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Fast carbon nanotube charging and actuation

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Short Text for Table of Contents (40 words):

Fast contraction and charging of carbon nanotube papers is shown, demonstrating that actuators and supercapacitors composed of these materials can exhibit very high power to mass, despite their reliance on ion transport.

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Carbon nanotubes change dimension in response to electrochemical charging. These changes and the tremendous tensile strengths of nanotubes suggest that the actuators will generate unprecedented work densities. Power density is low however. We demonstrate that carbon nanotube paper actuators can be surprisingly fast and powerful despite the need for ion transport. Stress changes of 1.1 MPa in 6 ms correspond to an apparent strain rate of 19 %/s and an instantaneous power density of 270 W/kg of nanotubes, surpassing human muscle. The fast response is the result of rapid charge injection into the carbon nanotube papers. The rapid charging demonstrates specific electrical power transfers of 450 kW/kg, an order of magnitude higher than is observed in commercial supercapacitors and two orders of magnitude higher than is found in batteries. Optimization of nanotube paper and electrolyte geometries is expected to lead to very substantial increases in power density.

A number of new and established technologies employ electrical stimuli to induce mechanical deformation in materials. [1] Carbon nanotube based actuators (CNT) have recently attracted attention due to their low voltage of operation (~ 1 V), high operating load (26 MPa to date) and high tensile strengths (1.8 GPa, possibly reaching 37 GPa in individual tubes). [2] However, CNT actuators tend to exhibit a full response on a time scale of seconds, rather than the milliseconds typical of electromagnetic actuators, piezoceramics and muscle. A key objective of this work is to push the limits of CNT actuation rate. A second objective is to observe charging rates. Carbon nanotube papers have been shown to exhibit specific capacitances on the order of 10^4 F/kg and higher. [3] If they can also be shown to charge and discharge rapidly, they will demonstrate particular promise for use as high power energy storage devices.

Previous work presented the use of resistance compensation to increase the rate of actuation in carbon nanotube devices. [4] The rate of actuation was found to be limited to 3 %/s. At high acceleration rates the inertia of apparatus appeared to be limiting rate. In the present work the rate of change in force is measured while carbon nanotube films are held at fixed length (isometric conditions). The advantage of measuring force changes under isometric conditions is that there are no moving parts and hence inertia does not limit the peak rates that can be observed.

Carbon nanotubes are formed into porous sheets or fibers which are immersed in electrolyte to form electrodes in an electrochemical cell. [2a] The application of potential causes the formation of an electrical double layer at the nanotube/electrolyte interface, in which the electronic charge stored in the carbon atoms is balanced by the ionic charge in the electrolyte. The accumulated nanotube charge and the resulting change in band structure is believed to cause a change in the C-C bond length during electron injection due to a number of factors including Coulomb repulsion. [2a] Assuming that these mechanisms are correct, it is the rate at which charge can be injected which determines the strain rate. The key to increasing rate is to increase current injected per unit volume. [5]

Achieving rapid charging rates is a challenge in fibers and sheets composed of carbon nanotubes because of the enormous capacitance of CNT electrodes, which is a consequence of the enormous internal surface area. This capacitance is more than 6

orders of magnitude higher than is observed in polyester capacitors, and similar to that of commercial super and ultracapacitors. [6] Internal resistances and ion transport rates prevent rapid charging and discharging, limiting the effectiveness of CNTs both as actuators and supercapacitors. Work by Niu and colleagues has shown that it is possible to obtain fast response times by using a combination of relatively thin porous carbon nanotube electrodes and high conductivity electrolytes. Charge and discharge times of 7 ms and specific powers of 8 kW/kg are reported. [7]

In this paper it is shown that fast response times can be obtained both for actuation and charging of carbon nanotube papers. In order to increase the rates of charging and actuation in thin porous CNT films, millisecond-long voltage pulses of up to ± 35 V in amplitude are applied. Potentials are much higher than the ~ 1V used in charging of CNT paper and fibre actuators and supercapacitors, and such large potential magnitudes would typically lead to parasitic reactions and degradation. However, if the solution resistance and any contact and lead resistance are significantly greater than the CNT paper impedance, most of the voltage drop will initially be across these, rather than the double layer within the nanotube films. [4,5a] The use of short pulses ensures that no overcharging of the nanotube double layer will occur, allowing rapid charging without unwanted reactions. The maximum allowable pulse duration is estimated by multiplying the desired potential change at the electrode (for example 1 V) by the electrode capacitance and dividing by the peak current observed following such the step change in cell potential. This relationship is derived from the electrical constitutive relationship for a capacitor, $V \cdot C = Q$, and conservatively assumes $Q = current \times time$. High voltage is only used to show what is possible when geometry is optimized.

