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Multi-walled carbon nanotubes plastic actuator

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Carbon nanotubes (CNTs) 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. A bimorph actuator composed of single-walled carbon nanotubes (SWCNTs), polyvinylidene difluoride (PVdF) and the ionic liquid (IL) 1-butyl 3-methylimidazolium tetrafluoroborate [BMIM][BF_4] with a polymer-supported internal IL electrolyte was previously demonstrated by Aida and coworkers. While several experiments were carried out using SWCNTs, PVdF and a number of ILs, the use of multi-walled carbon nanotubes (MWCNTs) instead of SWCNTs is, to our knowledge, a new result that will be presented here. Electrochemical characterizations by cyclic voltammetry (CV), and actuation tests performed applying a square wave of 4 V peak-to-peak at frequencies between 0.3 and 2 Hz are reported and discussed.

1 Introduction A new kind of actuator based on carbon nanotubes (CNTs) has been proposed as a 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 CNT 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 in 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 and coworkers [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 due to the possible specific interaction between the imidazolium ion component and the π–electronic nanotube surface [6–8]. This composite material was used to make a three layers bending actuator with a polymer-supported internal IL electrolyte layer which is sandwiched by bucky-gel electrode layers.

In this paper, we propose the use of multi-walled carbon nanotubes (MWCNTs)-based bucky-gels that are not subject to chirality-related restrictions on electrical properties and are significantly cheaper than single walled (SW) for preparing actuators. We report here the performance of a low-voltage driven electromechanical bending actuator composed of MWCNTs, the IL [BMIM][BF_4] and polyvinylidene difluoride (PVdF).

2 Experimental

2.1 Materials All chemicals were used as received from Nanocyl (MWCNTs, 95% C purity) and Fluka (PVdF $M_r = 530000$), (BMIM-BF_4, 97% purity), (tetrahydrofuran, 99.8% purity).

2.2 Preparation of the actuator The configuration of the cantilever actuator is shown in Fig. 1a, and it 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). Typically the electrolyte layer has a thickness of 0.1 mm and each of the two bucky-gel electrodes has a thickness of about 0.15 mm.

The bucky-gel electrode layers are composed of 30% of MWCNTs, 35% of PVdF and 35% of BMIM-BF_4 (molecular structure Fig. 1b), while the electrolyte includes 50% of BMIM-BF_4 and 50% of PVdF.

The mixtures were prepared as follows: for the electrodes 0.35 g of BMIM-BF_4 were grounded with 0.30 g MWCNTs with a mortar in an agata jar, 0.35 g PVdF dissolved in few drops of THF were added and the solution was stirred for 1 h.

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 h.

2.3 Displacement measurement Actuation tests were carried out by applying a square wave of 4 V peak-to-peak at frequencies between 0.3 and 2 Hz to a 17 mm × 2.5 mm sized actuator strip of 0.4 mm thickness clipped by two gold electrodes.

All the electrochemical measurements were performed with a PARSTAT 2273 potentiostat/galvanostat/frequency response analyser (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-gel electrode layers (ε) by using

$$\varepsilon = 2d\delta/(L^2 + \delta^2), \quad (1)$$

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 [8].

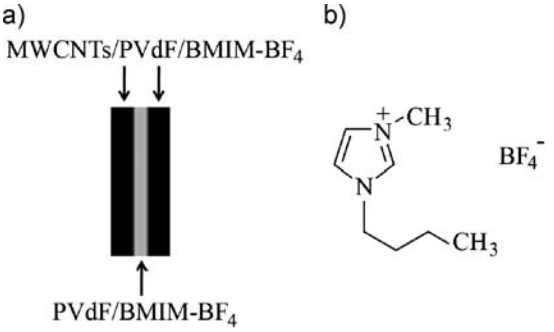

Figure 1 (a) Structure of the cantilever composed of a solid electrolyte layer sandwiched between bucky-gel electrode layers and (b) molecular structure of the IL BMIM-BF_4.

