glass and carbon electrodes showed excellent electrochemical activity toward methanol oxidation.18

Electrophoretic deposition is gaining increasing attention as a simple technique for fabricating a fuel cell electrode assembly.19–21 The advantages of electrophoretic deposition include uniform deposition of charged particles

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and control of film morphology by modulating the applied electric field.\textsuperscript{22–24} The pristine catalyst particles (e.g., Pt-loaded carbon particles) when suspended in a solvent become charged under the influence of a dc electric field and migrate toward the oppositely charged electrode. The film cast on the electrode surface is robust, and the amount of deposition can be controlled by changing the duration of the applied field. Similarly, the SWCNTs suspended in THF when subjected to a low dc field of \(\leq 80\) V/cm move toward the positive electrode and assemble in the form of a film.\textsuperscript{18} For an eventual fuel cell application, this method has the advantage that we can control the loading of carbon support and catalyst by simply varying the time and dc voltage used in the electrophoretic procedure and hence constitutes a convenient way to fabricate membrane electrode assemblies (MEA) for fuel cells.

We have now employed an electrophoretic deposition technique to cast films of SWCNTs on carbon fiber paper (Toray paper) for their end use in a hydrogen fuel cell. A schematic representation of our SWCNT-based proton exchange membrane assembly for a H\(_2\)/O\(_2\) based fuel cell is shown in Scheme 1. By employing cyclic voltammetry and impedance measurements, we have characterized the catalytic properties of electrophoretically deposited SWCNT/Pt films in half cell reactions. We have evaluated the performance of the fuel cell employing these electrodes to explore the possible role of SWCNTs in decreasing charge transfer resistance. Fabrication of proton exchange membrane assembly (MEAs) using a SWCNT/Pt catalyst and their performance in a fuel cell under normal operating conditions are discussed.

**Experimental Section**

**Solubilization of SWCNTs in THF.** A detailed procedure for the solubilization of the purified SWCNTs is reported in our earlier work.\textsuperscript{18} SWCNT (Nanocs Inc.) was solubilized by mixing 10 mg of SWCNTs with 100 mg of tetraoctylammonium bromide (TOAB) (Aldrich) or Nafion in 25 mL of tetrahydrofuran (THF) and sononating the mixture for 20–30 min. After the sample was subjected to centrifugation, the residue was resuspended in THF. This process of sonication/centrifugation was repeated for 3–4 cycles to remove excess TOAB/Nafion.

**Electrodeposition of SWCNTs and Platinum on Carbon Fiber Electrode (CFE).** The electrophoretic cell and the electrodes used for the MEA preparation are shown in Figure 1. We employed 2.25 \(\times\) 2.25 cm\(^2\) electrodes cut from carbon fiber paper (0.6 mm thickness) obtained from Fuel Cell Store (Bolzten, CO). Two carbon paper electrodes were kept \(\sim 5\) mm apart in a cell containing a SWCNT suspension in THF. When a dc voltage of \(\sim 40\) V is applied, we observed a slow movement of carbon nanotubes from the suspension toward the positive electrode and the assembly of nanotubes as a film on the CFE. The thickness of the films was controlled by varying the time of electrophoretic deposition. These films are quite robust and are suitable for electrochemical measurements.

The electrophoretic deposition approach was also employed to cast films of commercial carbon black (CB) and Pt black on carbon fiber paper electrode. CB and Pt black were obtained from Johnson Mathey and were suspended in THF containing 0.3 mL of Nafion solution (5% solution from Aldrich) per 100 mg of catalyst. Addition of Nafion to the suspended particles gives them a net negative charge, and both CB and Pt black particles migrate under the influence of an applied dc field toward the positive electrode and are deposited on the electrode surface. Control of the amount of metal catalyst and carbon support is achieved by controlling the dc voltage and time of deposition. After deposition, the electrode was vacuum-dried and weighed to determine if the desired loading has been achieved. If necessary, the process of deposition, drying, and weighing was continued until the desired loading (\(\leq 0.05\) mg/cm\(^2\)) was achieved.

