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Electrochemical and electromechanical properties of carbon black/carbon fiber composite polymer actuator with higher performance than single-walled carbon nanotube polymer actuator

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ABSTRACT

The electrochemical and electromechanical properties of poly(vinylidene fluoride-*co*-hexafluoropropylene) based actuators using carbon black (CB)/vapor grown carbon fiber (VGCF)/ionic liquid (IL) composite gel electrodes formed without ultrasonication were compared with those of actuators using only CB or VGCF. The double-layer capacitance of the CB/VGCF/IL electrodes was larger than that of the CB/IL electrodes and increased with VGCF content. The amount of strain exhibited by the CB/VGCF/IL actuators was also larger than that for the CB/IL actuators, with the highest strain being produced for an actuator with a CB:VGCF ratio of 1:1. This was slightly larger than that for a polymer actuator using single-walled carbon nanotubes (SWCNTs), indicating that the proposed actuators exhibit sufficiently high performance for real-world applications without the need for expensive SWCNTs. Furthermore, the frequency dependence of the displacement response of the CB/VGCF/IL polymer actuators was successfully simulated using an electrochemical kinetic model similar to that for SWCNT-based actuators. The results yielded the strain in the low-frequency limit and the time constant of the response.

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 actuators that can respond 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 a dry actuator [4–6] that can be simply fabricated by layer-by-layer casting of ‘bucky-gel’ [7], a gelatinous room-temperature ionic liquid (IL) containing single-walled carbon nanotubes (SWCNTs). The actuator has a bimorph configuration with a polymer-supported IL electrolyte layer sandwiched between 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 components with high electrochemical stability [8].

We previously reported the dependence of the electromechanical and electrochemical properties of such actuators on the type of IL, nanocarbon and polymer used [6,9–12]. We have previously speculated a bending mechanism [5]. When a voltage is applied between two electrode layers, the cations and anions in the gel electrolyte layer are transferred to the cathode and anode layers, respectively, and an electric double layer is formed with negatively and positively charged nanotubes. Such ion transport most likely results in swelling of the cathode layer and shrinkage of the anode layer.

Furthermore, we have recently shown that polymer actuators containing activated multi-walled carbon nanotubes (MWCNTs), or a combination of non-activated MWCNTs and a metal oxide surpassed the performance of SWCNT-based actuators in terms of strain and maximum generated stress [13–15].

SWCNTs require special preparation and are very expensive, while carbon black (CB) and vapor grown carbon fiber (VGCF) are very cheap. CB is routinely used as conductive particles in many types of batteries and supercapacitor electrodes, and has already been used as an electrode material in supercapacitors [16]. However, since the capacitance of CB is too low for use in an actuator,

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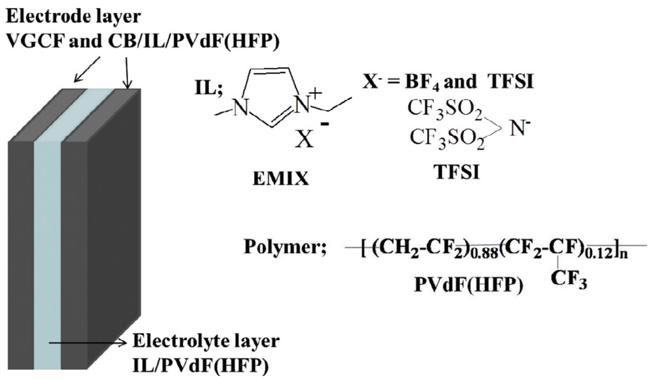

Fig. 1. Configuration of CB/VGCF/IL polymer actuator and the molecular structures of the ILs and polymer used.

we have previously reported a method of increasing its capacitance by the addition of MnO_2 [17].

VGCF is specifically designed to enhance the electrical and thermal properties of high-performance materials. A disadvantage of using SWCNTs in actuators is their poor dispersibility. In contrast, VGCF exhibits good dispersibility, together with high electrical conductivity and mechanical strength. However, its main disadvantage as an actuator material is its low capacitance [11]. Recently, we have reported that polymer actuators containing a mixture of VGCF and a metal oxide, formed without ultrasonication, surpassed the performance of a SWCNT-containing actuator in terms of the strain produced [18].

Optimizing the performance of the CB/VGCF/IL polymer actuators requires controlling the amount of CB and VGCF. To compete with the performance of SWCNT-based polymer actuators, we consider that the capacitance, electrical conductivity and Young's modulus for the CB/VGCF/IL polymer electrode is important factor for the high strain value.

In a previous study [6], we investigated the voltage–current and voltage–displacement characteristics of a bucky-gel actuator by applying a triangle waveform voltage of various frequencies. In order to quantitatively describe the frequency dependence of the strain generated in the actuator, we proposed an electrochemical equivalent circuit model consisting of the lumped resistance and capacitance of the electrode layer and the lumped resistance of the electrolyte layer.

In the present work, we developed an actuator that uses polymer-supported CB/VGCF/IL composite gel electrodes, and compared its electrochemical and electromechanical properties with those of polymer actuators that use only CB or VGCF.

2. Experimental

2.1. Materials

The CB (DENKA BLACK HS-100, Denki Kagaku Kogyo Inc.) and VGCF (VGCF-X, Showa Denko Co. Ltd.) were used as received. The CB was found to have a particle size of 48 nm and a surface area of 39 m^2/g. The VGCF had a fiber diameter of 10–15 nm, an average fiber length of 3 μm, and a surface area of 270 m^2/g. The ILs, 1-ethlyl-3-methylimidazolium tetrafluoroborate (EMI[BF_4]; Fluka) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMI[TFSI]; Merck), were used as received 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 CB/VGCF actuator is illustrated in Fig. 1. The combined CB + VGCF content was 20 wt% and CB:VGCF ratios of 1:0, 3:1, 1:1, 1:3, and 0:1 were used. The composition of the actuators was 20 wt% CB + VGCF, 48 wt% IL, and 32 wt% PVdF(HFP), and they were prepared using the following method. Fifty mg of CB + VGCF, 120 mg of IL and 80 mg of PVdF(HFP) were added to 9 mL of DMAc, and the mixture was stirred for more than 2 days until it became gelatinous. The electrode layer was fabricated by casting 1.6 mL of the electrode solution in a Teflon mold (2.5 × 2.5 × 0.7 cm^3) and evaporating the solvent. The residual solvent was then completely removed by heating *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 containing the IL and PVdF(HFP) (0.5 mmol/100 mg) in a mixed solution containing 1 mL of MP and 250 mg of PC in a Teflon mold (2.5 × 2.5 cm^2). This was again followed by solvent evaporation and complete solvent removal *in vacuo* at 80 °C. The thickness of the obtained gel electrolyte film was 20–30 μm. The actuator films were fabricated by hot pressing electrode and electrolyte layers containing the same IL. The typical thickness of an actuator film was 150–175 μm, which is less than the sum of the original layer thicknesses due to contraction during the hot-pressing process at 70 °C.

2.3. Displacement measurement [19]

The actuator experiments were conducted using an applied triangular voltage to a 10 × 1 mm^2 actuator strip clipped by two gold 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:

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

where L is the free length and d is the thickness of the actuator strip [20].

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). The morphology of the electrode film was observed by using scanning electron microscope (SEM) with JEOL JSM-6510.

3. Results and discussion

Fig. 2 shows the double-layer capacitance C (the gravimetric capacitance of the nanocarbon, $C_{CB+VBCF}$ = *C/(weight of the*