Carbon Nanofiber Hybrid Actuators: Part II – Solid Electrolyte-based

YUN YEO-HEUNG,[1] ATUL MISKIN,[1] PHIL KANG,[1] SACHIN JAIN,[1] SUHASINI NARASIMHADEVARA,[1] DOUGLAS HURD,[1] VISHAL SHINDE,[1] MARK J. SCHULZ,[1,*]
VESSELIN SHANOV,[2] PENG HE,[2] F. J. BOERIO,[2] DONGLU SHI[2] AND SUBRAHMIN SRIVINAS[2]

[1]Mechanical Engineering, Smart Structures Bio-Nanotechnology Laboratory, [2]Chemical and Materials Engineering University of Cincinnati, Cincinnati, OH 45221, USA

ABSTRACT: The objective of this study (Part II) paper is to develop a dry actuator for wider application than the wet actuator. To form a dry actuator, a carbon nanofiber (CNF) actuator is based on a solid polymer electrolyte (SPE). The SPE film is prepared from polymethyl methacrylate (PMMA), an ion-exchange material, a plasticizer, and a solvent by the solution casting method. Ion conductivity studies were carried out to characterize the electrochemical properties of the SPE. Electrochemical impedance spectroscopy was performed to understand the electrochemical cell of the dry actuator. The actuator was tested in a dry environment at various voltages and frequencies and the tip displacement was measured using a laser displacement sensor. Compared to previous single wall carbon nanotube buckypaper actuators, the dry-based CNF actuator requires a little higher voltage to actuate, but it is two orders of magnitude lower in cost. Compared to the liquid-based actuator, the solid electrolyte-based actuator is slower and the displacements are smaller. These results have verified the principle of the CNF dry actuator. Further development of this new smart material could lead to practical smart structures applications in which the CNF hybrid material could be used as a muscle layer on structures, or as the structural material itself.

Key Words: carbon nanofiber, electrochemical actuator, solid electrolyte, smart structural material.

INTRODUCTION

RESEARCHERS in the area of smart structures have been trying to overcome the limitation of the small strains or small forces produced by smart materials. With the help of biomimetic materials like the carbon nanotube (CNT), there is a potential to develop new actuators that will provide higher work per cycle than previous actuator technologies, and generate higher mechanical strength. In addition, CNTs offer high thermal stability, and this actuator with a suitable binder may be used in moderate temperature environments.

The first actuator made of CNTs was a macro-scale sheet of nanotubes termed 'buckypaper' (Baughman, 1996; Mazzoldi and Baughman, 2000; Roth and Baughman, 2002). This actuator produced strain due to the change in dimension of the nanotube in the covalently bonded direction caused by an applied electric potential. The charge injection leads to a change in the dimension of the nanotube paper causing the assembly to bend. This excess charge is compensated at the nanotube–electrolyte interface by electrolyte ions forming a double layer. Soon after the buckypaper actuator, their team demonstrated actuation of a single-wall (SW) CNT in which the SWCNT was suspended over a trench, and its edges fixed at the surface with a metal layer (Roth and Baughman, 2002).

Compared to the best-known ferroelectric, electrostrictive, and magnetostrictive materials, very low driving voltage for CNT actuation is a major advantage for various applications such as smart structures, multi-link catheters, micro-pumps, flaps for micro flying objects, molecular motors, or nano-robots. Another advantage is the direct conversion of electrical energy to mechanical energy along with high actuation strain, high strength, and high elastic modulus. Since faradic actuators basically come from the charge–discharge–charge method like a battery, it is also possible in theory to design a self-powered actuator which means this device can store and release charge and actuate motion without an external power source. Since these CNT actuators work in electrolyte, the bandwidth of the CNT actuator is low and applications thus far have been focused on artificial muscle (Tahhan et al., 2003; Han and Shi, 2004). On the other hand,

*Author to whom correspondence should be addressed.
E-mail: mark.j.schulz@uc.edu

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Von Klitzing's group in Germany used a solid electrolyte mixture for a harder actuator and a wider bandwidth.