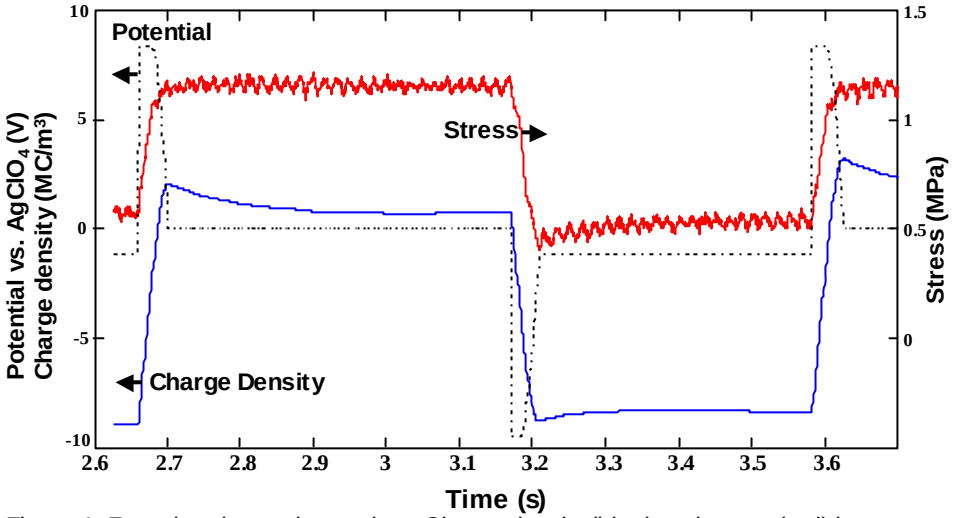

Figure 1: Fast charging and actuation. Charge density (blue) and stress (red) in response to a potential pulse (black). The stress rate is 19 MPa $\cdot s^{-1}$, corresponding to a strain rate of 2.1 % $\cdot s^{-1}$ (using a modulus of E=0.95 GPa).

Results from two CNT samples are presented. Sample 1 is 30 μm thick, 1.6 mm wide and 15 mm long between clamps. Sample 2 is 35 μm thick, 1.6 mm wide and 11 mm long between clamps. Twenty alternating positive and negative voltage pulses were applied to Sample 1. Figure 1 shows the voltage pulse profile, the input charge in response to the voltage pulse, and the resulting change in stress over the course of one cycle. Response was essentially identical in each cycle. Resistance compensation is used to increase the speed of response while maintaining the sample potential at or between -1 V or 0 V. [4,5a] As seen in Figure 1 the potential applied between the working and the reference electrode is much larger. This is because a substantial portion of the voltage is consumed by the resistive drop across the electrolyte.

Figure 1 also shows the charge induced change in stress. The average rate of change of stress over the period of maximum applied voltage is 20 $MPa \cdot s^{-1}$, corresponding to an apparent strain rate of 2.1 $\% \cdot s^{-1}$. The apparent strain rate is calculated using a measured modulus of E=0.95 GPa, which is found to be constant over the range of applied potentials. The use of resistance compensation has increased the rate of actuation by more than an order of magnitude.

The recorded charge and voltage are used to find the capacitance of the nanotube sample, the stored energy, and the power. Normalized by mass of the nanotubes alone, the capacitance was found to be $2.8 \pm 0.3 \times 10^4$ $F \cdot kg^{-1}$, which falls within the range of capacitances observed by Barisci et. al. in identically prepared nanotube papers. [3a] Given the applied change in double layer potential of 1 V, the electrical specific energy is 14 $kJ \cdot kg^{-1}$. The instantaneous electrical power to mass ratio is 470 $kW \cdot kg^{-1}$.

