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Development and characterization of single wall carbon nanotube–Nafion composite actuators

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Abstract

The development and characterization of thin film polymeric actuators has been performed for single wall carbon nanotube (SWNT)–Nafion composite systems. Previous work in our laboratory illustrated that incorporation of highly conductive SWNTs into an ionomeric matrix promoted an actuation response by enhancing the electro-osmotic effect at relatively low doping levels, ∼0.1% (w/w). Further investigation has shown the effects of frequency and applied voltage on the composite bimorph actuator systems. The results indicate a displacement response that is linearly dependent on voltage and inverse to frequency.

Keywords: SWNT; Nafion; Actuator

1. Introduction

Thin film polymeric actuators are an area of current research for various applications, including microelectromechanical systems (MEMS), artificial muscles, and micro-catheters [1]. Typical devices require an electrochemical stimulus to cause the mechanical bending of the structure by pH, osmotic, or redox effects. Although many conducting polymers have been investigated, [1] an ionomeric polymer, Nafion, has been shown to be a viable actuating material based on an electro-osmotic effect [2].

Nafion actuators which rely on the chemical reduction of noble metals on the surface of the ionomer film, have been reported by several groups [3–5]. Typical Nafion bimorph actuator devices operate in aqueous alkali metal electrolytes, although some work has been done with alkyl ammonium solutions [6]. Under an applied bias of a few volts or less, cations in solution are driven into the Nafion matrix of the cathode by the electric field. The solvated cations cause swelling of the cathode at a significantly higher degree than the anode. This differential swelling results in a bending of the tip towards the anode. The degree of electrode swelling is directly related to the water solvation sphere of the counter cation. It has been shown that selection of lithium as the counter cation will produce the maximum displacement for these actuators [3,7].

Attempts to improve actuator performance have been made by enhancing electrode roughness to increase metallized surface area, [8] modifying Nafion film thicknesses, [2] and varying the counter cation species in the electrolyte [6]. Recently, we described the effects of incorporating single wall carbon nanotubes (SWNTs) into the Nafion matrix as a means of significantly augmenting the film's conductivity [9]. Efficient dispersion of the highly percolating SWNTs in the Nafion matrix can foster a more uniform, conductive electrode. This is in contrast to chemically metallized-Nafion electrodes which are limited to enhancement of surface conductivity only. Since chemical metallization is a diffusion-limited process, the penetration depth of the noble metals is typically 1–10 μm [10]. Also, the problematic delamination of metal surface layers for metallized-Nafion electrodes is not a concern for SWNT–Nafion composite electrodes since the conductive network is dispersed within the polymer matrix.

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The previous displacement results were reported to be similar between highly metallized-Nafion actuators (i.e. >30% (w/w) metal), and significantly lower doped SWNT–Nafion actuators (∼5% (w/w) SWNTs). Also, the typical osmotic relaxation for metallized-Nafion actuators was not observed with SWNT–Nafion composite actuators [9]. In this report, we provide characterization data for the effects of applied voltage and operating frequency on the bimorph cantilever displacement of SWNT–Nafion composite actuators.

2. Experimental

Single wall carbon nanotubes were purchased from Carbon Nanotechnologies Inc., referred to as HiPco SWNTS or h-SWNTs [11]. Purification of the as-produced (AP) material was performed using a series of chemical and thermal oxidation steps based on the reported procedure [12]. In summary, ∼50 mg of AP h-SWNTs were heated to 225 °C in air for 16 h, followed by ultrasonication in ∼20 mL concentrated hydrochloric acid for 1 h. The solution was filtered through a 0.2 μm–47 mm Anodisc membrane filter and dried at 70 °C in vacuo for 1 h. The procedure was repeated at temperatures of 325 and 425 °C in air for 2 h, with ultrasonication in concentrated hydrochloric acid for each step at similar times. A final thermal oxidation at 425 °C for 2 h was performed to attain >95% (w/w) h-SWNTs, the desired purity. Characterization of the AP and purified h-SWNTs was performed using thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Raman spectroscopy. The TGA was performed on ∼1 mg samples under flowing air (60 sccm) at a ramp rate of 5 °C/min from room temperature up to 950 °C. SEM images were obtained with a Hitachi S-900 at an accelerating voltage of 2 kV with magnifications ranging up to 100,000×. Raman spectroscopy was performed with a JY-Horiba LabRam instrument at excitation wavelengths of 1.96 and 2.54 eV. The scan range was 50–2800 cm^{-1} with an attenuation filter during analysis to minimize localized heating of SWNT samples.

