

Electrochemical actuation of carbon nanotube yarns

Tissaphern Mirfakhrai¹, Jiyoung Oh², Mikhail Kozlov²,
Eddie Chi Wah Fok¹, Mei Zhang², Shaoli Fang²,
Ray H Baughman² and John D W Madden¹

Abstract

We report on actuation in high tensile strength yarns of twist-spun multiwall carbon nanotubes. Actuation in response to voltage ramps and potentiostatic pulses is studied to quantify the dependence of the actuation strain on the applied voltage. Strains of up to 0.5 % are obtained in response to applied potentials of 2.5 V. The dependence of strain on applied voltage and charge is found to be quadratic, in agreement with previous results on the actuation of single walled carbon nanotubes, with the magnitude of strain also being very similar. The specific capacitance reaches 26 F/g. The modulus of the yarns was found to be independent of applied load and voltage within experimental uncertainty.

¹ Department of Electrical and Computer Engineering and the Advanced Materials & Process Engineering Laboratory (AMPEL), University of British Columbia, 2332 Main Mall, Vancouver BC, Canada V6T 1Z4. E-mail: tissa@ece.ubc.ca

² NanoTech Institute, the University of Texas at Dallas, Richardson, Texas, USA, 75080.

1. Introduction

Individual carbon nanotubes (CNTs) offer exceptional properties. The tensile modulus of single walled carbon nanotubes (640 GPa) approaches that of diamond, while their tensile strength of approximately 20-40 GPa is about ten times higher than for continuous yarns or fibers of any type [1]. Many research groups have been working to make bulk assemblies or yarns that can approach the modulus and tensile strength of individual CNTs. Interest in nanotube assemblies expanded in a new direction when it was found that sheets of nanotubes (Bucky paper) actuate when used as an electrode in an electrochemical cell [2]. Since then actuation strains of up to 0.4 % [3] have been reported at effective strain rates of as high as 19 %/s [4].

Electrochemical double layer charge injection in the nanotubes is believed to induce actuation via quantum mechanical and electrostatic effects that dominate for small and large degrees of charge injection, respectively [2, 5]. This double layer charge injection, shown in Figure 1, is a non-faradaic process in which changing the charge on the carbon atoms results in changes of C-C bond lengths [6, 7]. The excess charge on the nanotubes is compensated at the nanotube-electrolyte interface by ions (cations or anions). The nanotubes act as double layer capacitors that are charged and discharged during actuation cycles.

Because the Young's modulus of individual CNTs is extremely high, a relatively small strain of actuation can result in high stress generation, producing unprecedented work densities per cycle [8]. The actuation process can potentially be fast if charge can be injected quickly, leading to high power to mass ratios [4]. CNTs are stable at temperature as high as 1000°C if sealed from oxygen, making them appropriate for high-temperature actuation. However, before any of this can be realized it is necessary to make macroscopic structures out of CNTs that preserve the superb mechanical and electronic properties of the component CNTs. Actuation of sheets of multiwall carbon nanotubes (MWNTs) has been reported [9], showing reasonable strain but having only moderate tensile strength. Another approach is to spin fibers of aligned nanotubes. The present paper reports the first actuation measurements made on MWNT yarns that have been recently developed by the NanoTech Institute of the University of Texas at Dallas [10]. A scanning electron micrograph of such a yarn is shown in Figure 2.

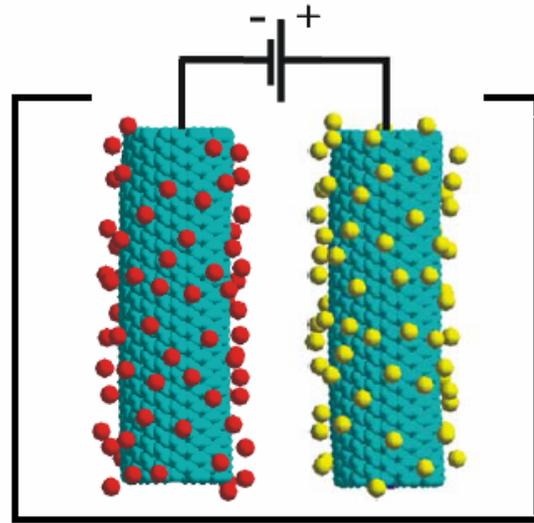


Figure 1: Ions of opposite charges are attracted to the CNT electrodes in an electrolyte when a voltage is applied, resulting in a change in the C-C bond length and actuation.

2. Methods

MWNT yarns were prepared by a dry spinning method [10], i.e., by drawing and twisting tubes from a forest. The MWNT forest was synthesized by catalytic CVD using acetylene gas as the carbon source. MWNTs, which are about 10 nm in diameter, are simultaneously drawn from the MWNT forest and twisted. The nanotube length in the forest is about 300 μm , resulting in yarn diameters between 1 and 60 μm , depending upon the forest width used for spinning. The twist is characterized by the helix angle (α), which depends directly upon the degree of twist and inversely on the yarn diameter. The degree of twist is typically 15,000 turns/m.