**Characterization of the Electrode Surface.** The CFE containing SWCNTs and Pt were characterized by scanning electron microscopy (Hitachi S-4500). The morphology of the SWCNTs on the carbon fiber was also confirmed by Raman spectroscopy. The Raman measurements were made on a Jasco RMP-210 Raman spectrometer. The laser power used was 10 mW. A radiation spot of 0.1 mm diameter was used in 180 degree backscattering geometry at room temperature. The excitation wavelength was 532 nm.

**Preparation of the Membrane Electrode Assembly (MEA).** Carbon nanotube and CB was deposited first on carbon fiber paper (Teflon treated) using the procedure described above. A second electrophoresis step was used to deposit the Pt black catalyst on the SWCNTs or CB film. These electrodes are referred to as CFE/SWCNT/Pt and CFE/CB/Pt electrodes, respectively. A Nafion membrane cut in the dimension of 5 \(\times\) 5 cm was prepared by boiling in a solution of 5% H\(_2\)SO\(_4\) and 1 M H\(_2\)O\(_2\) at \(80^\circ\)C for 20 min and washing several times with deionized water. The cathode and anodes were then pressed on either side of the pretreated Nafion 117 membrane at a pressure of 50 kg/cm\(^2\) and 127 \(^\circ\)C for 2 min.

**Electrochemical Characterization.** Half cell reactions were conducted in a three-arm electrochemical cell using the carbon fiber paper coated with SWCNTs and Pt black as an anode or cathode. Cyclic voltammetric experiments were carried out using BAS 100 electrochemical analyzer. The impedance spectra were recorded using a Gamry DC 101 frequency response analyzer, in the frequency range between 100 kHz and 100 mHz and an excitation signal of 10 mV (rms). The experiment was conducted in a potentiostatic electrochemical impedance spectroscopy (EIS) mode where we were able to record the impedance spectra at an open circuit potential or at controlled potentials. The numerical data were analyzed by fitting to an equivalent circuit model.

**Catalyst Evaluation in a Hydrogen Fuel Cell.** A single cell test fixture supplied by Electrocem Inc. was employed for evaluating the catalyst performance for a H\(_2)/O\(_2\)-based fuel cell. The MEA was inserted between two graphite plates that had a serpentine flow pattern. Two 0.24-mm-thick silicone gaskets were introduced between the membrane and the electrodes. A uniform torque of 55 inch-pounds was applied to each of the bolts used to assemble the cell. The fuel cell was connected to the test station (Scribner Associates, Inc., USA) that was equipped with a gas humidifier, a mass flow controller, and a temperature indicator controller. Humidified hydrogen and oxygen gases were fed into the cell at a flow rate of 200 cm\(^3\) min\(^{-1}\) and maintained at a...
temperature of 75 °C. The current–voltage (I–V) characteristics of the cell were evaluated at two different ambient temperature of 25 and 60 °C.

Results and Discussion

A good dispersion of the platinum catalyst on the carbon support is the precondition for achieving good electrocatalytic activity and subsequent fuel cell performance. One critical aspect to achieving a good dispersion is the surface area of the carbon supports and how much of that surface area is accessible. A commonly used support is CB with a measured BET surface area of between 79 and 81 m²/g. Carbon nanotubes in general are expected to have much higher surface areas. We determined the BET surface area of 244 m²/g for the Nanocs SWCNT sample that we used in the experiments below, which is almost three times that of CB. While the specific surface area of the carbon support is important, a number of other factors determine their catalytic activity, including the electrochemical active surface area, conductivity, and crystallinity of the support.