NASA's Jet Propulsion Laboratory tried to develop bimorph actuators and force sensors based on carbon nanotubes. This idea also came from double layer charge injection that causes bond expansion. The Nanoscale Science Research Group of UNC demonstrated that a double-layered cantilever using multi-wall (MW) CNT changed its curvature under a temperature change. This system is called a thermally actuated mobile system. This bilayer cantilever is an actuator/sensor which has two layers with different thermal stress or intrinsic stress between the two materials. They reported that greatest bending occurs at a thickness ratio 1 : 7 (thickness of aluminum/MWCNT) and the actuator is controlled by laser heating. However, other research is more focused on SWCNT (Spinks et al., 2001–2003; Wang et al., 2001; Minnett et al., 2002) and in a liquid electrolyte environment. To our knowledge, the electrochemical actuation properties of carbon nanofiber (CNF) have not been investigated yet, probably because of the difficulty in making CNF sheets like buckypaper. Buckypaper is formed by dispersing nanotubes/nanofibers in a solvent and evaporating the solvent to leave a thin paper of the nanotubes/nanofibers.

Part I of this article (Yeo-Heung et al., 2004) showed the actuation properties of CNF in a wet electrolyte. The objective of Part II is to develop dry-based actuators using a solid polymer electrolyte (SPE). The SPE enables operation in a dry environment instead of special media such as liquid electrolytes. The dry actuator is suitable for some replacement applications in which current smart materials are used. In this paper, we report the results of systematic studies of the CNF-SPE actuator with respect to the influences of materials and processing variables on the actuation properties and the actuation mechanism. Even though CNFs have a smaller actuation strain than SWCNT, the material is readily available in commercial quantities and is therefore a practical smart material. This paper describes the initial development of electrochemically driven CNF dry actuators.

ACTUATOR FABRICATION

Recently, various types of ionically conducting polymers, generally classified as polymer electrolytes or polymer ionics, have been developed. In order to develop an active material using carbon nanotube electrochemical actuation, we developed our own SPE. This gel-type film is prepared from PMMA-$LiBF_4$-PC (propylene carbonate), and an ion-exchange solid material. Polymethyl methacrylate (PMMA) used as a host polymer with an ion-exchange material was first reported five years ago (Rajendran and Uma, 2000a) where the kinetics and stability of lithium electrodes in PMMA-based gel electrolytes was studied.

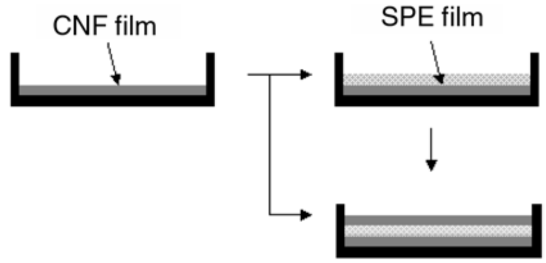

Figure 1. *The dry actuator using a gel-type electrolyte.*

The CNF is first dispersed in 20 mL of DMF by mechanical mixing for 5 h and ultrasonication using a tip sonicator at a level of 20 W and frequency of approximately 30 kHz for 2 h. The well-dispersed CNF solution is poured in the mold and evaporated to cast a CNF film (shown at left in Figure 1). On the surface of the CNF film, the SPE solution is poured in the mold and dried in a vacuum (shown at top right in Figure 1). After preparing this CNF-SPE film, one more layer of CNF is placed on the surface of CNF-SPE and hot pressed to form a CNF-SPE-CNF actuator (shown on bottom right in Figure 1). The CNF-SPE-CNF films can be used in single or multiple layers to form actuators that bend in two directions.

The SPE was developed using the procedure described next. Different types of SPE films made of PMMA-$LiBF_4$ in different mole ratios were prepared by the solution casting technique (Yeo-Heung et al., 2004). The PMMA, $LiBF_4$, propylene carbonate (PC), and acetonitrile (ACN) were dissolved under 70°C without any purification. The solution was stirred continuously until the mixture became a homogeneous viscous liquid. This solution was poured on the mold to cast the film. Then, the films were dried under a vacuum oven for 2 h. In an attempt to improve the ion conductivity, PC was used as a new plasticizer. The conductivity increases with the concentration of PC, and with high concentrations gel-electrolytes can be formed. CNF actuators with various SPEs were tested in a dry environment. The actuation properties are small compared to the same materials in a liquid electrolyte. There are several steps that can be taken to increase the dry actuator properties as well as the actuation performance in a liquid electrolyte.