The apparent power density was achieved by using resistance compensation, with more energy having been expended than is gained upon discharge. However, if the electrolyte and contact resistances were dramatically reduced, the enormous power densities would be obtained without needing to apply additional potential to overcome these internal resistances. In order to create a capacitor capable of discharging at the same rate observed in Figure 1, but without compensation, it is predicted that the spacing between CNT paper electrodes must be reduced to less than 100 μm. [5c] Still faster charge or discharge should be possible by further reducing electrode spacing.

In a complete device the capacitance per unit mass is reduced because the nanotubes are soaked in electrolyte (which increases their effective density by a factor of 3) and a counter electrode is needed, which halves the capacitance. The overall capacitance per unit mass of a two CNT electrode system with electrolyte is then approximately 4,500 $F \cdot kg^{-1}$. The specific energy at 1 V is 4.5 $kJ \cdot kg^{-1}$ and the power is expected to reach 160 $kW \cdot kg^{-1}$. The energy density is twenty times lower than that of lead acid batteries but the power is more than 100 times greater, and an order of magnitude greater than power densities reported in commercial supercapacitors. [6b,8]

Still faster response is obtained by applying large amplitude potential pulses. Figure 2 shows an average stress rate of 180 $MPa \cdot s^{-1}$ induced by applying 6 ms long 30 V pulses. This response corresponds to an apparent strain rate of 19 $\% \cdot s^{-1}$. The apparent instantaneous mechanical power density is 270 $W \cdot kg^{-1}$, exceeding the power density of human skeletal muscle and approaching the highest attained animals. [9]

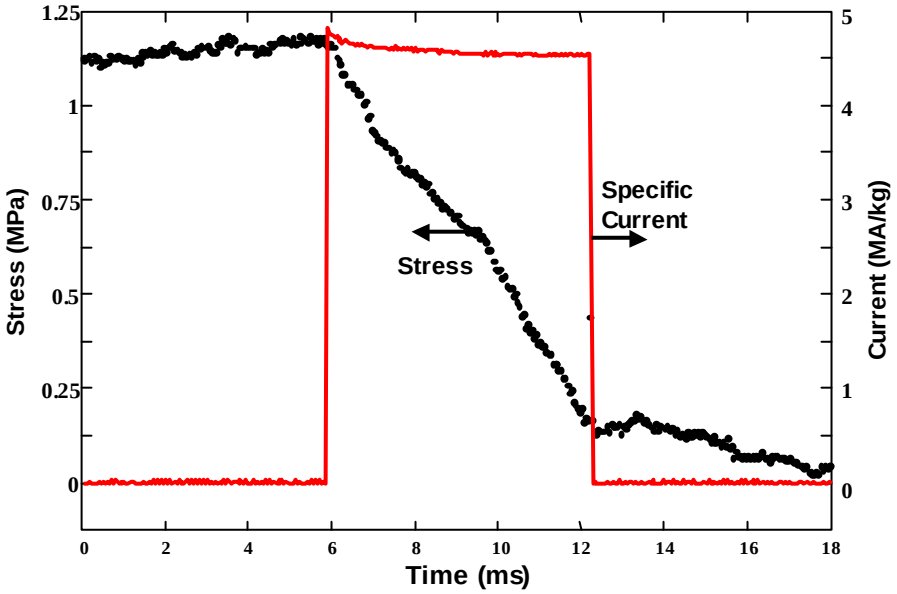

Figure 2: Fast actuation. The stress rate is 180 MPa $\cdot s^{-1}$, corresponding to a strain rate of 19 % $\cdot s^{-1}$ (using a modulus of 0.95 GPa).

A comparison of the mechanical and electrical power densities suggests that the efficiency of electromechanical conversion is mediocre. This efficiency can be greatly improved by recovering stored electrical energy. Increased electromechanical coupling can be obtained by operating at higher stress levels. [5b,5c] Work by Baughman and colleagues has demonstrated that actuation at 26 MPa is possible, increasing coupling by an order of magnitude, and suggests that further improvements are likely, given that tensile strengths in fibres have reached 1.8 GPa, and are estimated to be 37 GPa in individual tubes. [2b,2d,10]

