

Multi walled carbon nanotube actuators: Comparison of aqueous liquid and gelled ionic liquid electrolytes

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ABSTRACT

Carbon nanotube mats, so-called buckypapers, were studied for their in-plane (length) actuation in aqueous liquid (1 M NaCl) and non-aqueous gel electrolytes. As a gel electrolyte, a polymer gel consisting of PVdF-HFP and the ionic liquid BMITf was investigated and characterized by thermal analysis and measurements of ionic conductivity. Being an important parameter for the actuation, the electrical capacitance of multi walled carbon nanotube (MWCNT) buckypapers was evaluated in both electrolytes. Buckypapers and gel electrolyte were combined to manufacture non-volatile solid-state actuators. Actuation strain measurements under various tensile prestress levels have shown that the obtained maximum strains are comparable for both electrolytes tested.

Keywords: multi walled carbon nanotubes, MWCNT, buckypaper, actuator

1. INTRODUCTION

Electromechanical actuators – devices based on the direct conversion of electrical into mechanical energy – constitute significant elements for mechatronic applications like robotics, microscopic pumps, optical fiber switches and medical prosthetics. The ability of carbon nanotubes (CNT) to be actuated at low electrical potentials has already been known for a decade [1, 2]. CNT based actuators are typically assembled from buckypapers – mats of randomly oriented and non agglomerated CNTs – and operated in liquid electrolytes. Electrically charged CNTs are presumed to change their dimensions due to quantum chemical effects. The accumulated charges in the nanotubes cause increases in the C-C bond lengths during electron injection. This actuation can be amplified by surrounding nanotubes with counter ions, which allows the build up of an electric double layer leading to additional electrostatic effects.

State-of-the-art carbon nanotube actuators consist of single walled carbon nanotubes (SWCNTs). SWCNTs are anticipated to allow higher actuation strain as compared to multi walled carbon nanotubes (MWCNT) due to the former's higher specific surface area and lack of inner, electrochemically inaccessible tubes. For these reasons, MWCNTs have not yet been widely investigated for their actuation [3], although they are produced in large quantities at a fraction of the cost of SWCNTs.

So far CNT actuators have been examined predominantly in a laboratory environment and their performance assessed in a qualitative way. With regard to potential applications, significant research needs remain in investigating viable solutions when taking into account technical requirements, handling and manufacturability aspects. In this respect, replacing liquid by gel

electrolytes would represent a major advancement. Still being a contentious issue, the actuation mechanisms need to be understood more thoroughly in order to improve the performance of CNT actuator devices.

The overall object of this work is the development and characterization of MWCNT actuators based on either liquid or gel electrolytes and to compare their performance.

2. EXPERIMENTAL

2-1. Materials

MWCNTs (Baytubes C 150 P, 95 % purity, outer mean diameter 13 – 16 nm, length 1 – 10 μm), produced by catalytic chemical vapor deposition (CCVD), were obtained from Brenntag Schweizerhall AG (Bayer Material Science, Switzerland). For buckypaper preparation [4], the MWCNTs were used as received. 120 mg nanotubes were dispersed in 200 ml 1 wt-% aqueous sodium dodecyl sulfate and treated with a horn sonicator (Hielscher UP 200s Ultrasonic Processor) for one hour at the maximum power setting. After sonication, the suspension was centrifuged (Hettich Rotina 420R) for 30 min at approx. 4200 g. Buckypapers were prepared by vacuum filtration of the suspensions through a PTFE filter (pore size 0.45 μm , diameter 4 cm) and rinsing of the resulting mat with 200 ml deionized water and 100 ml methanol. After drying at ambient conditions the mats were peeled off the filter. The resulting buckypapers having a thickness of 0.10 – 0.12 mm were cut into strips of 3x20 mm.

