Sensors and Actuators B 173 (2012) 66–71

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Improved performance of an activated multi-walled carbon nanotube polymer actuator, compared with a single-walled carbon nanotube polymer actuator

Naohiro Terasawa*, Ken Mukai, Kinji Asaka

Health Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Article history:
Received 2 February 2012
Received in revised form 8 May 2012
Accepted 29 May 2012
Available online 19 June 2012

Keywords:
Polymer actuator
Rapid response
Large strain
Large maximum generated stress
MWCNT–NH_2

ABSTRACT

Actuators were developed using activated multi-walled carbon nanotube (MWCNT)–ionic liquid (IL) gel electrodes, and were compared with non-activated MWCNT- and single-walled carbon nanotube (SWCNT)-based actuators, in terms of their electrochemical and electromechanical properties. Furthermore, the effects of variations in the IL on the electrochemical and electromechanical properties of the activated MWCNT–NH_2/IL gel electrode actuators were investigated. The performance of the activated MWCNT–NH_2 polymer actuator surpassed that of the SWCNT actuator, in terms of the strain and maximum generated stress. For the MWCNT–NH_2 actuators, the strain and maximum generated stress were dependent on the IL species.

1. Introduction

Recently, much attention has been focused on soft materials that can directly transform electrical energy into mechanical work for a wide range of applications including robotics, tactile and optical displays, prosthetic devices, medical devices, and micro-electromechanical systems [1]. Low-voltage electroactive polymer (EAP) actuators, which can function quickly and are softly driven, are particularly useful, because they can be used as artificial muscle-like actuators for various bio-medical and human affinity applications [2,3]. We have previously reported [4–6] the first dry actuator that can be fabricated using 'bucky-gel' [7], a gelatinous room-temperature IL containing SWCNTs. The actuator has a bimorph configuration with a polymer-supported IL electrolyte layer sandwiched by polymer-supported bucky-gel electrode layers that allow quick and long-lived operation in air at low applied voltages. ILs have low volatility and exhibit high ionic conductivities and wide potential windows, which are advantageous for quick response actuators and high electrochemical stability components [8].

We previously reported the dependence of the electromechanical and electrochemical properties of actuators composed of polymer-supported bucky-gel electrodes and gel electrolyte layers on the IL, polymer and nanocarbon [6,9–12]. In addition, Biso and Ricci had reported a polymer-supported MWCNT–gel electrode for actuators containing an IL [13]. However, to the best of our knowledge, there was no MWCNT polymer actuator that surpasses the performance of SWCNT polymer actuators. SWCNTs are specially prepared compounds and are very expensive, while MWCNTs are very cheap and are commonly used in battery electrodes. Much attention has been focused on activated (acid treated) CNTs for electric double-layer capacitors (EDLCs), which have higher electrochemical capacitance than those based on non-activated CNTs [14]. Recently, we have reported that the performance of an activated (carboxyl functional group) MWCNT–COOH polymer actuator surpassed that of an SWCNT actuator, in terms of the strain and maximum generated stress; a common CNT MWCNT–COOH actuator can therefore be used to achieve good strain and maximum generated stress performance, without the use of specialized SWCNTs [15,16]. However, there have been no reports on the electrochemical and electromechanical properties of actuators containing activated (amino functional group) MWCNT–NH_2 polymer actuator.

In this work, we developed a polymer actuator using MWCNT–NH_2/IL gel electrodes; the electrochemical and electromechanical properties of this activated (amino functional group) MWCNT polymer actuator were compared with those of SWCNT and non-activated MWCNT polymer actuators. We investigated the effects of the IL species on the electrochemical and electromechanical properties of the MWCNT–NH_2/IL gel electrode actuators. The reasons for the superior performance of MWCNT–NH_2/IL actuators were also examined.

* Corresponding author. Tel.: +81 72 751 7914; fax: +81 72 751 8370.
E-mail address: terasawa-naohiro@aist.go.jp (N. Terasawa).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.05.092

Table 1
Average diameters and lengths for MWCNT–NH_2, MWCNTs and SWCNTs.

	Average diameter (nm)	Average length (μm)	–NH_2 functionalization (%)
NC3150 (MWCNT)	9.5	<1	–
NC3152 (MWCNT–NH_2)	9.5	<1	<0.5
SWCNT	~0.8–1.2	~0.1–1	–

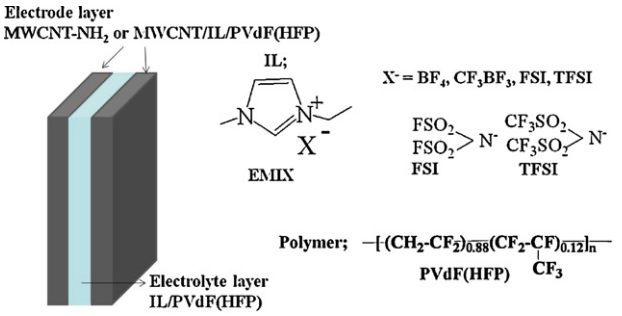

Fig. 1. Configuration of the polymer-supported MWCNT–NH_2/IL gel actuator, and molecular structures of ILs and polymer.

