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Fuel Cells

Polymer Electrolyte Fuel Cells Using Nafion-Based Composite Membranes with Functionalized Carbon Nanotubes**

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Polymer electrolyte membrane fuel cells (PEMFCs) continue to receive extensive attention because of their utility as a clean energy source for automotive, stationary, and portable applications.[1] The proton conductivity of the polymer electrolyte membrane (PEM) is one of the key factors limiting the performance of PEMFCs, which depends on the relative humidity, and controls the cost and durability.[2] Consequently, an improvement in the proton conductivity of the electrolyte membrane even by an order of magnitude could change the performance of fuel cells dramatically.[3] Currently, Nafion-based membranes are widely used as the PEM in fuel cells that operate from 60 to 80 °C. Although these membranes show good proton conductivities from 0.1 to 0.01 S cm^{-1} in a humid environment, they have many limitations, such as: 1) dependence on water for conductivity; 2) high methanol permeability; 3) a tendency to disintegrate in the presence of hydroxyl radicals, an intermediate in the cathode reaction; and 4) moderate mechanical and chemical stability.

To improve the performance of electrolytes used in PEMFCs, two different approaches have been adopted. First is the synthesis of alternative membranes that could operate at higher temperatures without the need for humidification. The phosphoric acid doped polybenzimidazole membrane is a widely exploited example in this category.[4,5] Second is the modification of Nafion membranes to increase their conductivity, chemical stability, and mechanical strength.[6–22] This is particularly significant for operation above 100 °C, where problems associated with CO poisoning are less pronounced.

The Nafion membrane is made up of a polytetrafluoroethylene (PTFE) backbone with side chains ending in sulfonic acid moieties, which form clusters with water at an approximate ratio of 70:1000.[6,7,10] It is the distribution of these sulfonic acid–water clusters that is the central reason for the celebrated proton transport of Nafion. Hence, any increase in the number of sulfonic acid groups could, in principle, help to increase the water content in the membrane. Many past attempts to achieve this by incorporating inorganic and/or organic additives have been successful only to a limited extent, although some of the membranes could retain water even up to 120 °C.[6–22] However, there are only very few reports on how to increase the sulfonic acid content, which would naturally also help to increase the number of acid–water clusters and therefore the proton conductivity of Nafion-based membranes.[23]

Herein, we present a chemical strategy to increase the sulfonic acid content of Nafion membranes by incorporating sulfonic acid functionalized single-walled carbon nanotubes (S-SWCNTs), and demonstrate the remarkable utility of this composite membrane as electrolyte in PEMFC applications. As these S-SWCNTs span the hydrophobic domains of the polymer matrix, they can exquisitely tune the extent of networking in the matrix. In addition, the mechanical stability of the composite membrane is enhanced by SWCNTs, which are well known for their high tensile strength and Young's modulus.[24]

The carbon nanotube (CNT)/Nafion composite has been used in different applications, such as actuators, microscopic pumps, sensors, and electrocatalysts.[25–31] Its use as electrolyte has been reported by Liu et al., with no significant improvement in performance despite higher mechanical stability.[32] In comparison, herein the CNT surface is functionalized with sulfonic acid groups to obviate possible high intrinsic electronic conduction. More significantly, the mere presence of 0.05 % of these functionalized SWCNTs is not adequate to form an electronically conducting network. Hence, it will be interesting to see what happens to the proton conductivity of Nafion membranes when CNTs prefunctionalized with sulfonic acid groups are introduced, because of the increased sulfonic acid content and better channel-like network for proton transport (Figure 1).

Figure 2a shows the temperature-dependent ionic conductivity of Nafion and Nafion/S-SWCNT composite membranes, and reveals an almost one order of magnitude higher conductivity for the composite than that of Nafion 1135, even above 100 °C. This finding can be attributed to the higher

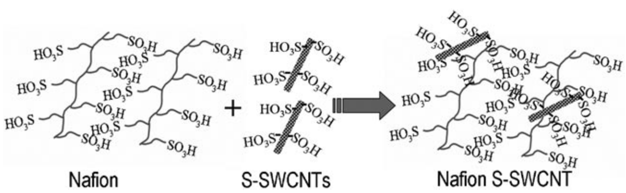

Figure 1. Preparation of the S-SWCNT/Nafion composite membrane by mixing solutions of the components in *N*,*N*-dimethylacetamide (DMAc).