In order to apply forces and record actuation forces and displacements generated by the CNT yarns, an Aurora Scientific ASI 300 muscle analyzer and its LabView-based software (www.aurorascientific.com) have been employed. Figure 3 is a photo of the apparatus used to apply force and of the yarn and clamping mechanism. The fiber is mounted between a lower fixed clamp and an upper movable motor arm. A computer-controlled potentiostat, similar to the one described in [11], is used to apply potentials. A data acquisition card (National Instruments 6036E) gathers the force and displacement data from the muscle analyzer and also logs the applied voltage and current. Figure 4 is a block diagram of the measurement setup with the yarn as one of the electrodes in the actuation cell. This configuration is referred to as Setup 1.

For some of the strain measurements a Perkin-Elmer DMA 7e with a custom sample holder and electrochemical cell was employed. The voltage was applied and current recorded via a Gamry Instruments potentiostat. This setup is referred to as Setup 2. All observed dimensional changes were normalized by sample length and are reported in percent.

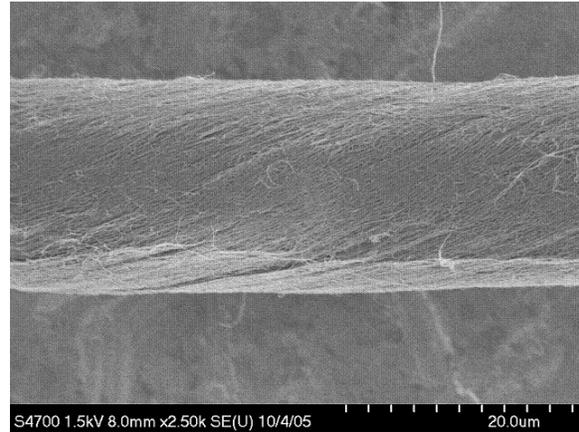


Figure 2: SEM micrograph of a twist-spun MWNT yarn

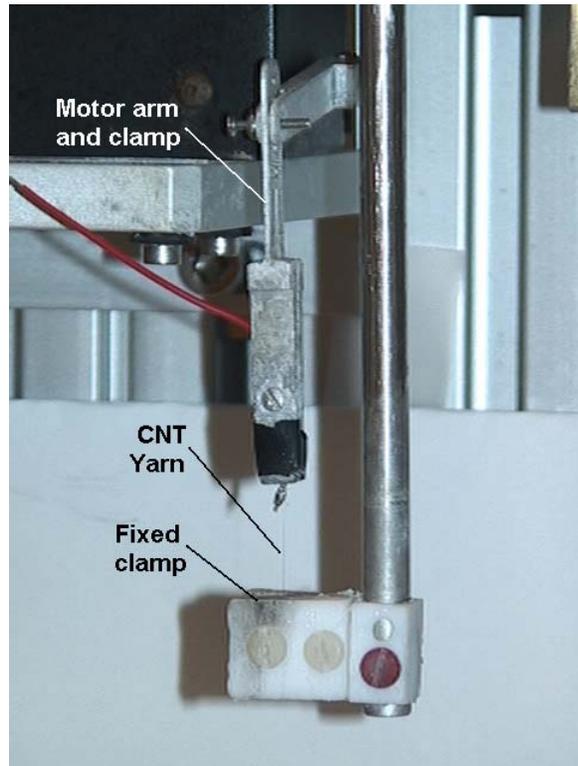


Figure 3: The CNT yarn mounted in the ASI muscle analyzer clamp.

All observed dimensional changes were normalized by sample length and are reported in percent.