2. Experimental

2.1. Materials

Activated MWCNT–NH_2[1] and non-activated MWCNTs[1] (Nanocyl Inc.) were used as-received and the results of characterization are given in Table 1. SWCNTs[2] were used as received (purified HiPco™ SWCNTs, Unidym Inc.). The ionic liquids (ILs), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI[BF_4]; Fluka) 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMI[FSI]; Dai-ichi Kogyo seiyaku) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI[TFSI]; Merck), were used as received and their chemical structures are shown in Fig. 1. 1-Ethyl-3-methylimidazolium trifluoromethyltriluoroborate (EMI[CF_3BF_3]) were synthesized according to the literature [17] and their chemical structures are shown in Fig. 1. Other reagents (poly(vinylidene fluoride-*co*-hexafluoropropylene) PVdF(HFP); Kynar Flex 2801, Arkema Chemicals Inc.), methyl pentanone (MP; Aldrich), propylene Carbonate (PC; Aldrich), and dimethylacetamide (DMAc; Kishida Chemical Co. Ltd.) were used as received.

2.2. Preparation of the actuator film [9]

The configuration of the nanocarbon actuator is illustrated in Fig. 1. The polymer-supported bucky-gel electrode layer was typically composed of 30 wt% MWCNT–NH_2, 35 wt% EMI[BF_4] or EMI[TFSI], and 35 wt% PVdF(HFP), and was prepared as follows: 90 mg of MWCNT–NH_2, 105 mg of EMI[BF_4] or EMI[TFSI], and 105 mg of PVdF(HFP) in 9 mL of DMAc were dispersed using ultrasonication for more than 5 h to produce a gelatinous mixture. In the case of the non-activated MWCNTs and SWCNTs, a casting solution was obtained using the same amount of DMAc (9 mL). The electrode layer was fabricated by casting 1.6 mL of the electrode solution in a Teflon mold ($2.5 \times 2.5\,cm^2$) and evaporating the solvent. The solvent was then removed in vacuo at 80 °C. The thickness of the obtained electrode film was 70–80 μm. Gel electrolyte layers were then fabricated by casting 0.3 mL of solutions composed of each IL and PVdF(HFP) (0.5 mmol/100 mg) in a mixed solution composed of 1 mL of MP and 250 mg of PC in a Teflon mold ($2.5 \times 2.5\,cm^2$) followed by solvent evaporation, and removal of the solvent in vacuo at 80 °C. The thickness of the obtained gel electrolyte film was 20–30 μm. The actuator film was fabricated by hot-pressing (N4018-60, NPa System Co. Ltd) the electrode and electrolyte layers with the same IL and nanocarbon under 120 N, at 70 °C for 60 s). The typical thickness of the actuator film was 150–175 μm, which is smaller than the sum of the two electrodes and electrolyte layer, due to the reduction in thickness of each layer caused by hot-pressing.

2.3. Displacement measurement [18]

The actuator experiments were conducted using an applied triangular voltage to a $10 \times 1\,mm^2$ actuator strip clipped by two gold disk electrodes. The displacement, at a point 5 mm away (free length) from the fixed point, was continuously monitored from one side of the actuator strip by using a laser displacement meter (Keyence, LC2100/2220). A potentio/galvanostat (Hokuto Denko, HA-501G) and a waveform generator (Yokogawa Electric, FC 200) were used to activate the bucky-gel actuator. The electrical parameters were simultaneously measured. The measured displacement δ was transformed into the strain difference between two bucky electrode layers (ε) by using the following equation, on the assumption that the cross sections are plane planar at any position along the actuator, i.e., there is no distortion of the cross section:

$$\varepsilon = \frac{2d\delta}{L^2 + \delta^2} \quad (1)$$

where L is the free length and d is the thickness of the actuator strip [19].

2.4. Characterization of the electrode and electrolyte

The double-layer capacitance of the polymer-supported bucky-gel electrode (φ7 mm) was estimated by cyclic voltammetry (CV), which was measured using a two-electrode configuration with a potentiostat (Hokuto Denko, HSV-100). The electrical conductivities of the electrodes were evaluated using the four-probe DC current method, where a linear sweep wave of current was applied from outer probe electrodes, and the voltage was measured by inner probe electrodes. Current–voltage curves were obtained using a potentio/galvanostat (Hokuto Denko, HA-151) with a waveform generator (Yokogawa Electric, FC 200). Young's moduli for the electrodes were estimated from the stress–strain curve, which was measured using a thermal stress–strain instrument (Seiko, TMA/SS 6000).

3. Results and discussion

Fig. 2 shows the CV for a cell system composed of an MWCNT–NH_2/EMI[TFSI] electrolyte sandwiched between two bucky-gel electrode layers (applied triangular voltage = ±0.5 V, sweep rate = 1 mV s^{-1}). This CV showed a capacitive wave at a sweep rate of 1 mV s^{-1}. The CVs for the other CNTs and ILs with different compositions also showed capacitive waves.

Fig. 3 shows voltage–current (V–I) ((a)10 Hz and (b) 1 Hz, ±2 V and 5 cycles) applied to the MWCNT–NH_2/EMI[TFSI]. At a triangular voltage of 10 Hz, the V–I curve showed a capacitive wave. In the case of other ILs, the V–I curves showed capacitive waves.

In previous paper [20], non-polymer actuators with a high-speed response under a high-frequency applied square-wave

[1] MWCNT–NH_2 and MWCNT (Nanocyl Inc.) http://www.nanocyl.com/en/Products-Solutions/Products/Research-Grades/Thin-Multi-Wall-Carbon-Nanotubes (accessed 17.01.12).
[2] SWCNT (high-purity HiPco™ SWCNTs, Unidym Inc.) http://www.unidym.com/products/materials.html (accessed 17.01.12).