Electrode Characterization. A Raman spectrum of the SWCNT film on CFE is shown in Figure 2. Spectra were obtained from multiple spots on the CFE surface, and no differences were seen in the spectra obtained from them. This indicates that the deposition of the SWCNTs on the CFE is uniform and the SWCNT retains its morphology intact following the process of electrophoresis. The ring breathing mode (RBM) and the G lines (shown as insets in Figure 2) are characteristic signatures of single-walled nanotubes. The profile and frequency of the RBM and the G lines are consistent with small diameter nanotubes on the surface. The profile and frequency of the G band has been used to distinguish between metallic and semiconducting SWCNTs. In our case, it suggests that the SWCNT sample as deposited on the carbon fiber surface has mainly metallic character with a main peak at 1581 cm⁻¹ and a shoulder at 1561 cm⁻¹.

As indicated in the experimental section, CFE/SWCNT/Pt electrodes were fabricated by sequential electrophoretic deposition of the nanostructured carbon support (SWCNT) on the carbon fiber paper electrode and Pt black. Scanning electronic microscopy (SEM) images taken before and after modification of CFE with SWCNTs and Pt catalyst are shown in Figure 3A–D. The SEM of carbon fiber paper shown in Figure 3A reveals a macroporous surface with interwoven carbon fibers, which are about 5 μm thick. These fibers provide the foundation to disperse the CNT and metal catalysts. Figure 3B (same magnification as Figure 3A) shows the CFE after deposition of SWCNTs. At this low magnification, it is difficult to identify the morphology of the carbon fiber surface. At high magnification (200×), the nanotubes interspersed within the carbon fiber network are clearly visible. Figure 3D shows the CFE/SWCNT surface at the same high magnification following electrophoretic deposition of Pt black. The platinum particles are well dispersed on the CFE/SWCNT electrode surface and provide an accessible surface for hydrogen adsorption and oxidation.

Hydrogen Evolution Reactions (HER) and Determination of Electrochemical Active Surface Area at CFE/SWCNT/Pt Electrodes. As indicated in the experimental section, we have compared the electrochemical behavior of the CFE/SWCNT/Pt with an electrode made from a conventional carbon support, in this case Johnson Matthey CB (CFE/CB/Pt). Electrophoretic deposition was used to deposit both the commercial CB and the SWCNT on the carbon Toray paper. Commercial Pt black from Johnson Matthey was used as the catalyst for the present study. In both cases, the loading of the electrocatalyst (Pt), carbon support, and the geometric area of the electrode was kept the same. To compare different electrocatalytic supports, it is important to

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**Figure 1.** Experimental setup for the electrophoretic deposition of SWCNTs. Items labeled 1, 2, and 3 are the quartz cell, carbon fiber paper (CFE), and Teflon spacer, respectively. The cell and its content (A) before and (B) after electrophoretic deposition of SWCNT on the carbon fiber paper (5 cm²) at an applied dc field of 80 V/cm for 2–5 min.

**Figure 2.** Raman spectra of SWCNTs electrodeposited on a CFE. The spectrum shown is an average of two acquisitions, and the CNT loading on the sample is estimated to be ~1 mg/cm². Insets show the ring breathing mode (RBM) and the G lines for the sample.
determine the electrochemically active surface area (ECSA) of each of the electrodes. ECSA of an electrocatalyst is a measure of the number of electrochemically active sites per gram of the catalyst and is determined by integrating the area under the potential window for H⁺ adsorption/desorption peaks after subtracting the charge from the double layer region. The cyclic voltammograms for the HER at CFE/SWCNT/Pt and CFE/CB/Pt electrodes were recorded in 1 M H₂SO₄ solution (Figure 4, panels A and B, respectively). The amounts of carbon support and the Pt catalyst in these two electrodes were maintained at 0.5 mg/cm², respectively. Both CFE/SWCNT/Pt and CFE/CB/Pt electrodes show two peaks in the cyclic voltammogram arising from hydrogen species adsorbed on the electrode surface. These two absorption peaks referred to as Hₛ and Hₜ arise from stronger and weaker adsorption sites, respectively, and are broad and not well resolved. The integrated area of the cyclic voltammogram represents Qₕ (charge arising from HER) and can be used to determine ECSA by employing the expression:

\[
\text{ECSA} \left[ \text{cm}^2 \text{ Pt/g of Pt} \right] = \frac{\text{charge} \left[ Q_{\text{H,}} \mu \text{C/cm}^2 \right]}{210 \left[ \mu \text{C/cm}^2 \right] \times \text{electrode loading} \left[ \text{g of Pt/cm}^2 \right]} \tag{1}
\]