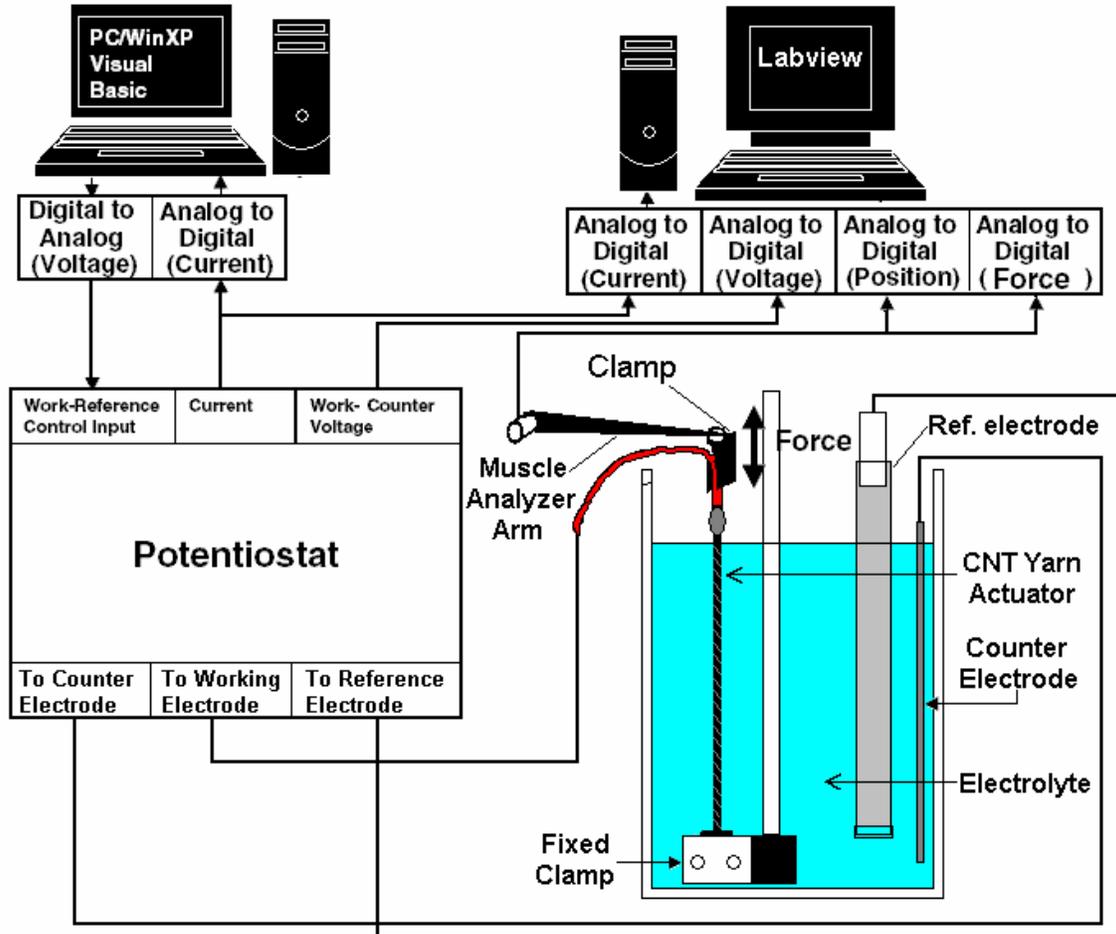


Figure 4: The experimental setup for measuring actuation of the yarns

3. Actuation

A 12 mm length of single-ply yarn with a diameter of $18\ \mu\text{m}$ was loaded to 11 MPa using Setup 1 and was left in the electrolyte to relax for 30 minutes. The electrolyte used is 0.2 M tetrabutylammonium hexafluorophosphate (TBAP) in acetonitrile (AN). Afterwards a triangular voltage input was applied at a scan rate of 1000 mV/s, and the resulting currents and strains were measured. The reference electrode was aqueous Ag/AgCl and the counter electrode was a sheet of polypyrrole. The charge transferred (Figure 5d) was calculated by numerically integrating the current (Figure 5c).

The strain during the CV is plotted vs. nominal charge per C atom (including atoms on the interior of the tube) in Figure 6 for charging and discharging half-cycles with a quadratic fit for the charging half-cycle superimposed. The number of atoms is calculated using the measured density of the yarns ($0.8\ \text{g/cm}^3$) and the molar weight of the carbon atom ($12\ \text{g/mol}$). The results match those obtained using sheets of carbon single walled nanotubes (SWNTs) [5] over the same range of nominal charge per atom. The similarity in actuation is consistent with the fact that the SWNTs are bundled, since charge injection occurs non-uniformly in both cases – on the outer SWNTs in a SWNT bundle and the outer wall of MWNTs. Although the MWNTs are also bundled, the surfaces of the MWNTs are largely exterior to the bundle, where double layer charge injection can occur.

The bold dots in Figure 6 represent the average strains reported by Hughes and Spinks [9] in MWNT sheets, and the error bars represent the range of strains. The similarity between the responses for MWNT sheets and the yarns suggests that the alignment of nanotubes and the degree of twist is not substantially influencing the magnitude of strain. This similarity is consistent with the proposed mechanism of CNT actuation in which strain is the result of charge induced changes in C-C bond lengths within the nanotube, rather than inter-tube interactions. Although strain in yarns and sheets is similar in magnitude, the much larger tensile strengths of the yarns makes them far more suitable for application.