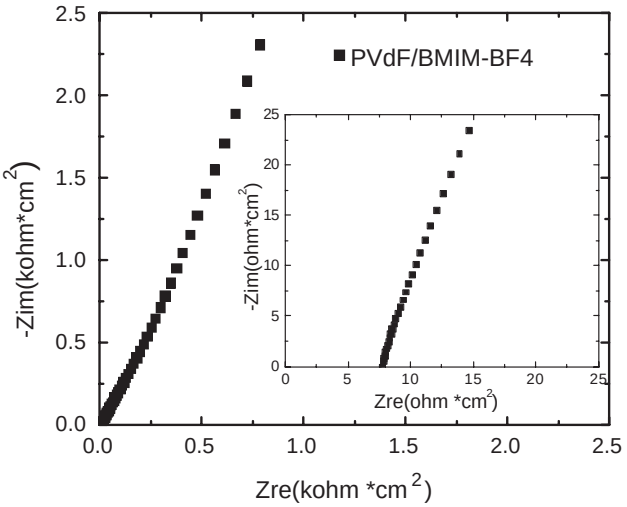

Figure 2 Nyquist plot at open circuit voltage in the 2 MHz to 100 mHz frequency range with 200 mV ac perturbation and ten points per decade acquisition of the electrolyte layer. The inset shows a magnification of the high frequency values.

2.4 Characterization of the electrode and electrolyte films The electronic conductivity of the 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 200 mV ac perturbation and ten 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. The cyclic voltammograms in the 5 mV/s to 1 V/s scan rate range at RT of the bucky-gel electrode were measured

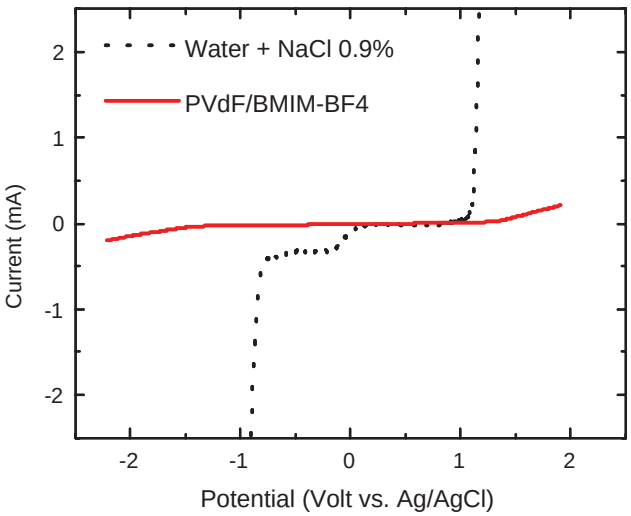

Figure 3 (online colour at: www.pss-b.com) Linear sweep voltammetries at 5 mV/s of PVdF/BMIM-BF_4 (solid line) and NaCl-based aqueous electrolyte (dotted line).

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 mV/s at RT by the slope of the electrode potential *vs* integral over time of the current. Scanning electron micrographs were acquired with a FEG-SEM (Jeol JSM-7500 FA).

3 Results and discussion The PVdF/BMIM-BF4 electrolyte layer showed an electronic conductivity of 4.3×10^{-4} S/cm; the presence of the IL assures the ionic conductivity, estimated by a Nyquist plot reported in Fig. 2 (value at high frequency, inset in Fig. 2), of 5.6×10^{-4} S/cm. The linear sweep voltammetries in the investigated electrolyte, reported in Fig. 3, indicate that its electrochemical stability window at RT is wide up to 4 V. This means that our actuator can work at 4 V peak-to-peak and this would be a great benefit because CNT-based actuator displacement is proportional to the applied voltage [1] and because no redox reactions could mean long life cycle.