The ECSAs calculated using eq 1 and integration of the voltammograms in Figure 4A,B are summarized in Table 1. The SWCNTs and the CB supports give reasonably similar values for the ECSAs with CFE/SWCNT/Pt exhibiting slightly higher values. We consider such a difference between ECSA values to lie within the margin of error, and thus it provides the basis for comparison of two carbon supports. The observed ECSA values are also similar to those observed earlier by Wang et al. It is interesting to note however that these values of ECSA are significantly higher than bare platinum (2.8 m²/g of Pt), reinforcing the importance of nanostructured carbon support.

The mechanism with which H₂ evolution occurs at a metal, M, involves an adsorbed H atom intermediate, MH_ads:

\[
\begin{align*}
\text{H}_3\text{O}^+ + e^- + M &\rightarrow \text{MH}_\text{ads} + \text{H}_2\text{O} \quad \text{(2)} \\
\text{MH}_\text{ads} + \text{H}_3\text{O}^+ + e^- &\rightarrow \text{H}_2 \uparrow + \text{H}_2\text{O} + M \quad \text{(3)} \\
2\text{MH}_\text{ads} &\rightarrow 2M + \text{H}_2 \uparrow \quad \text{(4)}
\end{align*}
\]

The sequence of these reactions is referred to as the Volmer step (reaction 2), the Heyrovsky step (reaction 3), and the Tafel step (reaction 4). These reactions are marked by the two shoulder peaks in the cyclic voltammogram. The separation between the adsorption and evolution peak potentials (E_H₄ − E_H₂ evolution) is a measure of the metal–hydrogen (M–H) bond strength. The voltammograms in Figure 4A,B indicate that the peak separation is larger

Several groups have reported desorption energies for hydrogen on carbon supports including graphite and SWCNTs. Dillon et al. reported a value of 19.6 kJ/mol for the hydrogen desorption energy on plain SWCNTs. Kuppers et al. reported a much higher value of 60 kJ/mol on graphite. However, these literature values are for the bare carbon supports as compared to our work with platinum on carbon support. We also carried out the HER on a CFE/SWCNT electrode without any platinum (Supporting Information, Figure S1). It is quite likely that the energetics of hydrogen adsorption/desorption in our case reflects additional energy barriers that arise from H interacting independently with both platinum and the SWCNT support. To further understand the differences in hydrogen desorption energies between the two carbon supports, we carried out Tafel polarization studies and impedance measurements.

Depending upon the overpotential window regime, a Tafel slope between 30 and 180 mV/decade was determined for the HER for the CFE/SWCNT/Pt and CFE/CB/Pt electrodes. The slopes as identified by two different overpotential regions are summarized in Table 2. The actual Tafel plots from which the slopes have been determined are included as Supporting Information (Figure S2). Region I corresponds to overpotential values that are close to equilibrium potential. For all three electrodes, we obtain reasonably similar values between 25 and 31 mV/decade in region I. This indicates that similar hydrogen adsorption mechanisms (eq 2) are operative at these electrodes in the lower potential regime. In region II corresponding to the overpotential range of 200–400 mV, the CFE/SWCNT/Pt has a Tafel slope of 190 mV. This slope is higher than the corresponding slope obtained with CFE/CB/Pt electrodes (120–135 mV/decade). Higher Tafel slopes indicate higher activation energy for hydrogen desorption on SWCNT supports as compared to CB, supporting our suggestion that hydrogen adsorption/desorption on SWCNT/Pt can be used to compare the interfacial kinetics of the two supports. Observed differences in electrode kinetic constants could then be attributable to the support. Figure 5A shows the impedance spectrum in Nyquist form for the CFE/SWCNT/Pt electrode. The data under open circuit conditions are shown as an inset in panels A and B. The experimental data are shown as circles, and the theoretical fits are shown as solid lines. The area of the electrode in all cases was 1.4 cm².