The ionic conductivity of a polymer electrolyte depends on the concentration of the conducting species and on their mobility. Up to 20% weight of PMMA in an electrolyte at room temperature can produce a homogeneous and transparent gel. In Rajendran and Uma (2000b) the ionic conductivity for PMMA polymer electrolytes was reported in the range of $0.6 - 5.5 \times 10^{-3}\,S\,cm^{-1}$ at room temperature.

Table 1. Conductivity values of the PMMA–ion-exchange material with gel polymer complex.

Polymer complex (PMMA-salt-PC wt)	Conductivity, σ ($\times 10^{-3}$ S cm^{-1}, RT)
Sample 1 (5-5-95)	4.6
Sample 2 (15-5-80)	6.1
Sample 3 (25-5-60)	4.3
Sample 4 (35-5-60)	1.1

The ionic conductivity values of electrolytes are measured using the four-probe method. Conductivity values of the PMMA–ion-exchange material developed in this article are given in Table 1.

In Table 1, conductivity values of PMMA–ion-exchange plasticizer material decrease with the increasing amount of PMMA and lie between 6.1 and 1.1 S cm^{-1} at room temperature. It is observed from Table 1 that conductivity increases with the increase in the concentration of plasticizer at some rate. This may be due to lowering of the viscosity with the increase of plasticizer concentration. The conductivity also decreases if the sample is dried more. Therefore, with the solid polymer electrolyte, it is important to control the viscosity to get stable conductivity. Thermal stability of the SPE is not considered in this paper. The film with a 100–500 μm thickness was peeled off the mold and cut into 0.7 cm (width) × 2 cm (length) films.

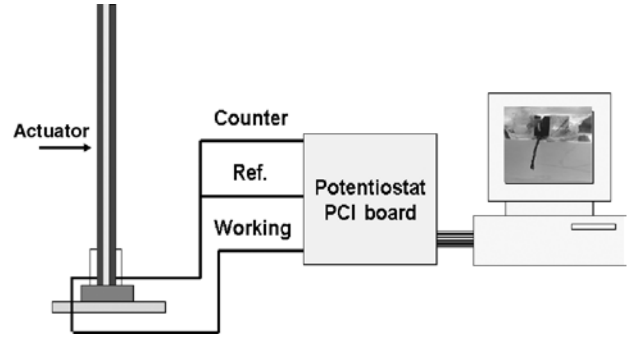

Figure 2. *Electrochemical analysis setup for the dry actuator using a Gamry system housed in a PC.*

ELECTROCHEMICAL IMPEDANCE

Electrochemical impedance spectroscopy (EIS) provides information about the complex electrochemical behavior of the actuator. The kinetics of ion-exchange and CNF electrode information can predict actuation performance and provide the parameters and values for the future modeling.

EIS was performed on two-electrode cells, one as the working electrode, and with the reference electrode and counter electrodes connected. EIS measurements were performed using a Gamry Potentiostat (Model PCI4/750) coupled with EIS (Gamry, EIS300) software based on Figure 2.

The dry actuator was recalibrated after each step, and impedance spectra were measured using 10 mV rms amplitude at frequencies between 0.01 Hz and 10 kHz. Figure 3 shows the EIS data (Nyquist plot) with imaginary versus real components of the complex impedance; we tested four different potentials 0.2, 0.5, 1, and 1.5 V.

Figure 3(a) represents the spectra for all frequencies between 0.01 Hz and 10 kHz. Small depressed semicircles were observed at higher frequencies in Figure 3(b), then second larger capacitive loops at lower frequencies occurred in Figure 3(a). The radius of these second