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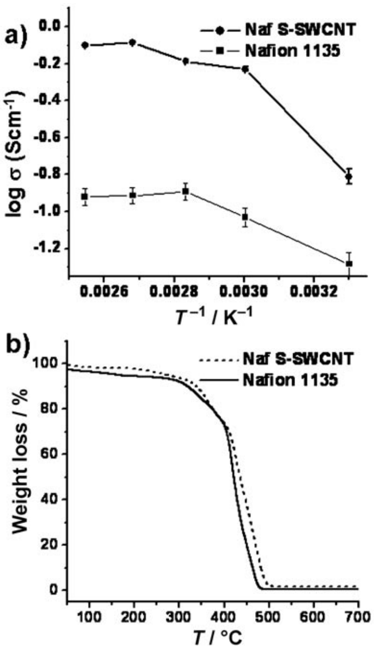

Figure 2. a) Temperature-dependent proton conductivity (σ) of Nafion 1135 and Nafion/S-SWCNT composite membranes at 100% relative humidity in the range of 1 MHz to 0.1 Hz. b) Thermogravimetric analysis of Nafion 1135 and Nafion/S-SWCNT membranes in air at a heating rate of 10 °C min^{-1}.

sulfonic acid content of the composite membrane, which facilitates more channels for proton transport. Furthermore, the activation energies calculated for the Nafion/S-SWCNT and Nafion 1135 membranes are 0.072 and 0.12 eV, respectively, which suggests that proton transport is more facile in the case of the composite membrane. These values are in excellent agreement with reported values ranging from 0.09 to 0.13 eV for Nafion membranes.[16,18]

The high proton conductivity of Nafion is attributed to a Grotthus-type mechanism, in which the reorganization of hydrogen bonds plays a key role. As the extra sulfonic acid moieties are anchored on the surface of the CNTs, these could provide more facile hopping of protons, which in turn would help to increase the proton mobility, thus accounting for the observed enhancement in conductivity. In contrast, an unmodified SWCNT/Nafion composite membrane does not show any improvement in proton conductivity (see the Supporting Information).

A comparison of the thermograms for the composite membrane and Nafion 1135 is given in Figure 2b. At up to 300 °C, only a small fraction of weight loss (ca. 5%) is observed for both membranes, which could be attributed to the loss of water. However, both the membranes disintegrate completely at 600 °C, which suggests that the incorporation of 0.05% S-SWCNTs does not increase the thermal stability of Nafion. Indeed, S-SWCNTs might act as a catalyst for the decomposition of the Nafion/S-SWCNT membrane because it takes places about 20 °C lower than that of Nafion 1135.

A smaller onset around 300 to 350 °C in the Nafion membrane corresponds to the degradation of sulfonic acid groups in the side chains.[33,34] In our composite membrane, two such onsets are observed in this region, which indicate the separate disintegration of sulfonic acid groups of the Nafion membrane and S-SWCNTs. These onsets can be clearly seen in the derivative plots (see the Supporting Information), which show a doublet corresponding to the two onsets at around 300 to 350 °C. Furthermore, the two-stage disintegration of both the membranes beyond 400 °C can be explained by the decomposition of polyether side chains and the PTFE backbone.[33,34] In comparison, the tensile strength of the composite (0.05% S-SWCNTs) is 7.6 MPa, which is smaller than that of Nafion 1135 (10.3 MPa). However, the yield point of the composite is surprisingly improved compared to that of Nafion 1135 (see the Supporting Information).

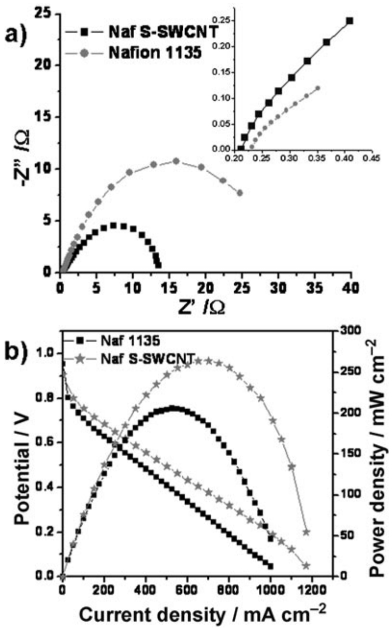

Figure 3. a) Nyquist impedance (Z) plots for MEAs made with Nafion 1135 and Nafion/S-SWCNT membranes. The measurements were carried out at room temperature with a flow of humidified H_2 and O_2. Inset: the high-frequency range at higher magnification. b) Polarization curves obtained with Nafion/S-SWCNT and Nafion 1135 membranes at 60 °C with humidified H_2 and O_2 (flow rate 0.4 slpm). The cells were conditioned for 30 min at open-circuit potential and at 0.2 V for 15 min before measurements.