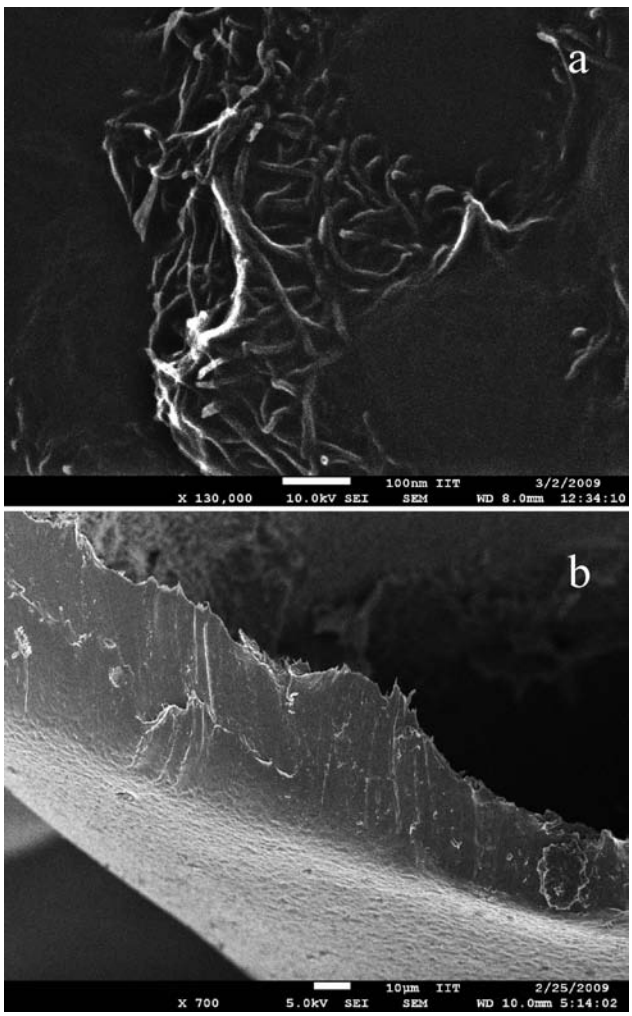

Figure 4 (a) SEM images of the bucky-gel electrode, where many nanotubes trapped in the PVdF matrix are visible. (b) Compact and homogeneous PVdF/BMIM-BF_4 electrolyte.

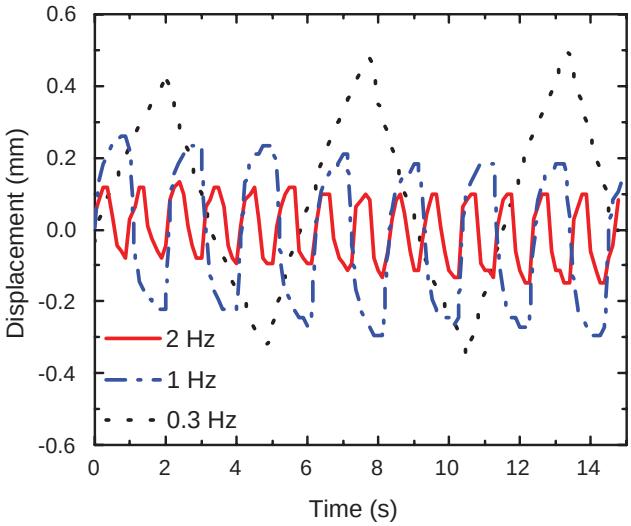

Figure 5 (online colour at: www.pss-b.com) Displacement at 4 V peak-to-peak during charge/discharge cycles at 2 Hz (solid line), 1 Hz (dash-dotted) and 0.3 Hz (dotted).

Figure 4 shows SEM images of the bucky-gel and electrolyte layer. In Fig. 4a, CNTs trapped in the polymeric matrix are well visible. The PVdF/BMIM-BF_4 layer shown in Fig. 4b appears homogeneous and compact.