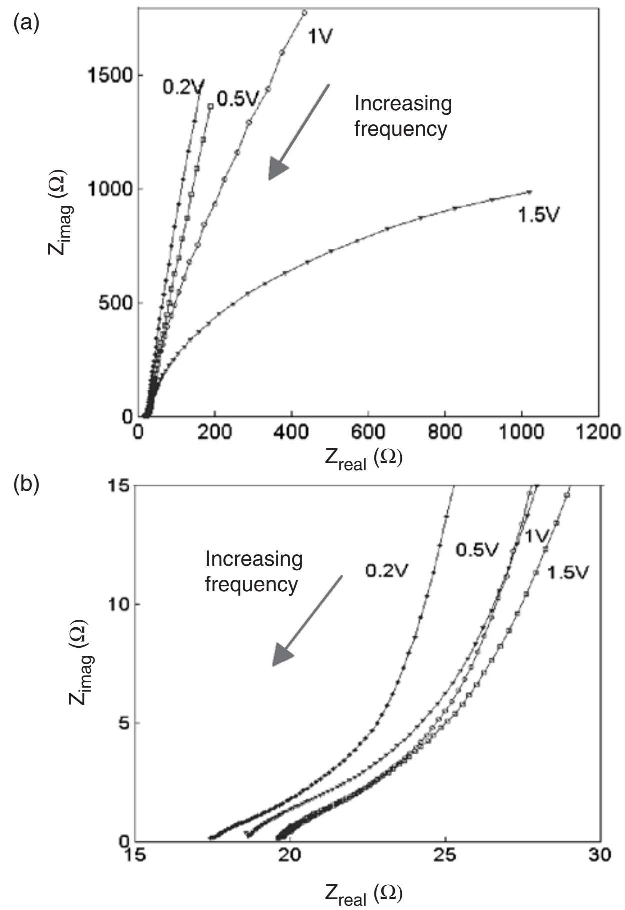

Figure 3. *Electrochemical impedance spectra for the dry actuator at cell potentials of 0.2, 0.5, 1, and 1.5 V: (a) frequencies between 0.01 Hz and 10 kHz and (b) enlarged view of high frequencies between 100 Hz and 10 kHz.*

larger capacitive loops at lower frequencies can explain the mass transport of the charge balancing ions. Lines drawn through the rising part of the second loops at 45° angles would represent the Warburg impedance which appears at intermediate frequencies. This Warburg impedance indicates the finite diffusion of ions in the dry actuator. It was also found that with a high open circuit potential at very low frequencies, the curving of

Table 2. Estimated values of Randles' circuit corresponding to four different potentials.

Open circuit potential (V)	R_p polarization resistance (kΩ)	R_s solution resistance (Ω)	C_d capacitance (F)
0.2	8.3	19	0.011
0.5	6.2	22	0.010
1.0	5.4	22	0.008
1.5	1.5	21	0.007

the plots returns to the real axis which indicates that the impedance is limited by convective steady state diffusion.

Since our interest for actuator applications is mostly at the lower frequencies, the impedance spectra were fit to Randles' circuit neglecting the small semicircles occurring at high frequencies. Randles' circuit is an equivalent circuit representing each component at the interface and in the solution during an electrochemical reaction for comparison with the physical components; C_d, the double layer capacitor; R_p, the polarization resistance; and R_s, the solution resistance. Randles' circuit can be expressed as (Park and Yoo, 2003):

$$Z(\omega) = R_s + \frac{R_p}{1+\omega^2 R_p^2 C_d^2} - \frac{j\omega R_p^2 C_d}{1+\omega^2 R_p^2 C_d^2} = Z_{real} + jZ_{imag} \quad (1)$$

The model for a dry actuator is different than the model for a wet actuator because of the different characteristics of the electrolyte. The values of the curve fit parameter are shown in Table 2. As shown in Figure 3, the response shows significant capacitive effect and Z_{imag} decreases at high frequency which may represent ion exchange at the working electrode. This behavior is described in Rajendran and Uma (2000b).

At higher frequencies, as shown in Figure 3(b), as the open circuit potential increases, the diameter of the semicircle increases which represents the increase of capacitance. In the case of the dry actuator, the capacitance has to be large enough to charge the ions and actuate the CNF. However, in order to get larger displacement, we have to apply higher voltage, and necessarily, it lowers the capacitance of the dry actuator. The higher voltage might degrade the life cycle of the dry actuator. At lower voltages, no fatigue of the actuator was apparent.

EXPERIMENTAL SETUP

Figure 4 shows the experimental setup to characterize the dry actuator. The displacement of the dry-based actuator is measured using a laser displacement sensor (Keyence, LC-2400 Series) as shown in the figure.