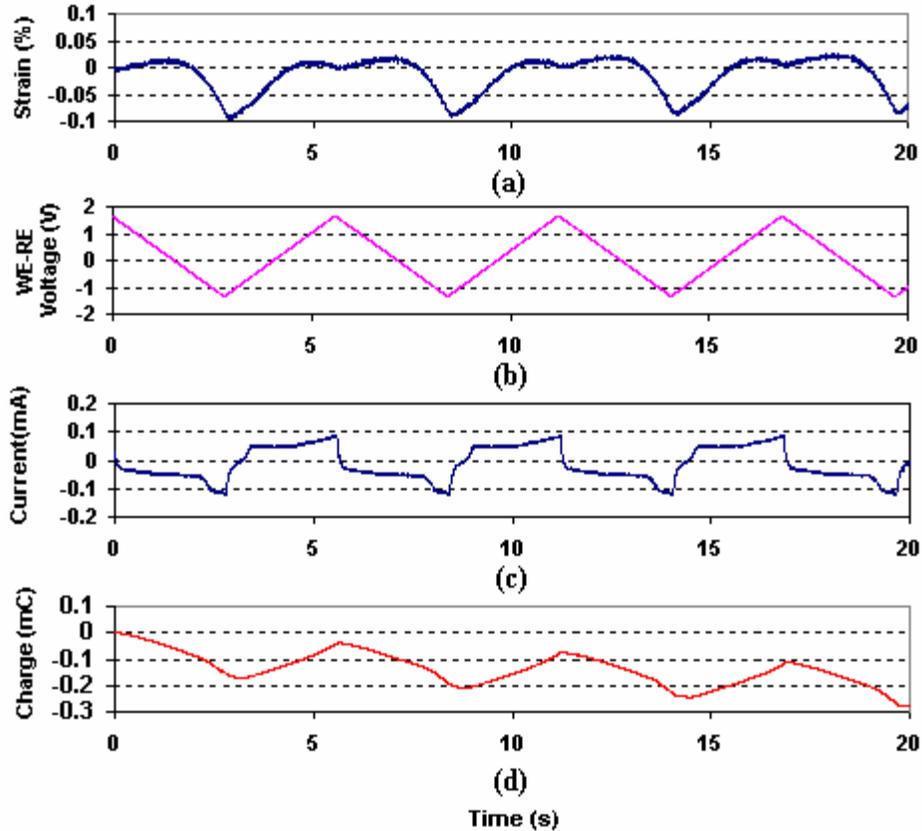


Figure 5: (a) Strain, (b) working electrode voltage, (c) cell current and (d) transferred charge during cyclic voltammetry of the MWNT yarn in 0.2 M TBAP in acetonitrile for an applied tensile load of 11 MPa.

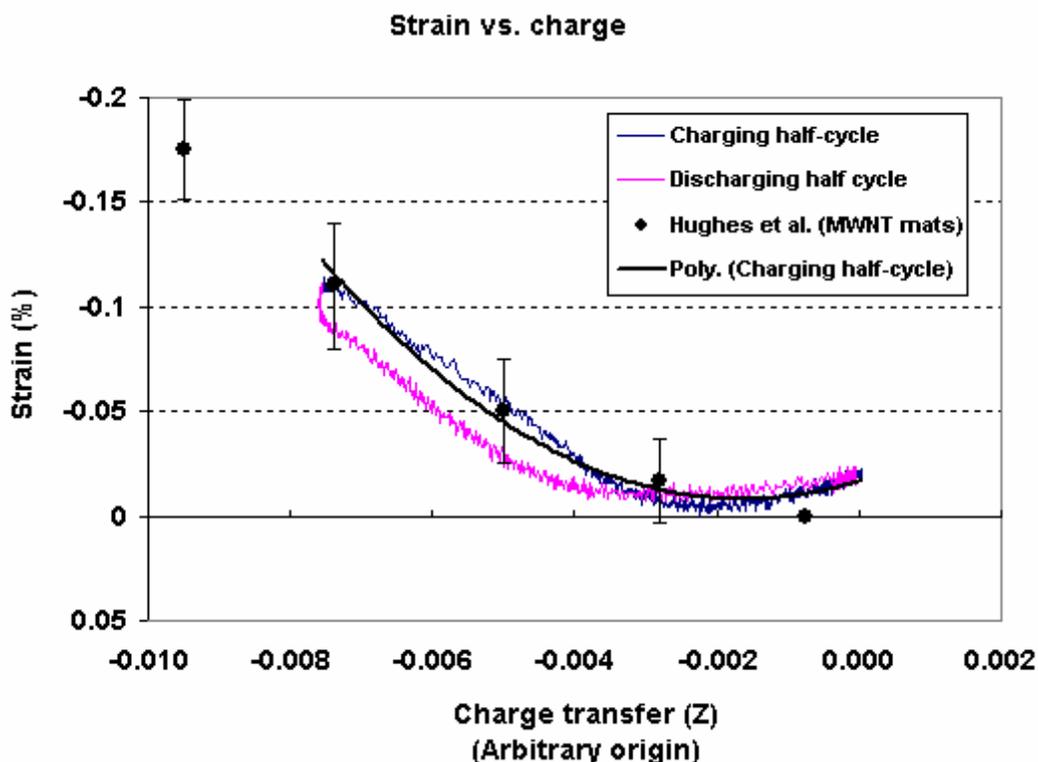


Figure 6: Strain vs. nominal charge per C atom during CV. The origin of the horizontal axis is arbitrary since the initial charge of the MWNTs is unknown. The dots represent strain to charge observed in MWNT sheets [9].

The experiment was repeated at a scan rate of 100 mV/s. The resulting currents for 1000 mV/s and 100 mV/s are plotted vs. the applied voltage (Figure 7a). The gravimetric capacitance of the yarn in TBAP in acetonitrile was estimated using the CVs to be 26 ± 5 F/g over a potential range of -0.7 V to $+0.7$ V, as shown by the square response of an ideal capacitor in Figure 7a. This high capacitance is very similar in magnitude to the capacitance observed in single wall carbon nanotubes [9], and suggests that the external surfaces of the MWNTs are largely accessible to electrolyte. The double layer capacitance of the nanotubes is estimated to be 0.17 F/m². This result is derived from the measured capacitance and an estimate for the surface area per mass of MWNTs having an outer diameter of 10 nm and 8 inner layers, where the MWNT geometry was measured by transmission electron microscopy. It has been assumed that charge injection is only to outer walls and that all outer walls are accessible for charge injection. The capacitance drops by about 20 % as the scan rate is increased from 100 to 1000 mV/s. This can be because of the existence of fast and slow charging processes in the yarn similar to those described in [12] or may be limited by the mass transport.