![Figure 4. Cyclic voltammograms for the HER at (A) CFE/SWCNT/Pt and (B) CFE/CB/Pt (scan rate: 50 mV/cm; electrolyte: 1 M H2SO4; reference electrode: SCE). The area of the electrode in all cases was 1.4 cm².](image4)

![Figure 5. The ac impedance spectrum in Nyquist form for HER at an overpotential of 100 mV at the (A) CFE/CB/Pt electrode and (B) CFE/SWCNT/Pt electrode. The data under open circuit conditions are shown as an inset in panels A and B. The experimental data are shown as circles, and the theoretical fits are shown as solid lines. The area of the electrode in all cases was 1.4 cm².](image5)

Table 2. Tafel slopes and exchange current density for the hydrogen evolution reaction on various electrodes

<table>
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<tr>
<th>Electrodes</th>
<th>Tafel slope (mV/decade)</th>
<th>Exchange current density (mA/cm²)</th>
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</thead>
<tbody>
<tr>
<td>CFE/CB/Pt</td>
<td>31</td>
<td>135</td>
</tr>
<tr>
<td>CFE/SWCNT/Pt</td>
<td>29</td>
<td>192</td>
</tr>
</tbody>
</table>


Figure 6. Linear sweep voltammogram for oxygen reduction reaction at (a) CFE/SWCNT, (b) CFE/Pt, (c) CFE/CB/Pt, and (d) CFE/SWCNT/Pt in 0.5 M H2SO4 saturated with oxygen. The carbon and metal catalyst content was kept constant at 1.0 mg/cm², and the scan rate was 20 mV/s (electrolyte: 0.1 M Na2SO4; reference electrode: SCE).

O2 Reduction Reaction (ORR) at CFE/SWCNT/Pt Electrode. To overcome the sluggish kinetic response of carbon/Pt-based electrodes in the ORR is a major challenge.36 New catalysts are being explored to promote ORR and employ them in a fuel cell operation.37,38 To probe the effectiveness of SWCNT in an ORR, we carried out half cell reaction in a O2 saturated solution. For the oxygen reduction experiments, a solution of 0.1 M Na2SO4 was purged with ultrapure oxygen for ~15 min to attain saturation in solution.

Figure 6 shows the linear sweep voltammograms for the ORR in a solution saturated with oxygen at CFE electrodes modified with SWCNT, SWCNT/Pt, and CB/Pt and Pt. Each electrode was scanned over a potential range from 700 to 0 mV several times to ensure reproducibility. The cyclic voltammograms in Figure 6 show that the magnitude of the oxygen reduction current obtained with the SWCNT-based electrodes is relatively higher (factor of ~1.5) than a CFE/CB/Pt electrode. Higher exchange current densities and lower Tafel slopes have been observed for the ORR at SWCNT-supported electrodes.36,38

Performance of SWCNT-Based MEA in a Fuel Cell. While the catalyst of choice for the fuel cell electrode reactions is Pt nanoparticles anchored onto a carbon support, achievement of efficient charge-transfer kinetics at the gas–liquid–solid boundary remains a major challenge. Cyclic voltammetry and impedance results presented in the preceding sections highlight the usefulness of carbon nanotubes as support materials for fuel cells.