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, Solef 11010) was obtained from Solvay (Belgium), 4-methyl-2-pentanone (MP) from SigmaAldrich (Switzerland) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMITf) from IoLiTec (Germany). Gel electrolyte films were manufactured by solution casting. In a first step, 1 g PVdF-HFP was dissolved in 28.16 g MP and stirred for 20 minutes at 80°C to yield a clear solution. Subsequently 1 g BMITf was mixed with 14.18 g of the polymer solution at 80°C. After stirring for another 20 minutes, the solution was cast on aluminum plates and dried for 30 minutes at ambient conditions. The gel films of ca. 5 μm thickness could easily be peeled off. Thicker films could be prepared by repeated casting of hot solution on dried films.

2-2. Characterization methods

Electrochemical experiments were conducted in liquid aqueous electrolyte (1M NaCl) and in gel electrolyte (PVdF-HFP/BMITf) using an AMEL Model 7050 Potentiostat-Galvanostat. Buckypaper strips were used for both working and counter electrode in a two-electrode setup; potentials are reported relative to the counter electrode (no standard reference electrode was used). Cyclic voltammograms were recorded at scanning rates of 100 mV/s in the potential ranges of -2 to 2 V for 1 M NaCl and -3 to 3 V in the gel electrolyte. Specific capacitances were evaluated under galvanostatic conditions at current densities of 1 A/g in the potential range of -0.4 to 1 V. The specific surface area was characterized by the Brunauer-Emmett-Teller (BET) method using a TriStar Micromeritics analyzer. Prior to measurements, samples were preconditioned under nitrogen for one hour at 150°C using a Flow Prep 060 Micromeritics. The morphology of bucky paper surfaces was examined with a Scanning Electron Microscope (SEM) Gemini LEO 1530.

The thermal stabilities of the gel electrolyte and of its individual components were studied using a Perkin Elmer Pyris 1 Thermal Gravimetric Analyzer (TGA). Temperature scans between 50°C and 800°C were performed under nitrogen atmosphere at a heating rate of 30°C/min. The melting points were measured using a Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC) between the temperature range of -50 to 100°C at a heating rate of 10°C/min. Sealed aluminum pans

were used as sample containers for all DSC measurements.

Ionic conductivity of the gel electrolyte at room temperature was determined from complex impedance spectra measurements using an HP 4194 A impedance analyzer in the frequency range from 100 Hz to 20 kHz. A conductivity cell containing two stainless steel blocking electrodes was used. The ionic conductivity σ of the gel films was calculated as:

$$\sigma = \frac{l}{R_b \cdot S}$$

where l is the thickness of the membrane, R_b the bulk resistance and S the area of the electrodes. R_b is given by the intercept on the real axis at the high frequency end of the spectrum [5, 6].

2-3. Gel electrolyte actuator manufacturing

Figure 1 shows the manufacturing process for a MWCNT in-plane gel electrolyte actuator: two buckypaper strips and two strips of aluminum foil (1) were electrically connected (2) using silver epoxy. The buckypapers were put on an aluminum plate coated with a dried layer of gel electrolyte (3), and impregnated by applying gel electrolyte solution. The impregnated and dried buckypapers (4) were arranged for the use as an in-plane actuator: One impregnated buckypaper was used as the working electrode to be measured, the second one (counter electrode) was prepared by lateral cuts to lower its stiffness in length direction such as not to interfere with the actuation of the working electrode. Both buckypapers were brought together using a few droplets of gel electrolyte solution (5). After drying, the gel electrolyte actuator possessed a total thickness of 0.3 mm and was ready to use (6).