A similar experiment was performed using Setup 2 in 0.5 M tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile (AN) again vs. Ag/Ag⁺ and with a Pt mesh/CNT counter electrode. The potential window was -2.5 to $+2.5$ V. The response to a triangular input scanned at 10 mV/s is shown in Figure 7.b. The voltammetry results suggest a capacitive response due to double layer charging of the nanotubes over a voltage range of approximately -0.7 V to $+0.7$ V vs. Ag/Ag⁺. The capacitance at 10 mV/s scan rate in TBATFB in acetonitrile is estimated at 22 ± 2 F/g. Beyond this potential range a kinetics-limited reaction appears to be contributing to the current. It may be the result of electrolyte degradation.

The CV plots are considerably less resistive compared to those of MWNT sheets reported in [9]. Better axial alignment of the nanotubes in the yarns and fewer defects in the MWNTs used in the yarns are likely causes of the better conductivity along the yarn axis, resulting in a much less resistive response. This makes the yarns a much better candidate to be used as a supercapacitor compared to the MWNT sheets.

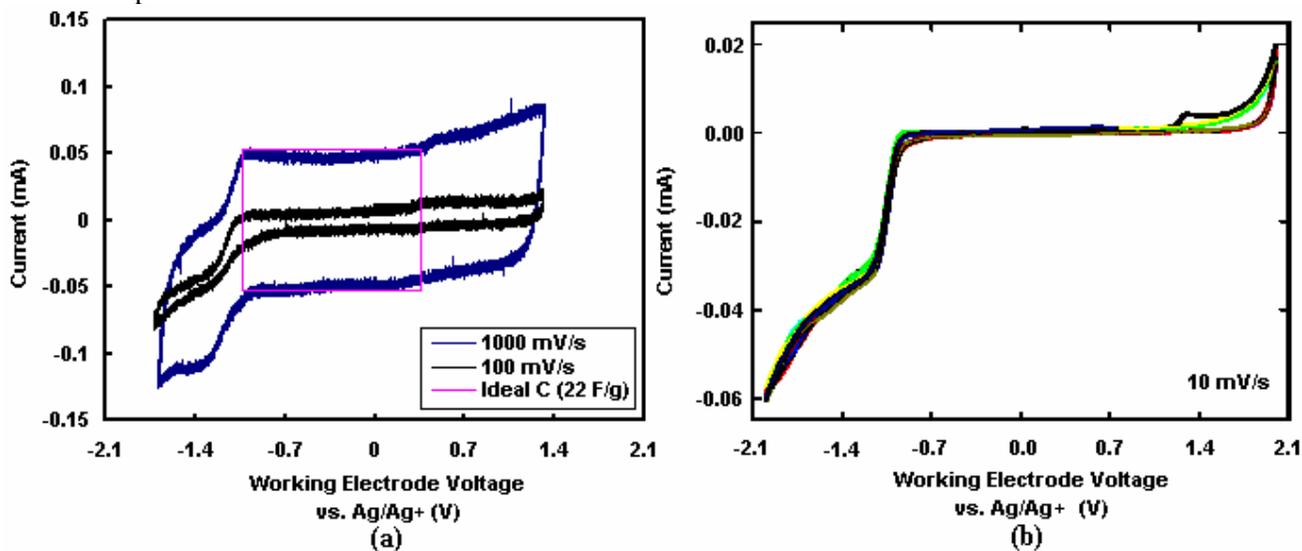


Figure 7: (a) Cyclic voltammogram for a 12mm-long single ply yarn at scanned at 1000 and 100 mV/s. The rectangle shows the ideal capacitor response for a gravimetric capacitance of ~ 26 F/g at 1000 mV/s. (b) CV of an 18 mm long yarn in 0.5 M tetrabutylammonium tetrafluoroborate (TBATFB) in acetonitrile (AN) at a scan rate of 10 mV/s

Figure 8 shows the actuation strain and the current in response to a series of voltage pulses with amplitudes between -2.5 V and +2.5 V. The electrolyte was 0.5 M TBATFB in AN. The maximum actuation strain achieved was measured to be 0.5 % using Setup 2. A similar experiment was performed using Setup 1. The voltages were applied using a Solartron SI 1287 electrochemical interface. The electrolyte was 0.2 M TBAP in AN, the reference electrode was aqueous Ag/AgCl and the counter electrode was a sheet of polypyrrole. The potential of the reference electrode stayed the same before and after the experiment. The pulses in each train had the same voltage amplitude. The experiment was repeated for voltage pulses relative to 0 V vs. Ag/AgCl of -2.5V, -2V, -1.5V, -1V, -0.5V, 0V, 0.5V, 1 V and 2 V. The maximum strain achieved is about 0.2 %.

