Fully plastic actuator based on multi-walled carbon nanotubes bucky gel

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Abstract— **Carbon nanotubes have electrical and mechanical properties that make them highly attractive for actuators. They have the ability to deform elastically by several percent, thus storing very large amounts of energy, thanks to their crystalline nature and to their morphology. We investigate the performance of a bimorph actuator composed of multi-walled carbon nanotubes (MWCNTs), polyvinylidene difluoride (PVdF) and the ionic liquid (IL) 1-butyl 3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$] with a polymer-supported internal ionic liquid electrolyte. Electrochemical characterizations by cyclic voltammetry (CV) linear sweep voltammetry (LSV), and actuation tests performed applying a square wave of 4 Volt peak-to-peak at frequencies between 0.3 Hz and 2 Hz are reported and discussed.**

Keywords- Carbon nanotubes (CNTs); Ionic liquids; Actuators; Soft materials; Artificial muscles

I. INTRODUCTION

A new kind of actuator based on carbon nanotubes (CNTs) has been proposed as demonstrator for the first time in 1999 [1], and while the technology is only at his early stage, it seems to be very promising and a strong effort in basic research is required for its full exploitation. A carbon nanotube actuator is basically an electrochemical cell in which CNTs are used as electrodes. The formation of an electrical double layer at the nanotube-electrolyte interface, by applying a potential, stores charge on CNTs and this drives the actuation. The principle of actuation is the change of volume of a CNT porous sheet immersed in an electrolyte when positive ions are injected [2]. Electrochemically one side of the device is charged negatively and the other positively; both sides expand, but the negative side expands more than the positive [3]. Thus the whole structure bends; this phenomenon is reversible and an opposite bias voltage induces the bending in the other direction. CNT based actuators are very promising because of the exceptional mechanical properties of CNTs due to the molecular structure nearly free from structural defects that leads to an enormous amount of elastic energy stored in each nanotube [4].

The main challenge in developing and designing a CNT based actuator is to find the way to extract a significant part of this elastic energy and convert it to useful motion by making the macroscopic structures as stiff as the microscopic ones [4]. Aida et al. [5] found that single-walled carbon nanotubes (SWCNTs) create a physical gel (called bucky-gel) when grounded with imidazolium-based ionic liquids (ILs); this is possibly due to a specific interaction between the imidazolium ion component and the π–electronic nanotube surface [6]. This composite material was used to make a three layers bending actuator with a polymer-supported internal ionic liquid electrolyte layer which is sandwiched by bucky-gel electrode layers [7,8,9,10].

In this paper, we propose the use of a bucky-gel based on multi-walled carbon nanotubes (MWCNTs) that are not subject to chirality-related restrictions on electrical properties and are significantly cheaper than SW for preparing the actuator. We report here the performances of a low-voltage driven electromechanical bending actuator composed of MWCNTs, the ionic liquid 1-butyl 3-methylimidazolium tetrafluoroborate [BMIM][BF$_4$] and polyvinylidene difluoride (PVdF).

II. EXPERIMENTAL

A. Materials

All chemicals were used as received from Nanocyl (MWCNTs, 95% C purity), Sigma-Aldrich (NaCl, 98% purity) and Fluka (PVdF M_r=530000), (BMIM-BF$_4$, 97% purity), (tetrahydrofuran, 99.8% purity).

B. Preparation of the cantilever actuators

The three-layer cantilever actuator can be readily fabricated through layer-by-layer casting on a glass plate at 60°C of electrodes and electrolyte by a solution of tetrahydrofuran (THF); the configuration of the cantilever is reported in Fig. 1a and the structure of the ionic liquid is reported in Fig. 1b. Typically the electrolyte layer has a thickness of 0.1 mm and each of the two bucky-gel electrodes have a thickness of 0.15 mm. The bucky-gel electrode layers are composed by 30% of MWCNTs, 35% of PVdF and 35% of BMIM-BF$_4$, while the electrolyte includes 50% of BMIM-BF$_4$ and 50% of PVdF. The mixtures were prepared as follows: for the electrodes 0.35g of BMIM-BF$_4$ were grounded with 0.30g MWCNTs with a agata mortar and pestle, 0.35g PVdF dissolved in few drops of THF