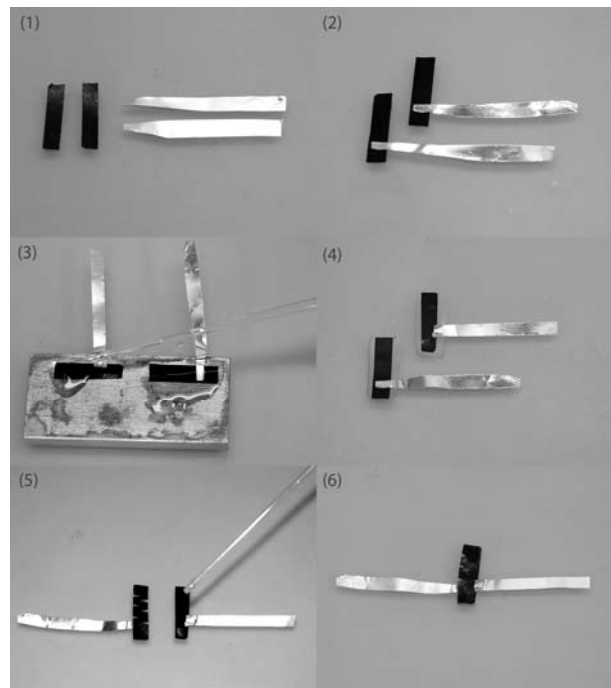


Figure 1: Manufacturing steps of a gel electrolyte actuator consisting of MWCNT mats and gel electrolyte (PVdF-HFP/BMITf); details see text.

2-4. Actuation strain measurement

In-plane (longitudinal) actuation strain of buckypaper strips in liquid and gel electrolyte was measured using a Dynamic Mechanical Analyzer (Perkin Elmer DMA 7e) in static mode with a modified procedure originally developed for the characterization of piezoelectric fibers [7]. Strips of either pure MWCNTs buckypapers immersed in 1 M NaCl or gel electrolyte impregnated buckypapers were clamped to have an active length of 6 to 7 mm (Figure 2, Figure 3). Nearly free-strain conditions were set up by applying a minimal tensile load of 10 mN required for stable tensile strain measurements. Experiments under non-zero tensile prestresses were performed by applying a static tensile load corresponding to the desired stress level, where stress was calculated based on the effective nanotube volume fraction in the buckypaper. A similarly sized buckypaper was used as counter electrode. Voltage steps (positive and negative potentials) of one minute duration were applied by the potentiostat, separated by one minute periods at zero potential. The measured displacements (average over step duration) were used to determine reversible actuation strain.

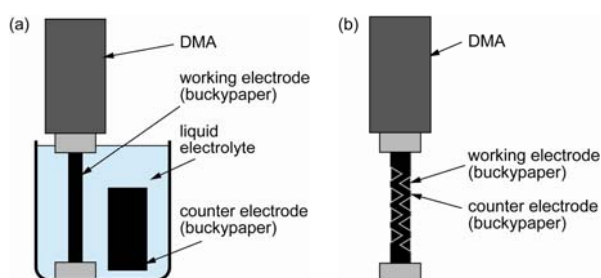


Figure 2: Actuation strain measurement: schematic of a MWCNT actuator in (a) liquid electrolyte; (b) gel electrolyte.

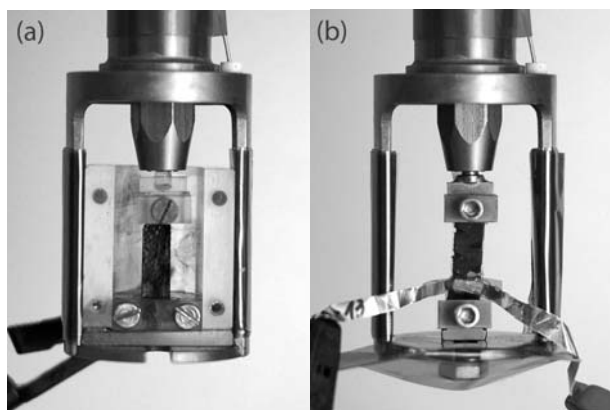


Figure 3: Actuation strain measurement: buckypaper strips with gauge length of 6 – 7 mm are clamped at the bottom, tensile load is applied and extension measured by the DMA probe at the top; (a) neat buckypaper immersed in aqueous liquid electrolyte (contacts and counter electrodes omitted for clarity); (b) buckypaper impregnated with gel electrolyte and laminated with counter electrode (metallic strips as contacts).

3. RESULTS AND DISCUSSION

3-1. Characterization of MWCNTs

Buckypapers produced exhibited a density of 0.45 g/cm³ (corresponding to a volume fraction of 25 %, assuming MWCNT density of 1.8 g/cm³) and a specific surface area of 174 m²/g. An earlier study had revealed a good correlation between the specific surface area and the electrical capacitance, which was found to play an important role in the actuation of buckypapers [4]. Considering, that only the outermost wall of the nanotubes is accessible to the nitrogen gas used for BET-measurements, it is unsurprising that MWCNTs have a smaller specific surface area when

compared to SWCNTs (510 m²/g).