Some creep is observed during actuation in both cases similar to what has been reported before [9, 13]. The creep seems to depend on the voltage amplitude and the actuation rate, but the nature of this dependence has not yet been studied. The creep rate is very close to the rate in [9] but the creep itself is smaller in this case over the same number of actuation cycles than the creep reported in [9]. This becomes more significant if we consider that actuation in this case takes place under up to 30 MPa of load as opposed to 200 kPa in [9], demonstrating one of the benefits of employing the yarns.

The amplitude of the resulting actuation strain is plotted vs. the applied voltage pulse amplitude in Figure 9. For comparison, the voltages are all plotted versus Ag/Ag+ by adjusting the voltages measured against Ag/AgCl by 0.335 V [14]. The plots from our two experiments look very similar. This implies that the size difference between the PF_6^- and BF_4^- ions has little effect on the actuation. The relationship is very close to a quadratic relationship, which is expected from

previous results in single wall carbon nanotubes and theory [2, 6, 7 and 13]. This supports the suggestions that the forces producing strain are primarily coulombic in nature when the amount of charge injection is large. The quadratic fit plotted in Figure 9 is calculated using all data points except the -3 V and -2.5 V. A different mechanism may be at work for these two points that are at one voltage extreme, where the actuation strain is much larger than what is predicted by the quadratic relationship. This mechanism may be related to the ‘pneumatic actuation’ due to formation of bubbles at high voltages as reported in [5].

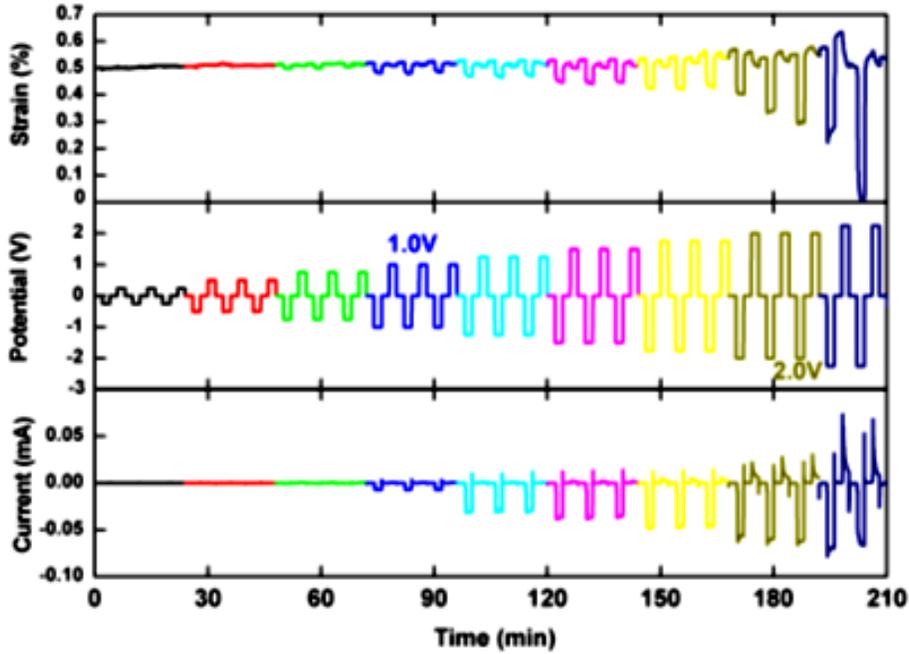


Figure 8: Applied voltage pulse trains vs. Ag/Ag⁺ and resulting actuation strains for actuation in 0.5 M TBATFB in AN

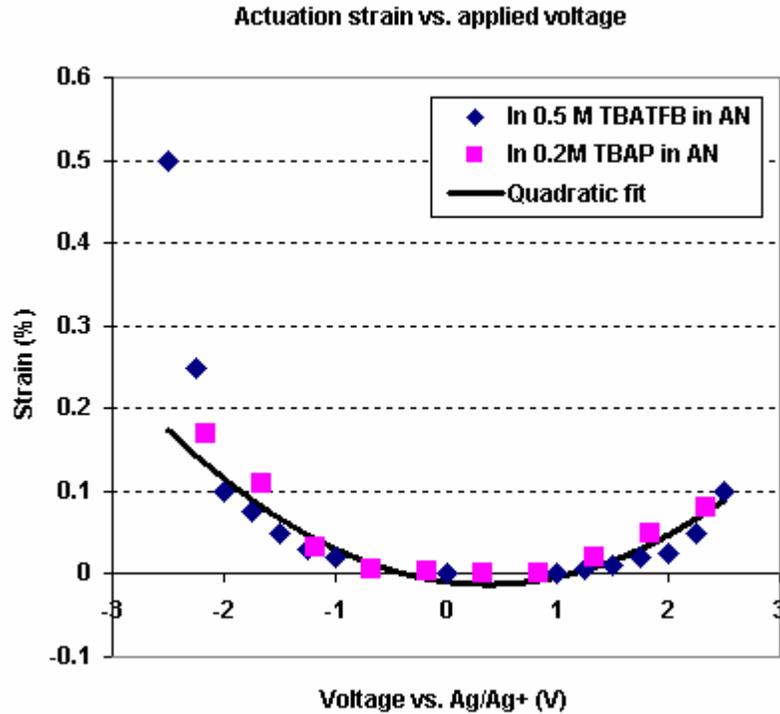


Figure 9: The strain amplitude plotted vs. the applied voltage amplitude.