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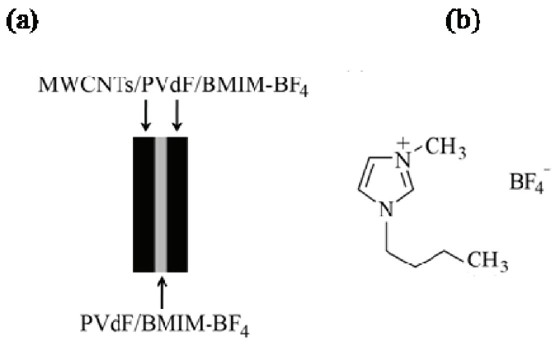

Figure 1. (a) Structure of the cantilever composed of a solid electrolyte layer sandwiched between bucky-gel electrode layers and (b) molecular structure of the ionic liquid BMIM-BF_4.

were added and the solution was stirred for one hour. For the electrolyte 3 g of PVdF were dissolved in 50 mL of THF under magnetic stirring, 3 g of BMIM-BF_4 were added and the solution was mixed for about 3 hours.

C. Actuation tests

Actuation tests were carried out by applying a square wave of 4 Volt peak-to-peak at 2, 1 and 0.3 Hz to a 17mm x 2.5mm sized actuator strip of 0.4 mm thickness clipped by two electrodes All the electrochemical measurements were performed with a PARSTAT 2273 potentiostat/galvanostat/frequency response analyzer (Applied Princeton Research).The displacement was continuously monitored with a camera mounted on a microscope and the displacement vs. time data was extracted from the video by using home-made tracking software. The measured displacement δ was transformed into strain difference between two bucky electrode layers (ε) by using the equation 1,

$$\varepsilon=2d\delta/(L^2+\delta^2) \tag{1}$$

where L and d are the free length and the thickness of the actuator strip respectively, on the assumption that the cross sections are plane at any position along the actuator as there is no distortion of the cross sections [10].

D. Characterizations of the electrodes and electrolyte films

Linear sweep voltammetries (LSV) at 5mV/s and room temperature using PVdF/BMIM-BF_4 sandwiched between platinum electrodes and ,for comparison, in NaCl-based aqueous electrolyte (0.9 % NaCl solution) were recorded in order to evaluate the electrochemical stability window (ESW) of the solid electrolyte . The cyclic voltammograms in the $5mVs^{-1}$ to $1Vs^{-1}$ scan rate range at RT of the bucky-gel electrode were measured by two-electrode configuration. The specific capacitance of the electrodes which featured 2.6 mg of MWCNTs was evaluated from the voltammetric discharges at 5 mVs^{-1} at RT by the slope of the electrode potential vs. integral over time of the current. The electrical conductivity of the PVdF/ BMIM-BF_4 based electrolyte was measured by four-point probe technique using a Keithley 2612 source meter. Impedance spectroscopy measurements in two-electrode mode at open circuit voltage in the 2 MHz to 100 mHz frequency range, with 200mV ac perturbation and 10 points per decade acquisition were carried out to evaluate the intrinsic ionic conductivity of the PVdF/BMIM-BF_4 electrolyte at room temperature (RT) with an Agilent E4980A precision LCR meter. Scanning electron micrographs were acquired with a FEG-SEM (Jeol JSM-7500 FA).

III. RESULTS AND DISCUSSION

LSV at room temperature of platinum electrodes in PVdF/BMIM-BF_4 were carried out to evaluate the ESW of the solid electrolyte and is shown in Fig.2 dashed line; the full line represents NaCl 0.9% aqueous electrolyte reported for a comparison. Fig. 2 indicates that ESW is wide up to 4 V, allowing to test the actuators at potentials where no faradaic reactions occur.

The PVdF/BMIM-BF_4 electrolyte layer showed an electronic conductivity of $4.3*10^{-4}$ Scm^{-1}. The presence of the IL assures the ionic conductivity, estimated from a complex impedance plot (Nyquist plot) reported in Fig. 3 where the intercept on the real axis is the bulk resistance of the polymer electrolyte film. So the conductivity of the polymer electrolyte can be calculated from the equation 2,

$$\sigma=L/(AR) \tag{2}$$

where A is the area of electrode, L the thickness of the film, and R the bulk resistance from ac impedance at high frequency (inset of Fig. 3). The conductivity of $5.6*10^{-4}$ Scm^{-1} was obtained at the ambient temperature.