The electrochemical reactions dictating the performance of hydrogen–oxygen fuel cell include at the anode

$$\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^- \quad (5)$$

and at the cathode

$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (6)$$

Despite the simplicity of reactions 5 and 6, a variety of factors such as inhomogeneity, surface roughness, and porosity of the carbon paper electrode. To overcome this effect, we employed an EQCRT scheme that includes a constant phase element.35

Table 3. Fitting Parameters Obtained Using the Equivalent Circuit

<table>
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<tr>
<th>carbon support</th>
<th>$R_s$ (Ω)</th>
<th>CPE</th>
<th>$n$</th>
<th>$R_c$ (Ω)</th>
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<tr>
<td>CB/Pt</td>
<td>4.67</td>
<td>0.000964</td>
<td>0.8</td>
<td>495.9</td>
</tr>
<tr>
<td>SWCNT-Pt</td>
<td>4.04</td>
<td>0.00367</td>
<td>0.76</td>
<td>44.44</td>
</tr>
</tbody>
</table>

and other experimental conditions were kept the same in both cases. The experimental impedance data are shown as open circles, while the solid line represents a theoretical fit obtained using an equivalent circuit model (EQCRT) illustrated in Scheme 2.

The model presented in Scheme 2 is a simple EQCRT that indicates the difference in the single electrode behavior. This model is similar to the one employed by Conway et al. and Armstrong and Henderson in their HER studies.32,33

The semicircles in Figure 5A,B do not center on the Z' axis as one would expect from a simple RC circuit combination.34 This discrepancy is likely to arise from the factors such as inhomogeneity, surface roughness, and porosity of the carbon paper electrode. To overcome this effect, we employed an EQCRT scheme that includes a constant phase element.35

Table 3 summarizes the fitting parameters obtained from this equivalent circuit.

Comparison of Figure 5A,B in the potential region for HER (at an overpotential of 100 mV) reveals that the charge-transfer resistance for a CFE/SWCNT/Pt electrode is about an order of magnitude less than that of a CFE/CB/Pt electrode. The EQCRT model yields the charge-transfer resistance values of 50 kΩ for the SWCNT support compared to 500 Ω for the CB support. The insets in Figure 5, panels A and B indicate the impedance at equilibrium under open circuit conditions. The CFE/CB/Pt electrode has a very high charge-transfer resistance under open circuit conditions, and it drops to 500 Ω at an overpotential of 100 mV. This behavior indicates sluggish interfacial kinetics at the electrode/electrolyte interface of the CFE/CB/Pt electrode. On the other hand, the electrode/electrolyte interface at the CFE/SWCNT/Pt electrode has more facile kinetics as manifested in the lowering of the charge-transfer resistance to 1 kΩ (inset in Figure 5B).

The stronger adsorption of H+ on the surface of the SWCNT/Pt as compared to the CB/Pt support is likely to play an important role in facilitating electron transfer kinetics. Since both these electrodes exhibit similar ESCAs (Table 1), we cannot attribute the differences in the kinetics and energetics of electrode processes to variations in ECSA but instead they are likely to arise from the inherent properties of the support. Further studies are underway to understand the interfacial kinetics of SWCNT-based electrodes at various overpotentials.

with the desired flow of H2 and O2, we monitored the similar loading of the catalyst. After attaining equilibrium while the cathode in all cases is commercial CB with and 1 mg/cm2 SWCNT and an anode back pressure of densities. A power density of 26 mW/cm2 was obtained for the rapid drop seen at higher current densities.

The cell resistance. Mass transport limitations account limitation of electrode kinetics. As the current density initially in the lower current density region due to SWCNT-based fuel cell exhibits an open circuit voltage of pressures of 0.103 MPa was attained at the anode. The voltage and current at a different applied load. A back pressure for SWCNT-supported assemblies has enabled us to achieve it. Even if we consider the improved mass transfer as the only reason for higher power density at greater anodic back pressures, the SWCNT support has enabled us to achieve it.

We also investigated the temperature dependence of the power densities and polarization curves using SWCNT-based MEA. Figure 9A shows the polarization curves at 25 and 60 °C for an MEA with a CFE/SWCNT/Pt anode while the cathode was commercial CB. Pt metal catalyst and SWCNT loading was 0.56 mg/cm2 and 1 mg/cm2, respectively, while the gas back pressure was maintained at 0.137 MPa. We obtained a maximum power density of 45 mW/cm2 at the higher temperature. We also fabricated an MEA using SWCNT support at both the anode and the cathode. The polarization data and power densities obtained with SWCNT support based MEA at 25 and 60

SWCNT concentration, an increase in the maximum power generated is also seen. These results show the importance of SWCNT support in achieving a better distribution of Pt catalyst and increase in the ECSA. The increase in the amount of the active surface available for hydrogen adsorption at higher SWCNT loadings is likely to increase the concentration of Hads on the surface.