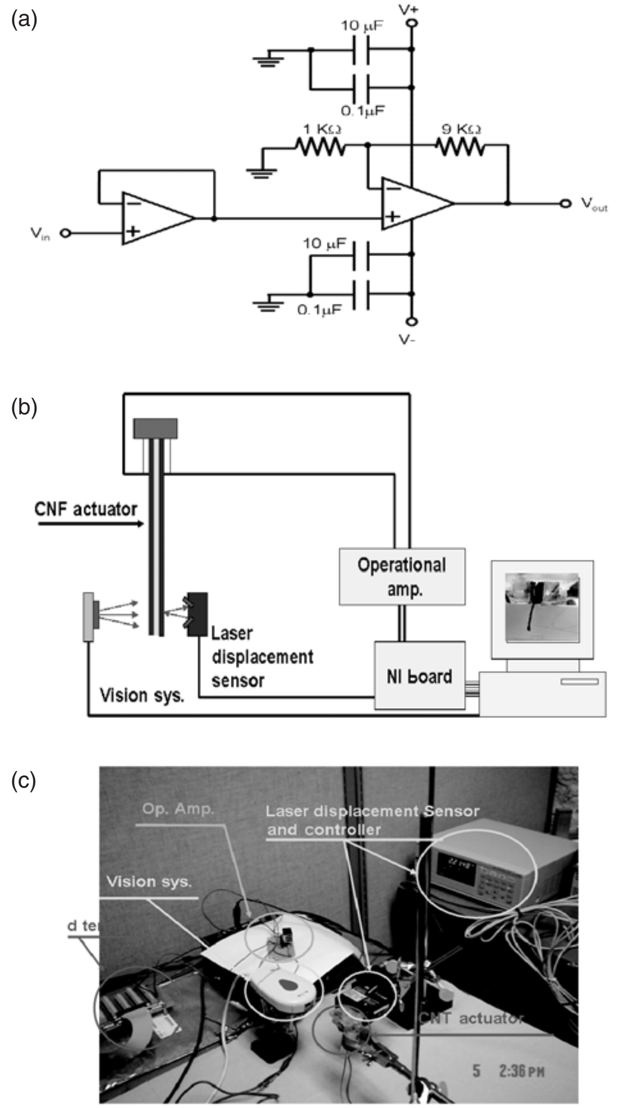

__Figure 4.__ Electrochemical actuation characterization system: (a) amplifier designed to drive the CNF actuator; (b) LABVIEW-based control system; and (c) a photo of the experimental setup.

Square wave potentials are applied between two electrodes using a National Instruments PCI board and a specially designed operational amplifier. Various square wave amplitudes are applied with frequencies ranging from 0.2 to 1 Hz. Figure 4(a) shows the operational amplifier circuit. In order to supply enough power from the NI board, a voltage follower using a noninverting amplifier was designed using an operational amplifier with a gain of 10 : 1.

Figure 4(c) shows the experimental hardware and the LABVIEW VI that was developed. This system simultaneously provides actuation, a laser measures the displacement, and a video camera captures the response of the actuator. The following types of measurements can be performed to characterize electrochemical systems: electrochemical impedance spectroscopy, cyclic voltammetry, and amperometric testing. Indirectly, the strain of the material can be determined based on the displacement. The strain response along with the electrical excitation can be used to determine coupled electromechanical constitutive equations for the material. When larger and more optimized material samples are fabricated, the constitutive equations will be developed.

Strain of a cantilevered beam actuator is calculated based on measured displacement as shown in Yeo-Heung et al., (2005). The strain ε is given by:

$$\varepsilon = \frac{3y(L-x)}{L^3}\delta \tag{2}$$

where y is the distance from the neutral axis, δ is the displacement of the beam, L is the length of the beam, and x is the distance where the strain is measured. Using the parameters of the actuator ($L = 15$ mm, $y = 1.5$ mm, $\delta = 0.12$ mm, $x = 0$) in Equation (2), the peak dynamic strain of the actuator is approximately 0.2%. The strain of the CNF actuator is difficult to determine for several reasons. The strain is non-uniform because the voltage decreases along the length of the actuator, the thickness of the actuator is difficult to measure due to compressibility of the material, and thermal expansion may also affect the strain.

RESULTS

Actuators can be built in a multilayer configuration. In unimorph bilayers, one electrochemical inert layer such as a 3 M tape (Scotch, #600) layer with buckypaper is needed to form a bending cantilever beam-type actuator. On the other hand, bimorph actuators use two buckypaper electrode layers with an SPE layer between the buckypaper layers. These actuator designs are used because electrochemical actuators expand due to applied voltage (bond expansion due to double layer charging), they do not contract when the opposite polarity voltage is applied, as in a piezoelectric material.