Fig. 4 reports cyclic voltammetries of a buckygel electrode taken starting from 100 mV/s up to 1000 mV/s and between -1.0V and +1.0V. The specific capacitance evaluated from the voltammetric discharges at 5 mVs^{-1} at RT by the slope of the electrode potential vs. integral over time of the current (not

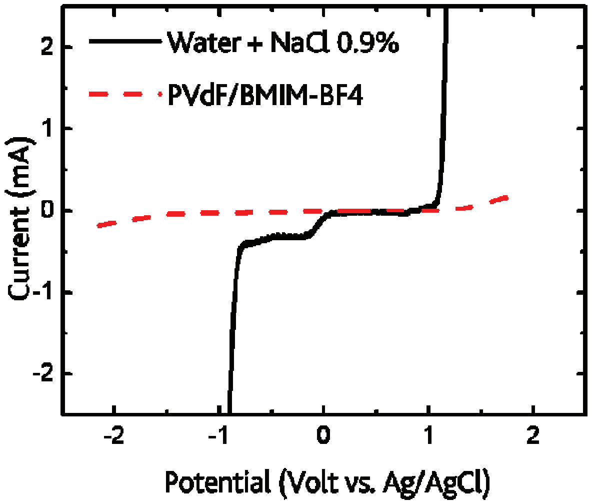

Figure 2. Linear sweep voltammetries at 5mV/s and room temperature of platinum electrodes in PVdF/ BMIM-BF_4 (dashed line) and NaCl based acqueous electrolyte (line).

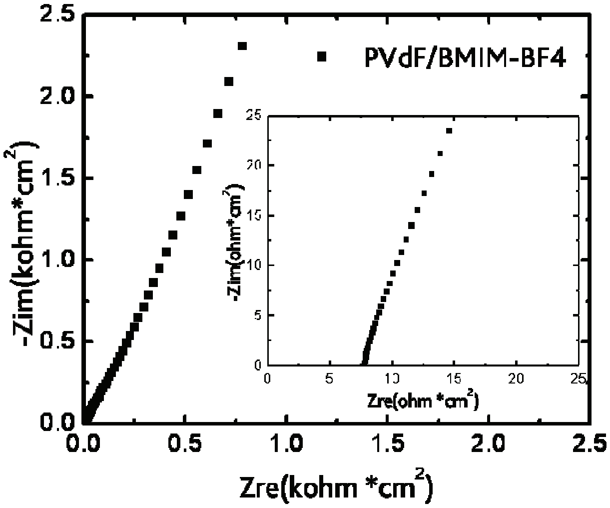

Figure 3. Nyquist plot at open circuit voltage in the 2 MHz to 100 mHz frequency range with 200mV ac perturbation and 10 points per decade acquisition of the electrolyte layer. The inset shows a magnification of the high frequency values.

shown here) is 10 F/g_{CNTs}.The capacitive properties of carbon nanotubes and the working principle of the device allow using it to eventually recover and store energy as in a super capacitor. Fig. 5 shows SEM images at different magnifications of the bucky-gel. Fig. 5a shows the surface structure of the composite material and in Fig. 5b, CNTs trapped in the polymeric matrix are well visible.

As suggested by Aida et al. [9] when a voltage is applied between the two electrodes $BMIM^+$ cations and BF_4^- anions in the electrolyte layer are transferred to the cathode and anode respectively and form a double layer with the charged nanotubes. This ion transport results in swelling of the cathode layer and shrinking of the anode layer and this drives the motion. Fig. 6 shows the displacement at 4V peak-to-peak during charge/discharge cycles at three different frequencies; 2Hz (line + circle), 1Hz (line + triangle) and 0.3Hz (line + square). An almost linear relation is found between the applied charge and the displacement of the device, it is shown in Fig. 7, where the linear fitting gives 7.0 ± 1.6 μm/mC. This suggests that the displacement of the cantilevers can be modulated by monitoring the amount of charge and this means that the actuation can be fairly well controlled. The maximum strain calculated using equation 1 is ca. 1% and this result is comparable with other works on SWCNTs based bucky-gel actuators [7-9].