Purified h-SWNTs were dispersed in Nafion solution (Aldrich) at appropriate mass doping levels for each composite by a series of mixing techniques. Initially, homogenization at 20,000 rpm occurred for five 10 min intervals, followed by mechanical stirring at room temperature for 72 h. The composite solutions were cast onto Teflon substrates, allowed to dry at room temperature for 24 h, and then placed at 70 °C in vacuo for 1 h. The resulting films displayed a thickness of ∼25 μm as observed by a cross-sectional analysis in the SEM.

Electrical contacts were applied to the SWNT–Nafion composite membranes by a mild platinization procedure described previously [9]. The composite membranes were then cut into strips with dimensions of 4 mm × 25 mm, and immobilized on opposite sides of an insulating 5 mm × 35 mm polyimide film (Fig. 1). Application of the SWNT–Nafion composite electrodes on the insulating polyimide substrate

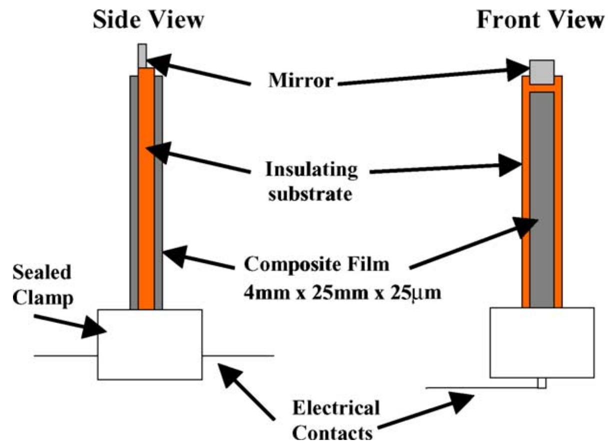

Fig. 1. Schematic representing the fabrication of bimorph cantilever actuators. On each side of the insulating substrate, SWNT–Nafion composite thin film electrodes were applied. Electrical leads in contact with the electrodes were protected by a sealed plastic clamp.

was intended to eliminate reported “curling” effects of metallized-Nafion actuators, [2,5,6,10,13] by isolating the electrodes to a flexible support. The bimorph cantilever actuator assembly was immersed in a 1 M $LiCl_{(aq)}$ solution. Displacement data was acquired using an optical lever whereby a 0.95 mW helium–neon laser was focused on an aluminum mirror and the reflected beam measured on a data collection board. Electrical stimulation of the actuator electrodes was performed using a Keithley 236 Source Measurement Unit at excitation sinusoidal voltages ranging from 0.025 to 2.0 V, and observable cycling frequencies from 1 to 50 Hz. The cantilever tip displacement was calculated using small-angle approximations by the following equation:

$$d = \frac{DL}{2B} \quad (1)$$

where d is the bimorph cantilever tip deflection, D the projected displacement on the data collection board, L the length of the cantilever arm measured from the center of the mirror to the base of the cantilever, and B is the distance between the bimorph cantilever tip and the data collection board. The experimental precision for the optical lever is ±5 μm at a distance, B, equal to 1 m.