A CNF-based bimorph actuator (dry actuator), is fabricated using the procedure shown in Figure 1 (CNF-SPE-CNF), and the CNF actuation property is tested. In the case of the all-solid actuator, the SPE interface with the CNF can provide load transfer. Figure 5 shows the deflection of the cantilevered CNF dry actuator when a voltage is applied between the two CNF electrodes (CNF actuators).

Figures 6 and 7 show the relationship between the strain of the cantilever beam tip and the voltage applied to the CNF actuator.

The applied potential has been found to influence the strain rate in electrochemically driven CNF dry actuators. These results have verified that increasing the magnitude of the applied potential increases the strain rate. Probably the higher potential increases the charge accumulation at the CNF–SPE interface and causes the faster response. However, too high of voltage would degrade the CNF dry actuator and decrease the lifetime. Therefore, there is a limitation to increasing voltage to achieve a high strain rate.

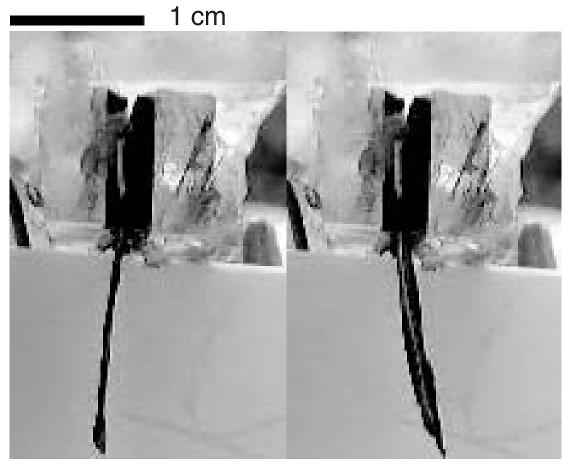

Figure 5. Bending motion of the CNF-SPE-CNF dry actuator before and after voltage is applied.

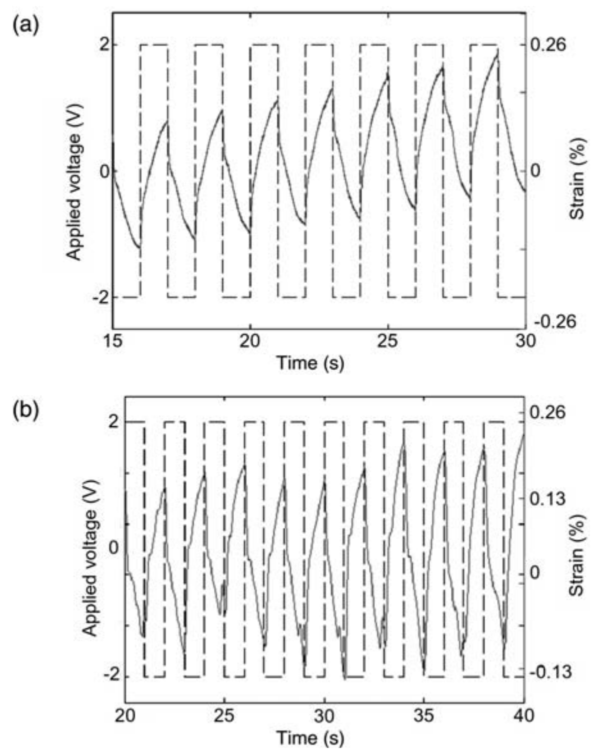

Figure 6. Deflection due to a square wave input (±2 V) at (a) 0.5 Hz and (b) 0.2 Hz. The dashed line (left axis) is the applied voltage, the solid line (right axis) is % strain.