To further substantiate the effect of hydrogen adsorption, we varied the back pressure at the anode (CFE/SWCNT/Pt). Figure 8 shows the comparison of the peak power density with the back pressure for a GEM/PEM, a CFE/CB/Pt CFE/SWCNT/Pt anodes. At low anodic back pressures of H2 (0 and 0.034 MPa), the CB exhibits a peak power density of 18 to 20 mW/cm2, which is slightly higher than SWCNT-based PEM. However, at greater anodic back pressures (0.068–0.137 MPa) the SWCNT-based assembly performs better, and we observe a peak power density of 28–30 mW/cm2 at 0.137 MPa. Under the same experimental conditions, the CB-based PEM assembly exhibits a power density of 22–24 mW/cm2. This pressure dependence observed with the nanotube support correlates with the electrochemical results from the HER. The Tafel slopes and the ΔG values from the HER show that there is an energy barrier associated with hydrogen adsorption/evolution on an SWCNT electrode at room temperature and pressure. This barrier results in the lower performance of SWCNT-based electrodes at lower pressures. However, with increasing hydrogen back pressure, the SWCNT electrodes exhibit a better performance. The possible reasons include a stronger adsorption and/or interaction with the SWCNT and reduced activation energies for hydrogen adsorption/oxidation and improved mass transfer. Even if we consider the improved mass transfer as the only reason for higher power density at greater anodic back pressures, the SWCNT support has enabled us to achieve it.

We also investigated the temperature dependence of the power densities and polarization curves using SWCNT-based MEA. Figure 9A shows the polarization curves at 25 and 60 °C for an MEA with a CFE/SWCNT/Pt anode while the cathode was commercial CB. Pt metal catalyst and SWCNT loading was 0.56 mg/cm2 and 1 mg/cm2, respectively, while the gas back pressure was maintained at 0.103 MPa. We obtained a maximum power density of ~45 mW/cm2 at the higher temperature. We also fabricated an MEA using SWCNT support at both the anode and the cathode. The polarization data and power densities obtained with SWCNT support based MEA at 25 and 60
of 0.2 mg/cm² (see Figure S3 in Supporting Information). Our comparison of CNT-based catalysts with the commercially available catalysts in the present study point out the salient features of CNT-based fuel cells. Although it is premature to ascribe this enhancement to SWCNT support in the cathode compartment, it is worthwhile to look into the ORR at the SWCNT support and find ways to achieve further improvement in the electrode kinetics. Efforts are underway to optimize the cell configuration and operating conditions.

Conclusions

The electrophoretic deposition of SWCNTs on a CFE (Toray paper) provides a simple and versatile technique to design a MEA for the fuel cell. SWCNTs serve as an excellent support to anchor Pt catalyst and carry out electrochemical oxidation and reduction reactions quite effectively similar to the existing commercial CB support. Our electrochemical studies demonstrate that hydrogen adsorption at SWCNT/Pt nanostructures can play an important role in improving the performance of H₂-based PEM fuel cells especially at higher pressures. Decrease in charge-transfer resistance and greater adsorption of hydrogen makes the SWCNT-based MEA attractive for developing next generation fuel cell devices. Efforts are necessary to overcome the activation energy barrier seen in the SWCNT-based electrodes. Indeed, the improved performance observed during the fuel cell operation at higher anodic back pressures shows promise in this direction.

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Supporting Information Available: HER cyclic voltammograms for the reference SWCNT and CB electrodes (Figure S1) and Tafel plot (Figure S2). S3 shows the fuel cell polarization data at high temperature using preconditioning procedure. These materials are available free of charge via the Internet at http://pubs.acs.org.