The electrochemical stability of MWCNTs in 1 M NaCl and gel electrolyte was found to be -1.1 to 1.6 V and -3 to 3 V, respectively. Specific double layer capacitance was determined from galvanostatic experiments at 1 A/g in the linear potential range of 0 – 0.6 V. Buckypapers in 1 M NaCl and neat BMITf exhibited highest capacitance (14 – 18 F/g), and in gel electrolyte slightly lower values (11 – 14 F/g). In accordance with the lower surface area of MWCNTs, their values of specific capacitance are lower than those of SWCNTs (35 F/g).

SEM images (Figure 4) disclosed a fibrous structure of the buckypapers with a fiber diameter of around 15 nm. Thus, the MWCNTs seem to be well dispersed and unbundled. The high aspect ratio of the nanotubes yields the mechanical entanglement resulting in cohesive CNT mats.

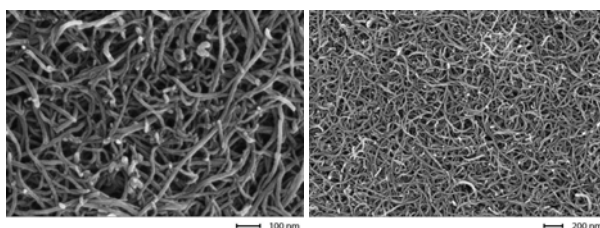


Figure 4: SEM images of MWCNTs (Baytubes) buckypapers at two different magnifications.

3-2. Characterization of gel electrolyte

Gel electrolytes consisting of a mixture of PVdF-HFP and BMITf possess the advantage of being electrochemically more stable and of not desiccating at ambient conditions as e.g. ionomers gelled with a volatile solvent do. An ionic liquid, such as BMITf, is a molten salt that does not evaporate at room temperature.

DSC heating and successive cooling traces of the gel electrolyte, PVdF-HFP and BMITf are shown in Figure 5. The melting point of the pure ionic liquid was found at 17.2°C confirming that BMITf is a room temperature molten salt. During the cooling scan, BMITf forms a supercooled liquid with a freezing point at -18.8°C. The melting and the freezing point are lowered by the presence of the PVdF-HFP, forming the gel electrolyte, down to 6.3°C and below -50°C, respectively. Hence, the gel electrolyte provides a useful ionic conductivity already at a lower temperature than the neat ionic liquid.

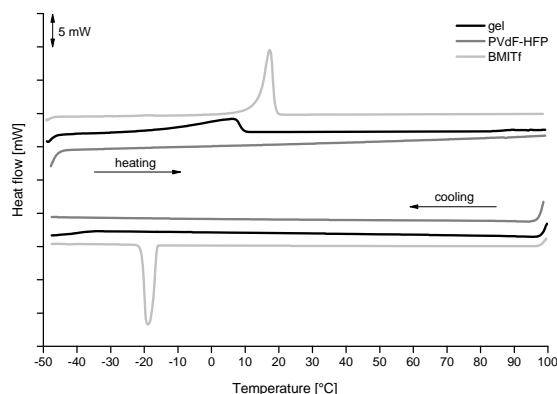


Figure 5: DSC scans of gel electrolyte, PVdF-HFP and BMITf.

Thermal stabilities of the gel electrolyte and its components as measured by TGA are shown in Figure 6. Decomposition onset temperatures of BMITf and PVdF-HFP are 404°C and 494°C, respectively. In the gel electrolyte a two-step decomposition was found at temperatures of 297°C and

406°C. Up to ca. 300°C no significant mass reduction was observed.