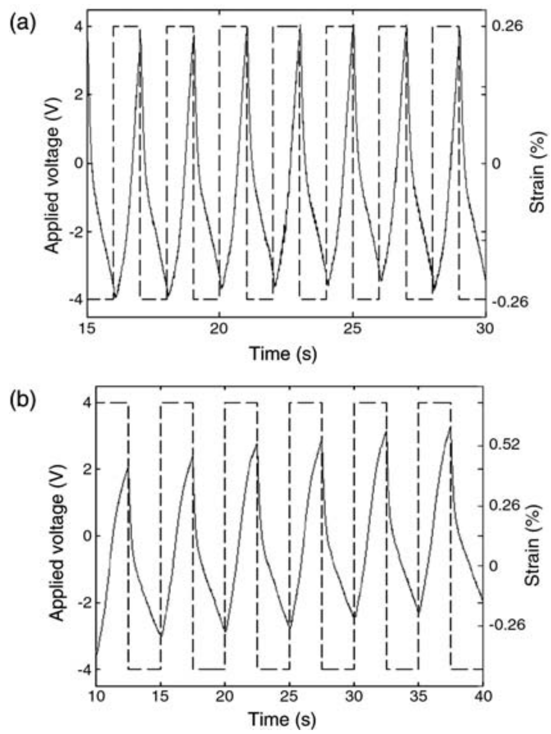

Figure 7. Deflection due to a square wave input (±4 V) at (a) 0.5 Hz and (b) 0.2 Hz. The dashed line (left axis) is the applied voltage, the solid line (right axis) is % strain.

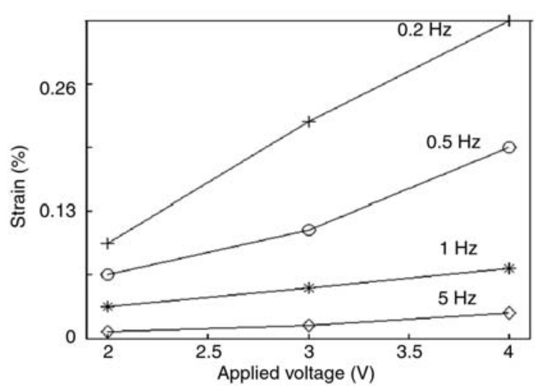

Figure 8. Deflection as a function of applied voltage at various frequencies for the dry actuator.

With the increase of frequency, deflection of the CNF actuator decreases as shown in Figure 8. Compared to the wet actuator, the CNF dry actuator has a lower bandwidth. Because the actuator is not hydrated, the actuation is slow and the amplitude is small compared to the wet actuator. Individually coating the CNF and uniformly dispersing, pressure casting, and aligning the CNF are techniques that will improve the actuation. Allowing the material to absorb a small amount of moisture would also improve the actuation.

A summary of the main properties of carbon nanotube and carbon nanofiber hybrid actuators is given in Table 3. This is the first time many of these material combinations have been tested, and much more detailed characterization is needed. There is room for great improvement in the results presented here.

FUTURE DIRECTIONS

There is a trade-off between developing large strains and large forces in electrochemical actuators. Future work will be directed toward optimizing these two properties. Plasma functionalization of the CNF and incorporation of the coated CNF into stronger polymers, along with the use of alternative solid polymer electrolytes and alignment of the CNF, offer the promise of greatly improving the performance of the actuator. A great advantage of the CNF material is that we are not constrained by cost. Large actuators and beams, plates, shells, and injection molded parts can be made and many experiments can be done at low cost. More details of the material tested in this article are given in the references in the Part I article (Yeo-Heung et al., 2004).

Although very futuristic, it is envisioned that smart structural materials will allow entire structures to change their surface shape to improve performance or modify their form and fit, and biomimetic intelligent structures will be able to actuate to relieve or redistribute loads to prevent damage. Also, the local actuation properties of the structural material will be useful to control various functional properties of materials such as cooling, stealth, optical properties, color, and any properties or functions that can be influenced by strain actuation and sensing of the base structural material.

CONCLUSIONS

This paper has verified that carbon nanofibers (CNF) have electrochemical actuation properties using a solid polymer electrolyte. A CNF-based dry actuator was fabricated using a solid polymer electrolyte and tested in this article. Tip displacement of a cantilever beam was measured using a laser displacement sensor and various input potentials and frequencies were used to drive the actuator. This testing showed that the actuator can be reversibly controlled and increasing the applied potential increases the strain rate in the CNF dry actuator. Compared to previous SWCNT buckypaper actuators, the dry-based CNF actuator will have wider applications and does not require a liquid for operation,

Table 3. Summary of properties of carbon nanotube and carbon nanofiber hybrid actuators.