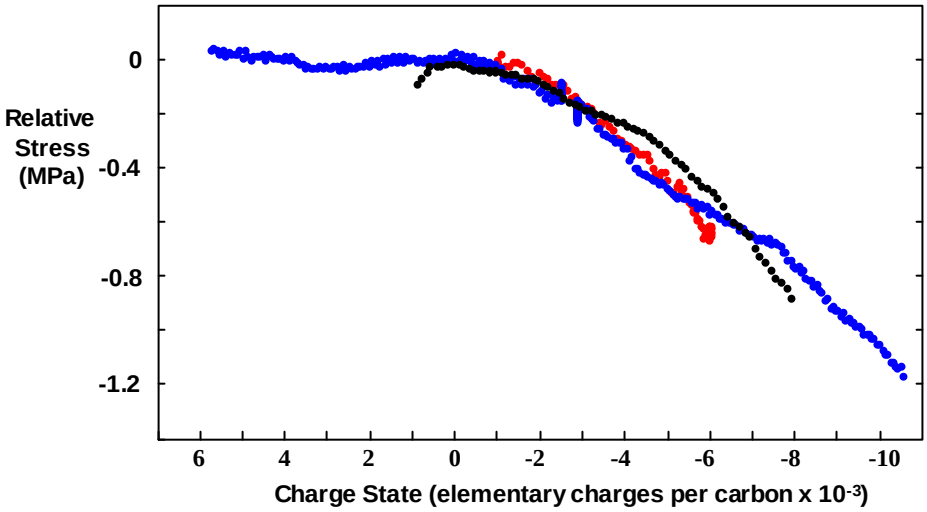

Figure 3: Stress to charge relationship. Observed in samples 1 (red) & 2 (blue) and compared with the strain to charge relationship from data presented in Baughman et. al. [2].

Previous work has shown that strain is a function of charge squared, and suggesting that this relationship is independent of time and dominated by Coulomb repulsion. The relationship between strain and charge per carbon atom published by Baughman et. al. [2a] has been recast in terms of stress vs. charge per carbon in Figure 3 (black dots) by multiplying strain by the elastic modulus. Stress and charge data obtained from Samples 1 and 2 activated at millisecond time scales are also plotted in Figure 3, showing that the relationship is essentially unchanged even at millisecond time scales. All observed deviations are within the ± 0.15 MPa experimental uncertainty in the stress measurements that results from the noise present in the measurement of force. The maintenance of the stress to charge ratio suggests that the mechanism of activation does not change, and that coupling between charge and deformation has not been degraded by the use of high voltage pulses. Previous work has shown an apparent limit on the rate of charging, which was thought to be due to limitations of the experimental set-up rather than intrinsic limits on the rate of actuation in the nanotube films. This work confirms the conjecture and demonstrates, within experimental uncertainty, that the effectively time-independent relationship between strain and charge proposed by Baughman et. al. [2a] is valid down to millisecond time scales. The data does not support the assertion that Coulombic forces dominate the actuation mechanism as the stress to charge relationship is not symmetric about the zero charge state, but rather there is no observable change in stress under negative charging. However, this asymmetry could be due to parasitic reactions which may be dominating the current during the application of positive potential steps.

Electrolytic processes are generally considered to be slow in comparison to electronics due to the relatively low mobilities of ions. Nevertheless, speed and power can often be improved by careful cell design, including ensuring short distances of ion transit, low electrolyte resistance and high electrode conductance. [5b,5c,10] How much faster can nanotube devices respond? Based on calculated time constants, [5c,10] it should be

possible to achieve charging and actuation in less than a nanosecond using 10 nm thick CNT samples. Such a charging and actuation time constant puts CNT performance far beyond any existing technology.

It is demonstrated that carbon nanotube papers can charge and actuate within milliseconds. These result support the assertion that there is a time independent relationship between charge and strain in these materials. It is simply the rate of charge insertion that limits response rate, and thus careful optimization of device geometry is predicted to lead to response reaching the nanosecond level, and unprecedented power densities. If combined with increases in the levels of active stress, including recent results demonstrating actuation at 26 MPa [2c], carbon nanotube based actuators will outperform all other actuator technologies both in work density and power density. The primary obstacle to reaching these goals is one of fabrication. Even without these improvements, power density in carbon nanotube film actuators exceeds that of human muscle. Furthermore, it shown that by reducing series resistance the electrical power density of carbon nanotube paper based capacitors greatly exceeds that of batteries and capacitor technologies. Despite their electrochemical nature, carbon nanotube electrodes can respond surprisingly quickly.