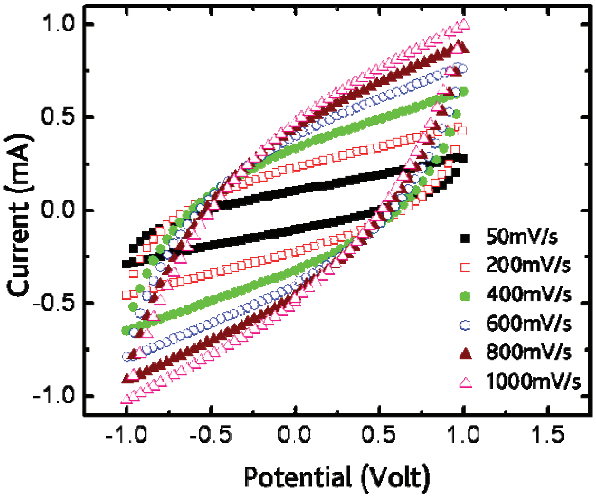

Figure 4. Cyclic voltammetries from 50 mV/s up to 1V/s of a bucky-gel electrode at room temperature while cycling between -1.0 V and +1.0 V.

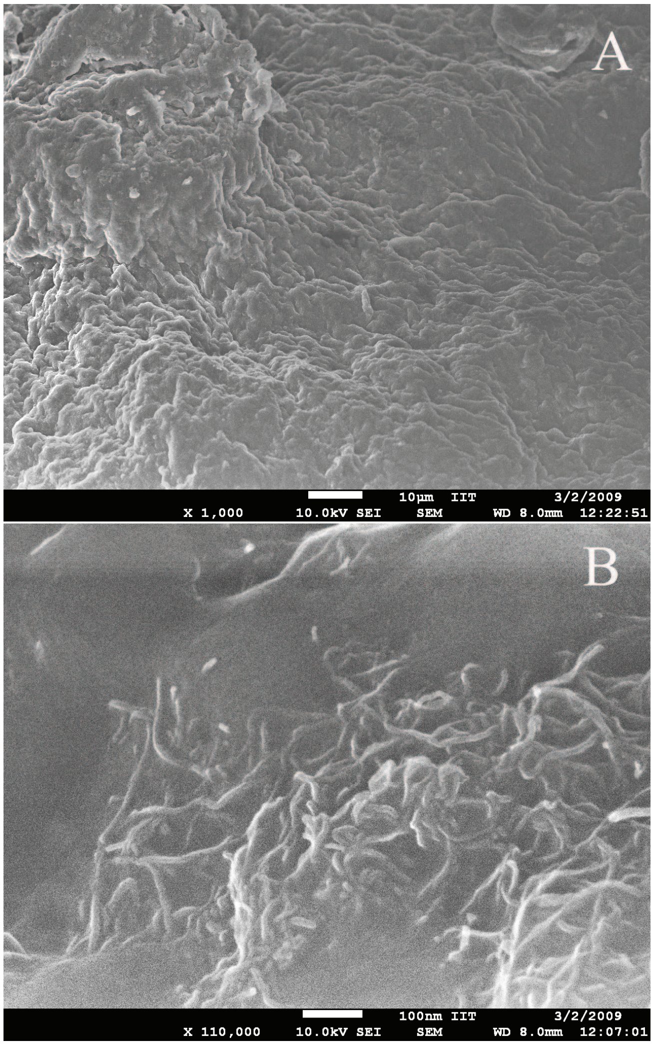

Figure 5. SEM images of bucky-gel electrode, (a) lower magnification and (b) higher magnification, CNTs are visible in the PVdF matrix.