As suggested by Aida and coworkers [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.

Figure 5 shows the displacement at 4 V peak-to-peak during charge/discharge cycles at three different

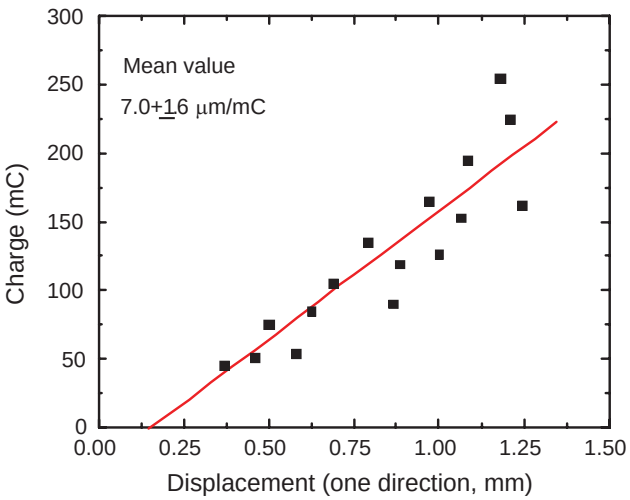

Figure 6 (online colour at: www.pss-b.com) Almost linear relation found between the applied charge and the displacement of the device, experimental dots (square) and linear fitting (line).

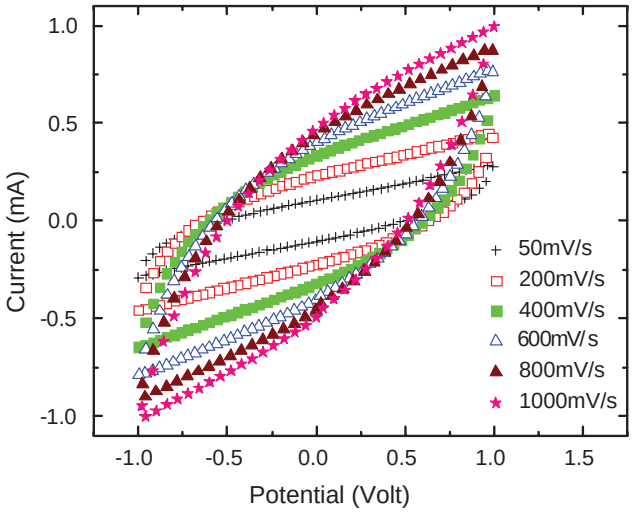

Figure 7 (online colour at: www.pss-b.com) Cyclic voltammetries at different scan rates of a bucky-gel electrode at RT between −1.0 and +1.0 V.

frequencies: 2 Hz (solid line), 1 Hz (dash-dotted) and 0.3 Hz (dotted).

An almost linear relation is found between the applied charge and the displacement of the device and it is shown in Fig. 6, where the linear fitting gives 7.0 + 1.6 μm/mC. This suggests that the displacement can be modulated in a quite precise way. The maximum strain calculated using Eq. (1) is approximately 1%. Figure 7 reports cyclic voltammetries of a bucky-gel electrode starting from 50 upto 1000 mV/s while cycling between −1.0 and +1.0 V. The specific capacitance evaluated from the voltammetric discharges at 5 mV/s at RT by the slope of the electrode potential *vs* integral over time of the current (not shown here) is 10 F/g of CNTs. The material has quite good capacitive properties that do not change much raising the scan rate; this fact suggests that this kind of device could eventually be used to recover and store energy as in a super-capacitor.

4 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, 10]. 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 capacitive properties of CNTs and the working principle of the device allow to use it to eventually recover and store energy as in a supercapacitor. The solid gel electrolyte was also characterized by impedance spectroscopy, linear sweep voltammetry and four-point probe measurement, showing a good conductivity, a wide electrochemical stability window and enabling to work up to 4 V without faradaic reactions occurring.

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