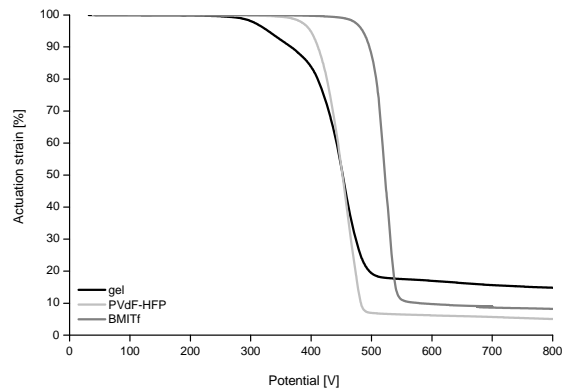


Figure 6: TGA of gel electrolyte, PVdF-HFP and BMITf.

From impedance spectroscopy, the ionic conductivity of the gel electrolyte was found to be 0.07 mS/cm, whereas neat BMITf and 1 M NaCl have conductivities of 3 and 74 mS/cm, respectively. The relatively small ionic conductivity of the gel electrolyte compared to the liquid electrolytes did not impose any significant limitations to the following actuation experiments (see below).

3-3. Actuation in liquid and gel electrolyte

The actuation strain measurements on the buckypaper strips in liquid and gel electrolyte were conducted by applying a sequence of constant potential signals of increasing magnitude, each of 1 min duration, separated by 1 min periods at zero potential. This procedure additionally allowed to examine the reversibility of the actuation. Figure 7 shows the actuation strains of a liquid electrolyte actuator (a) and a gel electrolyte actuator (b) within the potential range of 0 to -1.1 V and 0 to -3 V, respectively.

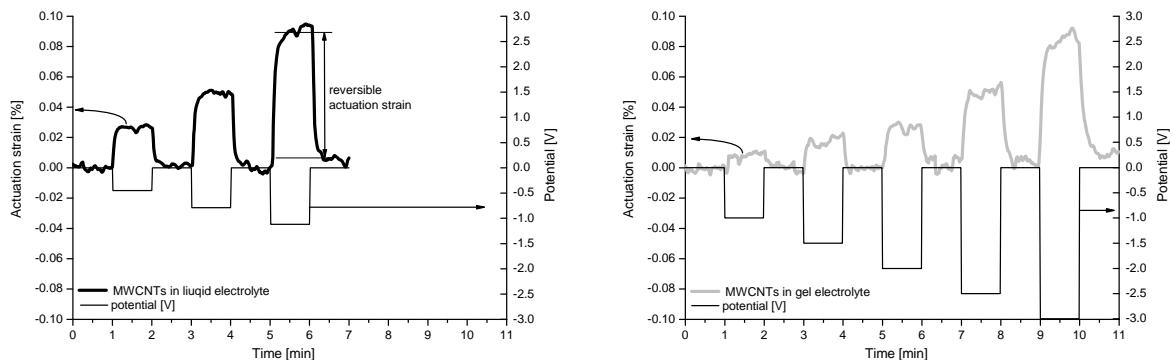


Figure 7: Actuation steps of MWCNT buckypapers under free-strain conditions (negative potential shown only): (a) in liquid electrolyte (1 M NaCl), (b) in gel electrolyte.

Reversible free-strain actuation (at zero tensile prestress) for both actuators is plotted in Figure 8. Actuation was found to be highest at the negative end of the potential range for both liquid and gel electrolyte (at -1.1 V and -3 V, respectively). For positive potentials no actuation could be found for the gel electrolyte actuators, and only marginal actuation for the liquid electrolyte actuators.

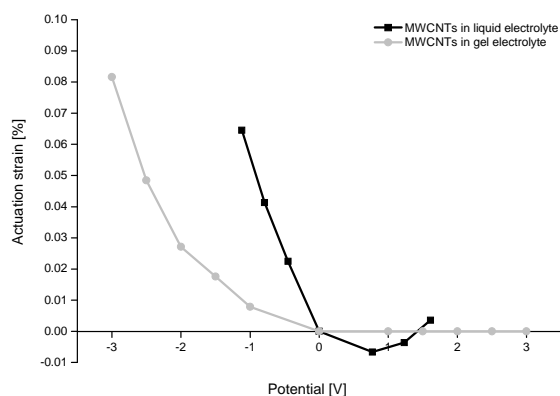


Figure 8: Actuation of MWCNT buckypapers in liquid and gel electrolyte.