4. The Young's modulus as a function of the oxidation state

The magnitude of isotonic actuation strain (i.e., for fixed load) can be influenced by potential-induced changes in modulus, as seen in polypyrrole [15]. The dependence of the Young's modulus on the charge state of the MWNTs was therefore studied.

The ASI 300 muscle analyzer was used to obtain stress/strain curves at a number of fixed potentials. The yarn was elongated by 0.1 % over 0.5 s and then brought back to its original length. The applied strain waveform and the resulting stresses are plotted in Figure 10. Lines were fit to the resulting stress vs. strain curves for loading and unloading half-cycles. The relative slopes of these lines provide the effective Young's moduli of the yarn during loading and unloading.

The measured Young's moduli under the loads of 35, 60 and 70 MPa are plotted in Figure 11. Within experimental error, no significant change in modulus is observed as the oxidation state is changed between -1.5 V to 1.5 V. A. The modulus in that range of voltages is 16 ± 5 GPa, but it seems to drop at the two extremes of voltage (-2 V and 2 V). This variation is within the range of experimental uncertainty, however. Nevertheless the uncertainty in modulus is large enough that it could induce a strain comparable to the actuation strains in Figure 9. The present results

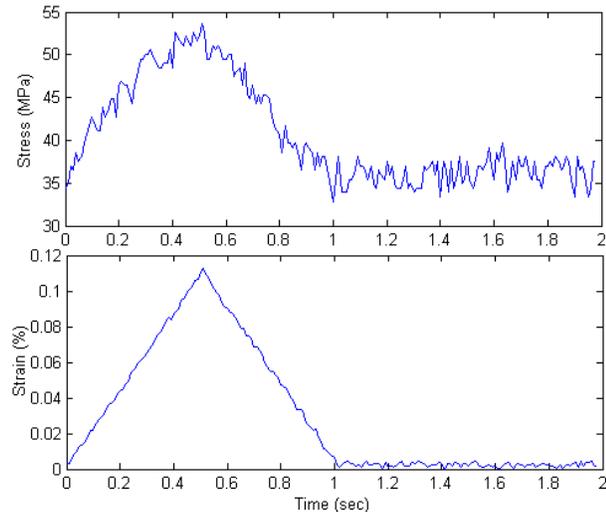


Figure 10: Applied strain waveform and the resulting stress to measure the Young's modulus of the yarns. The prestress was 35 MPa

provide a first bound on the variation. If modulus is changing at extreme voltages (e.g. due to bubble generation inside the yarn) it could explain the 0.5 % strain observed in Figure 9 and the deviation from the quadratic response.