3. Results and discussion

The purity of the SWNTs prior to dispersion in the Nafion matrix is an important consideration during composite preparation, directly affecting conductive percolation limits. Therefore, it was imperative to reproducibly attain high purity, >95% (w/w) h-SWNTs. As seen in Fig. 2, SEM images representative of the (a) AP h-SWNTS, and (b) purified, >95% (w/w) h-SWNTs, display significant removal of the amorphous carbon coatings from the purification process. In addition to this qualitative analysis, we have shown using TGA that the iron catalyst impurities can be reduced to <3%

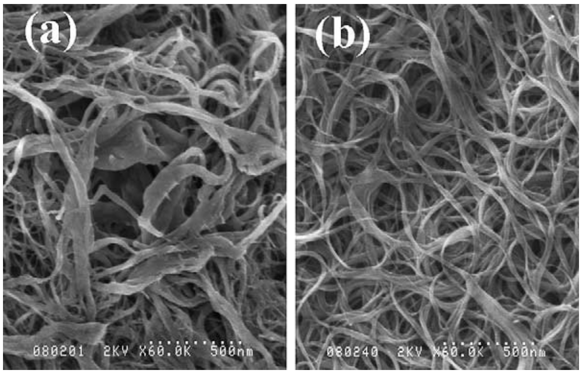

Fig. 2. SEM images of (a) as-produced h-SWNTs, and (b) purified, >95% (w/w), h-SWNTs. Removal of the carbonaceous coatings from the as-produced material during the purification process is distinctly observed between images (a) and (b). Magnification is 60,000× for both images.

(w/w) [9]. Raman spectroscopy was performed to determine any changes in the diameter distributions of AP h-SWNTs during the purification process. Shown in Fig. 3 is the Raman data for AP h-SWNTs (gray) and purified, >95% (w/w) h-SWNTs (black). The data in Fig. 3a and b represents the radial breathing modes (RBM) for laser energies of 1.96 and 2.54 eV, respectively. This spectral region directly relates to the diameter distribution and type (metallic or semiconducting) of SWNTs [14,15]. The following relationship between diameter (d, nm) and Raman shift (ω_{RBM}, cm^{-1}) has been reported for bundled SWNTs [16]:

$$\omega_{\mathrm{RBM}} = \left(\frac{224}{d}\right) + 14 \quad (2)$$

For both Fig. 3a and b, the Raman shifts for AP h-SWNTs occur between 180 and 320 cm^{-1} indicating diameters corresponding to 0.73–1.35 nm and the presence of both metallic and semiconducting SWNTs. The purified h-SWNTs have a diameter range of ~1.0–1.3 nm containing both metallic peaks (at 190, 216, and 253 cm^{-1} in Fig. 3a) and semiconducting peaks (at 199 and 223 cm^{-1} in Fig. 3b).

Preparation of the SWNT–Nafion composite solutions was performed as previously reported at various percent by weight SWNT doping levels [9]. The characteristic relationship of displacement as a function of doping level for SWNT–Nafion composite actuators is shown in Fig. 4. For an applied voltage of ±0.5 V and an operating frequency of 1 Hz, the resulting displacement is observed to increase as the percent by weight SWNTs is increased. These results, at relatively low voltages, offer tip displacements that are approaching reported values for metallized Nafion actuators, ~1 mm [3]. However, it is important to consider that a more accurate comparison of the displacement results between actuator types would require a standardization of the cantilever dimensions and applied electrical stimulus.

The actuator tip deflection for metallized Nafion actuators has been shown to be dramatically improved by altering the applied voltage [8]. Similarly, for a 10.8% (w/w) SWNT–Nafion composite actuator, the effects of a varying sinusoidal voltage on displacement at a constant frequency of 1 Hz were also measured from 0.025 to 2.0 V. As seen in Fig. 5, SWNT–Nafion actuators exhibit a linear dependence of tip displacement by voltage. This compares to the

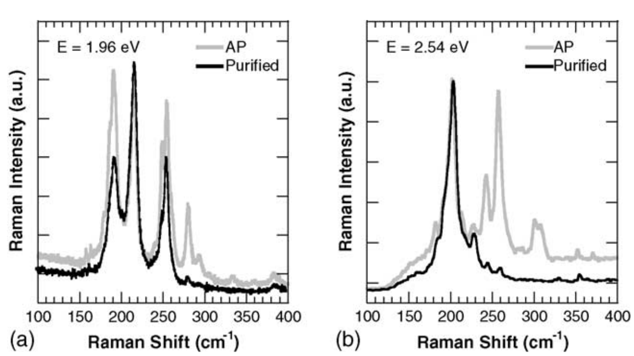

Fig. 3. Shown is the radial breathing mode (RBM) from the Raman spectra of AP (gray) and purified, >95% (w/w) h-SWNTs (black), for incident laser energies of (a) 1.96 eV and (b) 2.54 eV.