IV. CONCLUSIONS

MWCNTs based bucky-gel actuators were successfully prepared using gel electrolyte layers sandwiched between bucky-gel electrodes. The electrochemical and electromechanical properties of the actuators were studied by cyclic voltammetries and potentiostatic steps techniques. A strain of ca. 1 % was achieved and this result is comparable with other works on SWCNTs based bucky-gel actuators [7-9]. The displacement of the cantilevers can be modulated by

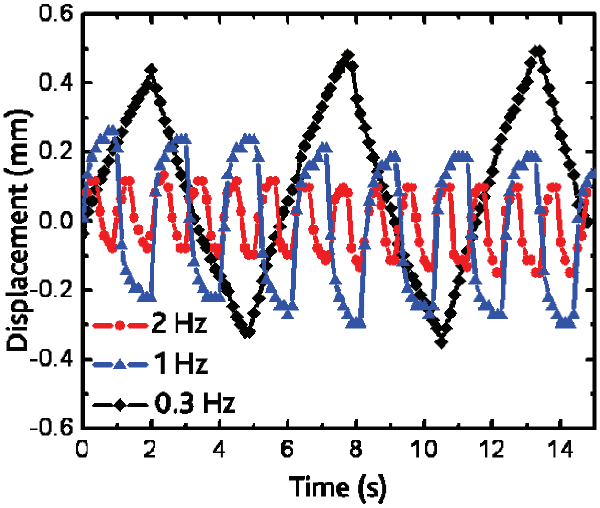

Figure 6 Displacement at 4V peak-to-peak during charge/discharge cycles at 2Hz (line + circle), 1Hz (line + triangle) and 0.3Hz (line + square).

monitoring the amount of charge and this means that the actuation can be fairly well controlled. The capacitive properties of carbon nanotubes and the working principle of the device allow using it to eventually recover and store energy as in a super capacitor. The solid gel electrolyte was also characterized by impedance spectroscopy, linear sweep voltammetry and four point probe measurement, showing a high conductivity, a wide ESW and enabling to work up to 4 Volt without faradaic reactions occurring.

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REFERENCES

[1] R. H. Baughman, C. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth and M. Kertesz, Science **184**, 1340 (1999).

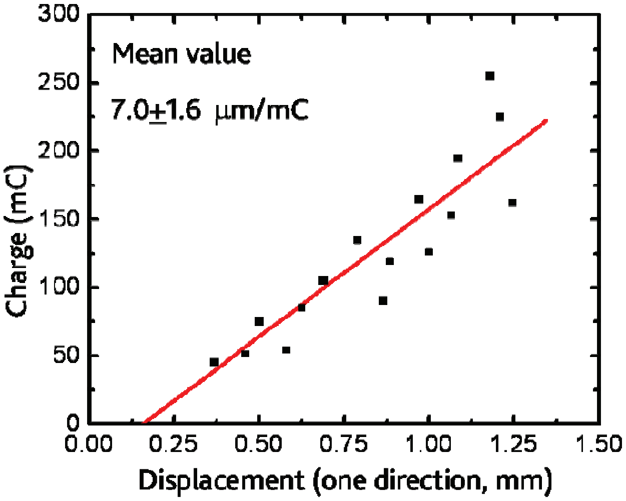

Figure 7. Almost linear relation found between the applied charge and the displacement of the cantilever, experimental dots (square) and linear fitting (line).

[2] J. D. W. Madden, J. N. Barisci, P. A. Anquetil, G. M. Spinks, G. G. Wallace, R. H. Baughman, I. W. Hunter Adv. Mater. **18,** 870 (2006).

[3] J. Fraysse, A. I. Minett, O. Jaschinsky, G. S. Duesberg, S. Roth, Carbon **40**, 1735 (2002).

[4] J. D. Madden, Science, **318,** 1094 (2007).

[5] T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, Science **300,** 2072 (2003).

[6] T. Fukushima, T. Aida, Chem. Eur. J. **13,** 5048 (2007) .

[7] T. Fukushima, K. Asaka, A. Kosaka and T. Aida, Angew. Chem. **117**, 2410 (2005).

[8] I. Takeuchi, K. Asaka, K. Kiyohara, T. Sugino, N. Terasawa, K. Mukai, T. Fukushima and T. Aida, Electrochim. Acta **54**, 1762 (2009).

[9] K. Mukai, K. Asaka, K. Kiyohara, T. Sugino, I. Takeuchi, T. Fukushima and T. Aida, Electrochim. Acta **53**, 5555 (2008).

[10] K. Mukai, K. Asaka, T. Sugino, K. Kiyohara, I. Takeuchi, N. Terasawa, D. N. Futaba, K. Hata, T. Fukushima and T. Aida, Adv. Mater. **20**, 1 (2009).