Type of actuator	Wet environment (electrolyte solution)	Dry environment (with an SPE)
SWCNT buckypaper	Fastest, large strain, expensive, good cohesion property to make buckypaper, low strength	Dry has slower response and smaller actuation than wet
MWCNT buckypaper	Good actuation strain, lower cost than SWCNT	Same as above
CNF buckypaper	Low cost, difficult to make buckypaper, low mechanical strength, needs higher voltage and current to actuate	Dry has slower response, requires larger voltage, good mechanical loading with SPE
CNF plasma coated to form buckypaper	Improved mechanical loading, similar actuation properties as CNF buckypaper	Same as above
SWCNT with PMMA polymer	Faster, large strain, best among nanotube composites, expensive	–
MWCNT with PMMA	–	–
CNF with PMMA polymer	Need higher voltage and current, better mechanical properties, dispersion needs improving, smart structures applications	–

but a higher actuation voltage is needed. Because of the low cost and potential for incorporating the CNF into stronger polymers, large structures that actuate may become feasible.

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REFERENCES

Baughman, R.H. 1996. "Conducting Polymer Artificial Muscles," *Synthetic Metals*, 78:339–353.

Han, G. and Shi, G. 2004. "Conducting Polymer Electrochemical Actuator made of High-strength Three-layered Composite Films of Polythiophene and Polypyrrole," *Sensors and Actuators B*, 99(2):525–531.

Mazzoldi, D.D. and Baughman, R.H. 2000. "Electro-mechanical Behavior of Carbon Nanotube Sheets in Electrochemical Actuators: Electroactive Polymer Actuators and Devices," In: *7th SPIE International Symposium*, Smart Structures and Materials, pp. 25–32.

Minett, A., Fraysse, J., Gang, G., Kim, G.-T. and Roth, S. 2002. "Nanotube Actuators for Nanomechanics," *Current Applied Physics*, 2(1):61–64.

Park, S.-M. and Yoo, J.-S. 2003. "Electrochemical Impedance Spectroscopy for Better Electrochemical Measurement," *American Chemical Society*, 75:455–461.

Rajendran, S. and Uma, T. 2000a. "Characterization of Plasticized PMMA-LiBF4 based Solid Polymer Electrolytes," *Bull. Mater. Sci.*, 23(1):27–29.

Rajendran, S. and Uma, T. 2000b. "Conductivity Studies on PVC-PMMA-LiAsF-DBP Polymer Blend Electrolyte," *European Polymer Journal*, 36:2617–2620.

Roth, S. and Baughman, R.H. 2002. "Actuators of Individual Carbon Nanotubes," *Current Applied Physics*, 2(4):311–314.

Spinks, G.M., Wallace, G.G., Fifield, L.S., Dalton, L.R., Mazzoldi, A., De Rossi, D., Ilyas, I., Kharyrullin, I.I. and Baughman, R.H. 2002. "Pneumatic Carbon Nanotube Actuators," *Advanced Materials*, 14(23):1728–1732.

Spinks, G.M., Wallace, G.G., Lewis, T.W., Fifield, L.S., Dai, L. and Baughman, R.H. 2001. "Electrochemically Driven Actuators from Conducting Polymers, Hydrogels, and Carbon Nanotubes," In: *8th SPIE International Symposium*, Smart Structures and Materials, pp. 223–231.

Spinks, G.M., Zhou, D., Liu, L. and Wallace, G.G. 2003. "The Amounts Per Cycle of Polypyrrole Electromechanical Actuators," *Smart Materials and Structures*, 12(3):468–472.

Tahhan, M., Truong, V.-T., Spinks, G.M. and Wallace, G.G. 2003. "Carbon Nanotube and Polyaniline Composite Actuators," *Smart Materials and Structures*, 12(4):626–632.

Wang, Z.L., Gao, R.P., Poncharal, P., de Heer, W.R., Dai, Z.R. and Pan, Z.W. 2001. "Mechanical and Electrostatic Properties of Carbon Nanotubes and Nanowires," *Materials Science and Engineering C*, 16:3–10.

Yeo-Heung, Y., Miskin, A., Kang, P., Jain, S., Narasimhadevara, S., Hurd, D., Shinde, V., Schulz, M.J., Shanov, V., He, P., Boerio, F.J., Shi, D. and Srivinas, S. 2005. "Carbon Nanofiber Hybrid Actuators, Part I: Liquid Electrolyte-Based," *J. Intelligent Material Systems and Structures*, same issue as this paper.

Yeo-Heung, Y., Miskin, A., Kang, P., Shanov, V.N. and Schulz, M.J. 7-2004. Invention Disclosure, In: "*Carbon Nanofiber Hybrid Actuators*," University of Cincinnati.