Figure 3a shows typical impedance spectra in Nyquist form for membrane-electrode assemblies (MEAs) fabricated with both Nafion 1135 and Nafion/S-SWCNT membranes using a standard formulation of 20% Pt/C along with Nafion binder in the catalyst layer as electrodes. Undoubtedly, MEAs with a Nafion membrane incorporating S-SWCNTs show less electrolyte resistance in comparison with that of Nafion 1135, which is in excellent agreement with the activation energies measured from Figure 2a. The enhanced conductivity for MEAs based on a composite membrane can be attributed solely to the membrane, as the contribution from other components of the electrodes will have an insignificant value because they are kept identical during fabrication. The conductivity values are 0.0155 and 0.0101 $\mathrm{S\,cm^{-1}}$ for composite membrane and Nafion 1135, respectively.

Moreover, the semicircles for H_2 oxidation and O_2 reduction overlap, and hence it is difficult to extract separate kinetic parameters from these data. However, the composite membrane forms a smaller semicircle for the O_2 reduction reaction, which indicates the decreased charge-transfer resistance and hence enhanced exchange current density. As the catalyst is the same in both cases, there will also be contributions from the change in surface properties resulting from the addition of S-SWCNTs.

Figure 3 b shows the polarization plot for a MEA fabricated using 20 % Pt/C for both anode and cathode in a single-cell experiment at 60 °C with a humidified H_2/O_2 gas flow rate of 0.4 slpm (standard liters per minute), which reveals a significantly better performance for the composite than that of the Nafion 1135 membrane. The open-circuit voltage (OCV) obtained with the composite membrane is 0.9 V at 60 °C, whereas for Nafion 1135 it is 0.96 V. However, the activation loss and ohmic loss (which are much more important for sustaining a large current density) in the case of the composite membrane are considerably lower than those of Nafion 1135. For example, the Nafion/S-SWCNT membrane gives a maximum power density of 260 $\mathrm{mW\,cm^{-2}}$ at 0.42 V, whereas the Nafion 1135 membrane gives 210 $\mathrm{mW\,cm^{-2}}$ at 0.39 V.

As the electrode composition and preparation procedures followed for the MEAs were same for both, the increase in performance could be exclusively credited to the Nafion/S-SWCNT membrane. These results have profound implications in PEMFC research as the incorporation of SWCNTs can give better durability, and also the performance enhancement could reduce the cost of the H_2/O_2 fuel cell itself because the same amount of Pt catalyst is used in both cases.

In conclusion, our approach of using S-SWCNTs incorporated in a Nafion matrix as a PEM in H_2/O_2 fuel cells offers an unprecedented opportunity to obviate many limitations of currently used Nafion membranes, thus opening new possibilities of tailoring the properties and stability of PEMs to give enhanced fuel-cell performance. Apart from a remarkable improvement in proton conductivity, these composite membranes are also capable of increasing the mechanical stability, which could arise from the incorporation of SWCNTs along with a decrease in methanol permeability. However, several challenges have to be overcome before these advantages can be commercially exploited, including a rigorous evaluation of the chemical stability and durability of the membranes, lifetime studies of MEAs, and possible corrosion problems of the electrode materials because of the higher sulfonic acid content. Nevertheless, these results present enough scope to design polymer electrolyte fuel cells with better overall system efficiencies and simplified balance-of-plant using this new generation of composite electrolytes.

Experimental Section

Sidewall functionalization of SWCNTs with sulfonic acid groups was effected by a surface functionalization strategy as reported by Wang et al. (see the Supporting Information).[35] Composite membranes were prepared by dissolving precast Nafion membrane (520 mg; 5 % Nafion solution in 2-hydroxypropane, Fuel Cell Stores Inc.) in DMAc (10 mL) and mixing with a solution (520 µL) of S-SWCNTs in DMAc. The mixture was stirred for 4 h at 60 °C and dried in an oven at 70 °C. The resulting membrane (100–110 µm in thickness) was pretreated with sulfuric acid by boiling the membrane for 1 h in H_2O_2, water, H_2SO_4, and water in sequence. Gas diffusion layers (GDLs) were prepared by applying a carbon ink made by mixing carbon, PTFE, cyclohexane, and water. A catalyst ink was prepared by mixing 20 % Pt/C (Arora Matthey), Nafion, isopropyl alcohol, and water and this ink was applied to the GDLs. The resulting electrodes were coated with a thin layer of Nafion before uniaxial compaction with the membranes to fabricate the MEAs.

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