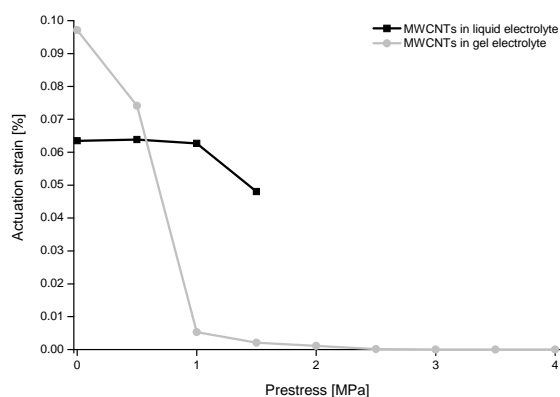


Figure 9: Reversible actuation strain vs. tensile prestress of buckypapers in liquid and gel electrolyte at -1.1 V and -3 V, respectively.

When applying a small tensile prestress of up to 1.5 MPa, actuation of buckypapers in liquid electrolyte was little affected; however, they mechanically failed already at 2 MPa (Figure 10). Gel electrolyte actuators performed worse, with a significant reduction of reversible actuation strain already at 0.5 MPa accompanied by considerable creep. Between 1 and 4 MPa no more reversible actuation was observed but creep behavior only. They eventually failed at 4.5 MPa. In both liquid and gel electrolytes, actuators showed highest performance and reversible actuation strain under zero tensile prestress.

4. CONCLUSIONS

This work presents the preparation of a novel MWCNT in-plane gel electrolyte actuator, consisting of a laminate of impregnated MWCNT mats and a gel film of the polymer PVdF-HFP with the ionic liquid BMITf. Furthermore, liquid (1 M NaCl) and gel electrolyte (PVdF-HFP/BMITf) actuators were compared regarding their actuation strain with and without tensile prestress.

For both liquid and gel electrolyte actuators, maximum actuation strains of 0.064% and 0.081% were found at zero prestress and at the negative end of the electrochemical stability window for the given experimental setup at -1.1 and -3 V, respectively. The higher actuation strain for the gel electrolyte actuator is primarily due to its superior electrochemical stability. The actuation ability of both actuator types rapidly decreased when applying low tensile prestresses, for liquid electrolyte actuators at 1.5 MPa and for gel electrolyte actuators at 0.5 MPa. Therefore the presented actuators

are only suitable for use in low load applications like optical devices.

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REFERENCES

1. Baughman, R. H., Cui, C., Zakhidov, A.A., Iqbal, Z., Barisci, J.N., Spinks, G.M., et al, "Carbon Nanotube Actuators", *Science* Vol. 284, pp. 1340-1344 (1999).
2. Baughman, R.H., Zakhidov, A.A., de Heer, W.A., "Carbon Nanotubes - the Route Toward Applications", *Science* Vol. 297, pp. 787-792 (2002).
3. Hughes, M., Spinks, G., "Multiwalled Carbon-Nanotube Actuators", *Advanced Materials* Vol. 17(4), pp. 443-446 (2005).
4. Suppiger, D., Busato, S., Ermanni, P., "Characterization of single-walled carbon nanotube mats and their performance as electromechanical actuators", *Carbon* Vol. 46(7), pp. 1085-1090 (2008).
5. Watanabe, M., Sanui, K., Ogata, N., Kobayashi, T., Ohtaki, Z., "Ionic conductivity and mobility in network polymers from poly(propylene oxide) containing lithium perchlorate", *Journal of Applied Physics* Vol. 57(1), pp. 123-128 (1985).
6. Monk, P.M., "Fundamentals of Electroanalytical Chemistry", Chichester: John Wiley & Sons LTD (2001).
7. Belloli, A., Heiber, J., Clemens, F., Ermanni, P., "Novel Characterization Procedure for Single Piezoelectric Ceramic Fibers", submitted to *Journal of Intelligent Material Systems and Structures* (2008).