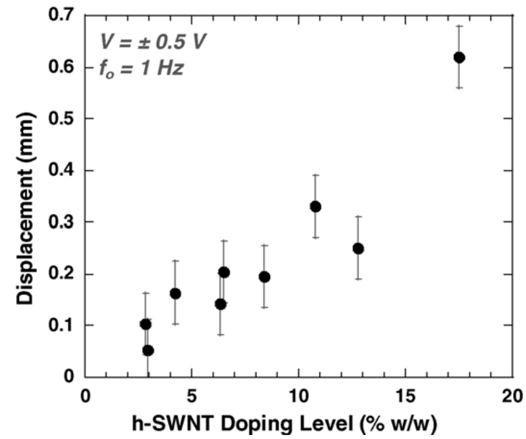

Fig. 4. Bimorph cantilever tip displacement data for varying percent by weight h-SWNT–Nafion composite actuators at an applied voltage of ±0.5 V and an operating frequency of 1 Hz.

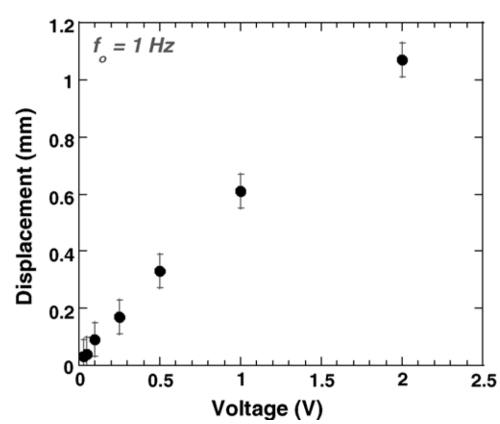

Fig. 5. Bimorph cantilever tip displacement data for a 10.8% (w/w) h-SWNT–Nafion composite actuator as a function of voltage at an operating frequency of 1 Hz. The plot shows the linear dependence of applied voltage on tip displacement.

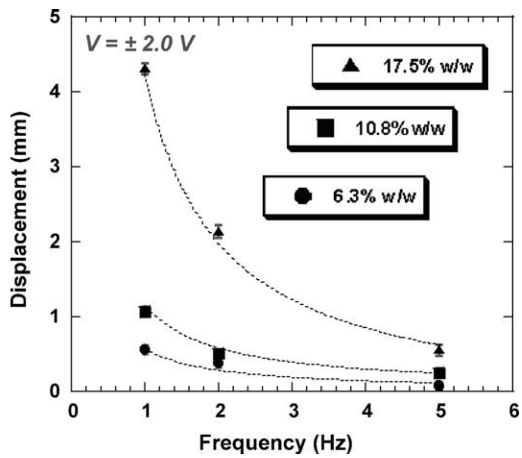

Fig. 6. Bimorph cantilever tip displacement (*d*) data for 6.3, 10.8, and 17.5% (w/w) h-SWNT–Nafion composite actuators at an applied voltage of ±2.0 V as a function of the operating frequency (*f*). The dashed curves represent the relationship, $d = 1/f$.

reported behavior of platinum–Nafion actuators where an "almost proportional" relationship between displacement and voltage was observed [4]. Therefore, the results indicate that variation in the potential difference between electrodes can impact the flux of solvated cations. (As described earlier, a higher degree of solvated cation diffusion into the composite electrodes will induce a larger degree of differential swelling and corresponding bending of the tip [3].) This applied voltage effect offers the potential for controlled manipulation of tip displacements for SWNT–Nafion composite actuators.