Experimental

Materials: Single-wall CNT dispersed in water with Triton X100 (www.sigmaaldrich.com) were obtained from Tubes@Rice (Rice University) with purity better than 90%. The material consists of hexagonally packed bundles of 1.2 to 1.4 nm diameter nanotubes. Each bundle is composed of between 30 and 100 nanotubes and has an average diameter of 50-140 nm. Bundles are several micrometers in length. [11] Acetonitrile, silver perchlorate, tetrabutylammonium perchlorate (TBAP) and tetrabutylammonium hexafluorophosphate (TBAHFP) were supplied by Sigma-Aldrich (www.sigmaaldrich.com).

CNT Paper Synthesis: The fabrication of the CNT films or papers, [2a] begins with vacuum filtration of the aqueous single-wall CNT suspension on a membrane filter, followed by washing with water and methanol, air drying, and removal of the formed film from the filter. Removal of impurities from the CNT sheet was carried out by thermal annealing under argon gas at 850°C for 1 h, followed by cooling to room temperature overnight.

Electromechanical Testing: CNT films immersed in 0.2 M tetrabutylammonium hexafluorophosphate/acetonitrile electrolyte are held at fixed length. Two clamps provide both electrical and mechanical contact. Force on the films is measured via a load cell (ELFS-T3E-10N, www.entran.com) whose output is conditioned (www.vishay.com, Model 2311) and recorded via an analog to digital converter (A/D, E-series, www.ni.com). A high resolution stepper motor driving a linear stage (20 nm per step) (www.compumotor.com, LN Drive; www.neat.com, LM-50 precision linear stage) is used to set the initial sample stress, which is close to 1 MPa. Once the desired stress is reached, shaped potentials are applied to samples under computer control (PC/Windows XP running Visual Basic 6.0). Current and potential are recorded via A/Ds. Current is integrated to determine the extent of charging. Capacitance is found by dividing the

accumulated charge by the change in open circuit potential. Actuation rate is judged by the rate of change in stress. Measurements demonstrate that sample stiffness is constant over the range of applied potentials used in this experiment enabling strain rate to be estimated by dividing the average rate of stress change by the elastic modulus. Films were found to have an elastic modulus of 0.95 GPa, which is constant over the range of potentials employed.

Sample 1 results were obtained using a cell with a stainless steel counter electrode. A silver/silver perchlorate reference electrode in acetonitrile was used with a potentiostat in order to control the CNT potential. [12] A resistance compensation algorithm was used to enable potentials of between ±10 V to be applied without degrading the sample or inducing parasitic reactions. [4,5a] In Sample 2 the counter electrode is a second CNT film surrounding the first on three sides and separated from it by approximately 5 mm. Six millisecond long 30 V amplitude pulses were applied between the two electrodes. In the resistance compensation method used the sample to reference voltage is first stepped up to + 8.5 V from the initial -1 V potential. The current is then measured immediately and the series resistance provided by the solution is estimated by dividing the change in voltage by the current. The voltage is subsequently adjusted so that the applied potential minus the product of the current and the estimated resistance does not exceed 0 V vs. the reference. The applied voltage drops to 0 V after approximately 35 ms, at which point the current is nearly zero and thus the resistive drop across the solution is also close to zero. After approximately 0.45 s a -9.5 V change in voltage is applied, and again resistance compensation is used. The applied voltage settles at -1 V before the next pulse sequence begins.

The charge traces in Figure 1 show that current reverses slightly once either the 0 V or -1 V set points are reached. The cell resistance is measured to be 32 Ω of which less than 5 Ω are due to the electronic resistivity the CNT sample, and thus most of the resistance is in series, as assumed by the resistance compensation algorithm. However, the sample resistance does introduce some error in the series resistance measurement, and likely explains the reverse current. The rate of charging is nearly constant at the beginning of each pulse where the applied potential is constant. This response is consistent with RC charging behaviour.

During cycling there is a gradual decrease in the mean stress level and an increase in charge over the time period of the measurement. The drift in charge appears to be the result of parasitic electrochemical reactions, while the drop in stress is likely a relaxation process.

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