Sensors and Actuators B 139 (2009) 624–630

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Electrochemical properties and actuation mechanisms of actuators using carbon nanotube-ionic liquid gel

Naohiro Terasawa[a,*], Ichiroh Takeuchi[a], Hajime Matsumoto[b]

[a] Research Institute for Cell Engineering, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
[b] Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Article history:
Received 19 January 2009
Received in revised form 19 March 2009
Accepted 24 March 2009
Available online 31 March 2009

Keywords:
Single-walled carbon nanotube (SWNT)
Ionic liquid (IL)
Actuator
Gels
$EMI[N(CN)_2]$
van der Waals volume

ABSTRACT

In this study, we investigated the dependence of anionic species of ionic liquid (IL) on electrochemical properties and actuation mechanism of the actuator using the carbon nanotube-ILs gel electrode. 1-Ethyl-3-methylimidazolium (EMI^+) was selected as a cation for ILs. As a result, DCA ($[N(CN)_2]^-$) anion performed much better as an actuator using polymer-supported bucky-gel electrode containing internal IL. In low frequencies, the generated strain of polymer-supported bucky-gel electrode of the actuator depended on the size of anion of IL. It, which was the small van der Waals volumes of IL anions (BF_4^- and $[N(CN)_2]^-$), was considered to be large for the usual bending mechanism and the charge injection, in addition, for other bending mechanism of the intercalation/deintercalation into the diameter of the single-walled carbon nanotube (SWNT) and into the SWNT bundles. In addition to that, we compared the actuator using polymer-supported bucky-gel electrode to the actuator using non-polymer-supported bucky-gel electrode. As a result, the generated strain of polymer-supported bucky-gel electrode of the actuator was considered to be attributed to the volume-change for polymer-IL gel of the cathode and that of the anode.

1. Introduction

Recently, much attention has been focused on soft materials that can directly transform electrical energy into mechanical work, because they allow a wide range of applications including robotics, tactile and optical display, prosthetic devices, medical devices, micro-electromechanical systems and so forth [1]. Especially, electromechanical polymer actuators, which can work quickly and softly driven by low voltage are very useful, since they can be used as artificial muscle-like actuators for various bio-medical and human affinity applications [2,3]. In previous papers [4–6], we have reported the first dry actuator that can be fabricated using 'bucky-gel' [7], a gelatinous room-temperature IL containing SWNTs. Our actuator has a bimorph configuration with a polymer-supported internal IL electrolyte layer sandwiched by polymer-supported bucky-gel electrode layers, which allows the quick and long-lived operation in the air at low applied voltages. ILs are less-volatile and show high ionic conductivities and wide potential windows, which are advantageous for the quick response in the actuation and the high electrochemical stability of the components, respectively [8].

Conductive polymer actuators and ionic polymer metal composites (IPMCs) using ILs as electrolytes were reported by several authors [8–12]. In our previous reports, the dependence of cationic species of ILs on the electromechanical and electrochemical properties of the bucky-gel actuators composed of the bucky-gel electrode and the gel electrolyte layers containing internal five IL cations have been reported [6]. We measured the frequency dependence of the displacement response of the bucky-gel actuator and it can be successfully simulated by the electrochemical kinetic model. Both the steric repulsion effects due to the transfer of ions to the electrode and 'the charge injection' [13] gives the bending motion of the bucky-gel actuator. The volume-changes of the cathode and anode change according to the sizes of the cation and anion, respectively. In high frequencies, the ion size gives the dependence of the bending motion of the bucky-gel actuator on the internal cationic species. The actuator containing $EMIBF_4$ shows better performance. However, the performance of the actuator using $EMIBF_4$ was not enough to apply actual applications, and the anion dependence of electromechanical behavior of the carbon nanotube actuator in various ILs has not yet been reported. Furthermore, the exact van der Waals volume of anion and cation species for ILs is not estimated.

The purpose of this paper is to prepare the bucky-gel actuators composed of the bucky-gel electrode and the gel electrolyte layers containing various internal IL anions of EMI series, and to study their electromechanical and electrochemical properties for exploring the details of the actuation mechanism, and to investigate much better performance of the actuator containing internal IL anions of EMI series. In particular, it is considered that it is

* Corresponding author. Tel.: +81 727 51 7914; fax: +81 727 51 8370.
E-mail address: terasawa-naohiro@aist.go.jp (N. Terasawa).

0925-4005/$ – see front matter
doi:10.1016/j.snb.2009.03.057

important to investigate the relation between the generated strains of the bucky-gel electrode of the actuator and the ion size of IL anion. In addition to that, we compare the actuator using polymer-supported bucky-gel electrode containing three kinds of internal ILs to the actuator using non-polymer-supported bucky-gel electrode containing three kinds of internal ILs, and investigated the role of PVdF(HFP)–IL gel in the generated strain.

2. Experimental

2.1. Materials

ILs used were 1-ethyl-3-methylimidazolium dicyanamide (EMI[N(CN)]$_2$) (MW = 177.21), 1-ethyl-3-methylimidazolium bis (fluoromethylsulfonyl)imide (EMIFSI) (MW = 291.29), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF$_4$) (MW = 197.97), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMICF$_3$SO$_3$) (MW = 260.23) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) (MW = 391.31) and 1-ethyl-3-methylimidazolium bis(pentafluoromethylsulfonyl)imide (EMIPFSI) (MW = 491.33), of which the chemical structures are shown in Fig. 1. Imidazolium-based ILs were from Fluka or Dai-ichi Kogyo Seiyaku Co., Ltd., which were used as received. Other reagents were used as received from Carbon Nanotechnologies Inc. (high-purity HiPco^{TM} SWNTs), Arkema Chemicals Inc. (PVdF(HFP): Kynar Flex 2801), Aldrich (methyl pentanone (MP) and propylene carbonate (PC)), Kishida Chemicals Co. (Dimethylacetamide) (DMAc).