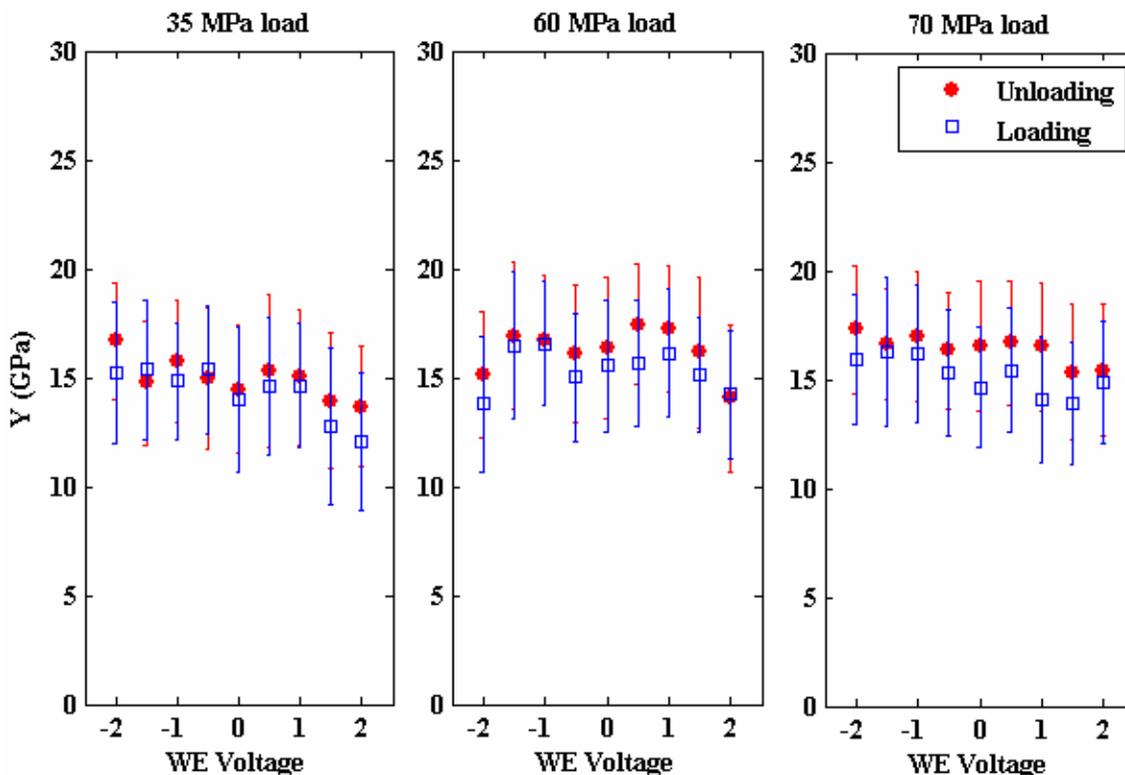


Figure 11: The Young's modulus of the CNT yarn as a function of the oxidation state under the loads of (a) 35, (b) 60 and (c) 70 MPa. The horizontal axes in all the plots indicate a working electrode voltage ranging from -2V to 2 V.

5. Conclusions

The actuation behavior of yarns spun from multiwall carbon nanotubes was studied. The yarns were found to actuate as a result of applied voltage. The actuation strain changes almost quadratically with applied voltage, as has been observed in single wall nanotubes, suggesting a coulombic interaction as the primary mechanism of actuation. A maximum actuation strain of 0.5 % is reported at an applied voltage of -2.5 V. The gravimetric capacitance of the yarn is found to reach 23 F/g. The dependence of the tensile modulus on oxidation state has been studied and it is concluded that the Young's modulus is not strongly dependent on the oxidation state within experimental uncertainty. Since modulus does not measurably change with charge injection, actuation strain should be insensitive to applied load.

Acknowledgements

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References

- [1] Baughman, R H, Zakhidov A A and de Heer W A 2002 Carbon nanotubes—the route towards applications *Science* **297** 787-92
- [2] Baughman, R H, Cui C, Zakhidov A A, Iqbal Z, Barisci J N, Spinks G M, Wallace G G, Mazzoldi A, De Rossi D, Rinzler A G, Jaschinski O, Roth S and Kertesz M 1999 Carbon nanotube actuators *Science* **284** 1340-44
- [3] Barisci J N, Spinks G M, Wallace G G, Madden J D, and Baughman R H 2003 Increased actuation rate of electromechanical carbon nanotube actuators using potential pulses with resistance compensation *Smart Mater. Struct.* **12** 549-55
- [4] Madden J D W, Barisci J N, Anquetil P A, Spinks G M, Wallace G G, Baughman R H and Hunter I W 2006 Fast carbon nanotube charging and actuation *Advanced Materials* **18** 870-73
- [5] Spinks G M, Wallace G G, Baughman R H and Dai L 2004 in *Electroactive Polymers (EAP) Actuators as Artificial Muscles, Reality, Potential and Challenges*, ed Y Bar-Cohen, (Bellingham WA: SPIE press) 261-95
- [6] Chan C T, Kamitakahara W A, Ho K M and Eklund P C 1987 Charge-transfer effects in graphite intercalates: ab initio calculations and neutron-diffraction experiment *Phys. Rev. Lett.* **58** 1528-31
- [7] Pietronero L and Strässler S 1981 Bond-length Change as a Tool to Determine Charge Transfer and Electron-Phonon Coupling in Graphite Intercalation Compounds *Phys. Rev. Lett.* **47** 593-96
- [8] Madden J D W, Vandesteeg NA, Anquetil P A, Madden P G A, Takshi A, Pytel R Z, Lafontaine S R, Wieringa P A and Hunter I W 2004 Artificial muscle technology: physical principles and naval prospects. *IEEE Journal of Oceanic Engineering* **29** 706-728.
- [9] Hughes M and Spinks G M 2005 Multiwalled carbon-nanotube actuators *Advanced Materials* **17** 443-46
- [10] Zhang M, Atkinson K R and Baughman R H 2004 Multifunctional Carbon Nanotube Yarns by Downsizing an Ancient Technology *Science* **306** 1358-61
- [11] Madden J D, Cush R A, Kanigan T S and Hunter I W 2000 Fast contracting polypyrrole actuators *Synthetic Metals* **113** 185-92
- [12] Oren Y and Soffer A 1985 The electrical double layer of carbon and graphite electrodes part II. Fast and slow charging processes, *J. electroanal. Chem.*, **186** 63.
- [13] Haque M H, Hying K, Kolaric I, Wallmersperger T and Kröplin 2006 Theoretical and experimental investigations of fundamental effects in carbon nanotube sheet actuators, *Smart Structures and Materials 2006: Electroactive Polymer Actuators and Devices (EAPAD)*, *Proc. of SPIE* **6168**, 61681I
- [14] Meites L, ed. 1963 *Handbook of Analytical Chemistry*, McGraw Hill, NY Sect. 5.

[15] Spinks G M, Liu L, Wallace G G and Zhou D 2002 Strain response from polypyrrole actuators under load *Advanced Functional Materials* **12** 437-40