Characterization of the bimorph cantilever actuator tip displacement as a function of operating frequency was conducted at constant voltage. Analysis of the frequency effects on displacement for representative doping levels (6.3, 10.8, and 17.5% (w/w) SWNTs) is displayed in Fig. 6. There is an observed reduction in displacement for each doping level as frequency increases. Also, characteristic of each doping level is an inverse relationship between displacement and frequency. The dashed lines in Fig. 6 represent displacement as a 1/frequency relationship, similar to the data points for each composite. As expected, the response time of the actuator is limited by the frequency at which the potential bias is alternated. Previous data by others also show decreasing displacement results for metallized-Nafion actuators [17]. However, there may exist other contributing factors for SWNT–Nafion composite actuators which effect tip displacement as a function of frequency. At low frequencies there are potentially mechanical restrictions inherent to the SWNT–Nafion electrodes and insulating polyimide substrate which prevent complete displacement during the applied stimulation. For high frequencies, it is proposed that cation diffusion would be the limiting factor responsible for an observable maximum frequency. In the series of SWNT–Nafion composites analyzed, the highest frequency observed using the optical analysis station was 50 Hz at ±2.0 V for the 17.5% (w/w) composite.

4. Conclusions

Characterization of SWNT–Nafion composite actuators as a function of applied voltage and operating frequency was performed. It was observed that a linear dependence on tip displacement from applied voltage exists with these devices. Also, the tip displacement was shown to vary inversely with frequency. Therefore, applied voltage and operating frequency offer two possible parameters for control over device performance. Overall, the ability to operate these actuator systems at controlled conditions, lends itself towards future development in MEMS switches.

Acknowledgements

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References

[1] R.H. Baughman, Synth. Met. 78 (1996) 339.
[2] K. Kim, M. Shahinpoor, Polymer 43 (2002) 797.
[3] Y. Abe, A. Mochizuki, T. Kawashima, S. Yamashita, K. Asaka, K. Oguro, Polym. Adv. Technol. 9 (1998) 520.
[4] N. Fujiwara, K. Asaka, Y. Nishimura, K. Oguro, E. Torikai, Chem. Mater. 12 (2000) 1750.
[5] M. Uchida, M. Taya, Polymer 42 (2001) 9281.
[6] K. Onishi, S. Sewa, K. Asaka, N. Fujiwara, K. Oguro, Electrochim. Acta 46 (2001) 1233.
[7] K. Asaka, N. Fujiwara, K. Oguro, K. Onishi, S. Sewa, J. Electroanal. Chem. 505 (2001) 24.
[8] T.G. Noh, Y. Tak, J.D. Nam, H. Choi, Electrochim. Acta 47 (2002) 2341.
[9] B.J. Landi, R.P. Raffaelle, M.J. Heben, J.L. Alleman, W. VanDerveer, T. Gennett, Nano Lett. 2 (2002) 1329.
[10] M. Shahinpoor, K. Kim, Sens. Actuators A 96 (2002) 125.
[11] P. Nikolaev, M.J. Bronikowski, R.K. Bradley, F. Rohmund, D.T. Colbert, K.A. Smith, R.E. Smalley, Chem. Phys. Lett. 313 (1999) 91.
[12] I.W. Chiang, B.E. Brinson, R.E. Smalley, L. Margrave, R.H. Hauge, J. Phys. Chem. B 105 (2001) 1157.
[13] M. Shahinpoor, Electrochim. Acta 48 (2003) 2343.
[14] M.S. Dresselhaus, G. Dresselhaus, A. Jorio, A.G. Souza Filho, R. Saito, Carbon 40 (2002) 2043.
[15] L. Alvarez, A. Righi, T. Guillard, S. Rols, E. Anglaret, D. Laplaze, J.L. Sauvajol, Chem. Phys. Lett. 316 (2000) 186.
[16] A.M. Rao, J. Chen, E. Richter, U. Schlecht, P.C. Eklund, R.C. Haddon, U.D. Venkateswaran, Y.K. Kwon, D. Tomanek, Phys. Rev. Lett. 86 (2001) 3895.
[17] K. Jung, J. Nam, H. Choi, Sens. Actuators A 107 (2003) 183.