2.2. Preparation of the actuator film

The configuration of our bucky-gel actuator is illustrated in Fig. 2. Typically, the polymer-supported bucky-gel electrode layer composed of 20 wt% of SWNTs, 48 wt% of EMIBF$_4$ and 32 wt% of PVdF(HFP) was prepared as follows. The mixture of 50 mg of SWNTs, 120 mg (0.6 mmol) of EMIBF$_4$ and 80 mg of PVdF(HFP) in 9 ml DMAc was dispersed in ultrasonic bath for more than 24 h. Then, a gelatinous mixture composed of SWNTs, EMIBF$_4$ and PVdF(HFP) in DMAc was obtained. In the case of the other ILs, the casting solution was obtained by mixing 0.6 mmol of an IL with the same amount of other components in 9 ml of DMAc. The electrode layer was fabricated by casting 1.6 ml of the electrolyte solution in the Teflon mold (an area of 2.5 cm × 2.5 cm) and evaporating the solvent, perfectly. The thickness of the obtained electrode film was 70–80 μm. The gel electrolyte layers were fabricated by casting 0.3 ml of the 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 the Teflon mold (an area of 2.5 cm × 2.5 cm) and evaporating the solvent, perfectly. The thickness of the obtained gel electrolyte film was 20–30 μm. An actuator film was fabricated by hot-pressing the electrode and electrolyte layers which have the same internal IL. The thickness of the actuator film was 150–175 μm, which are smaller than the sum of those of two-electrode and one electrolyte layers, since the thickness of each layer decreases by being hot-pressed. Fig. 3 shows the schematic representation of the fabrication method of actuator film; hot-pressing the electrode and electrolyte layers which were prepared by casting the solution and evaporating the solvent perfectly. Typically, the non-polymer-supported bucky-gel electrode layer composed of 29 wt% of SWNTs and 71 wt% of EMIBF$_4$ was prepared as mentioned.

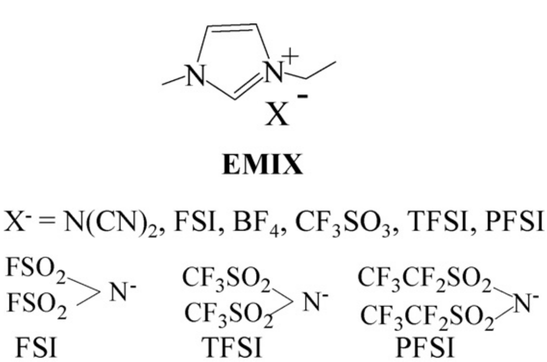

Fig. 1. Molecular structure of the ionic liquids used.

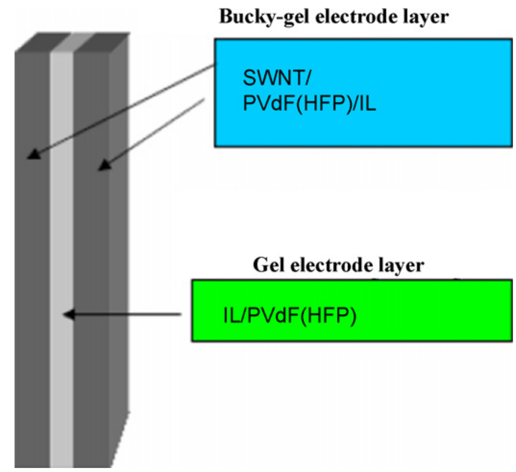

Fig. 2. Configuration of the polymer-supported bucky-gel actuator.

2.3. Displacement measurement

As shown in Fig. 4, the actuator experiments were conducted by the applied triangle voltages to a 10 mm × 1 mm sized 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 model LC2100/2220). A Hokuto Denko Potentio/Galvanostat model with a YOKOGAWA ELECTRIC model FC 200 waveform generator was used for activating the bucky-gel actuator. The electric 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 at

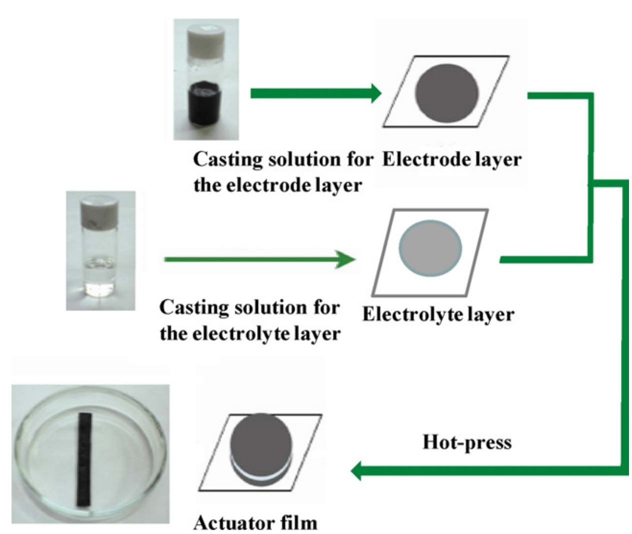

Fig. 3. Schematic drawing of the preparation method of the bucky-gel actuator by hot-pressing the electrolyte film sandwiched by two-electrode films.