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The effects of Li salts on the performance of a polymer actuator based on single-walled carbon nanotube-ionic liquid gel

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ABSTRACT

The effects of Li salts (Lithium tetrafluoroborate (Li[BF_4]) and Lithium bis(trifluoromethanesulfonyl)imide (Li[TFSI])) on the electrochemical and electromechanical properties of an actuator using a polymer-supported single-walled carbon nanotube (SWCNT)-ionic liquid (IL) gel electrode were investigated. The ionic conductivities of the gel electrolyte layers with molar ratios of Li[BF_4]/1-ethlyl-3-methylimidazolium tetrafluoroborate (EMI[BF_4]) = 0.1 and 0.5, and Li[TFSI]/1-ethlyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI[TFSI]) = 0.1 and 0.3 were higher than those containing only EMI[BF_4] and only EMI[TFSI], respectively. We found a large capacitance value 65–96 F/g at a slow sweep rate 1 mV s^{-1}. The actuator containing Li salt/IL performed much better than that containing only IL. It is considered that the higher ionic conductivity of the gel electrolyte layer containing Li salt/IL produces the quick response actuator, and that the large capacitance gives a large generated strain.

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, low-voltage electroactive polymer (EAP) actuators, which can work quickly and softly driven 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 ionic liquid (IL) containing single-walled carbon nanotubes (SWCNTs). Our actuator has a configuration with a polymer-supported internal IL electrolyte layer sandwiched by polymer-supported bucky-gel electrode layers, which allow 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].

In our previous reports, the dependence of IL species on the electromechanical and electrochemical properties of the bucky-gel actuators composed of the polymer-supported bucky-gel electrode and the gel electrolyte layers have been reported [6,9]. 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' [10] gives the bending motion of the bucky-gel actuator. The generated strain of the polymer-supported bucky-gel electrode of the actuator is considered to be attributed to the volume-change for polymer-IL gel of the cathode and that of the anode [9]. In addition to that, we show that polymer-IL gel of the electrolyte is important factor in the field of the low-voltage electroactive polymer (EAP) actuator [11]. However, the performance of the actuators using only 1-ethlyl-3-methylimidazolium tetrafluoroborate (EMI[BF_4]) and only 1-ethlyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide (EMI[TFSI]) was not enough to apply actual applications (e.g. tactile display).

While, rechargeable Li batteries are a ubiquitous energy device that is being used worldwide in many types of portable electronic equipment. In the state-of-the-art technologies of 4V-class rechargeable Li batteries, a mixture of organic aprotic solvents and the conducting salt lithium hexafluorophosphate ($LiPF_6$) is generally used as a non-aqueous electrolyte. Moreover, much attention has been focused on the polymer battery using Li ion polymer gel electrolyte [12]. We pay attention to an electrode and electrolyte for a high-energy density device, such as an EAP actuator and electrochemical capacitor using Li salt/IL. It is expected that the ionic conductivity of the gel electrolyte layer containing Li salt/IL is higher than that containing only IL, and that the double-layer capacitance of

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the polymer-supported bucky-gel electrode containing Li salt/IL is larger than that containing only IL. Furthermore, it is expected that the higher ionic conductivity of the gel electrolyte layer containing Li salt/IL produces the quick response actuator, and that the large capacitance gives the large generated strain in the actuator.

In this paper, we investigated the effect of Li salts (Li[BF_4], Li [TFSI]) on electrochemical and electromechanical properties of the actuator using the polymer-supported SWCNT-IL gel electrode (viz. "using the polymer-supported bucky-gel electrode").

2. Experimental

2.1. Materials

Li salts used were Lithium tetrafluoroborate (Li[BF_4]) and Lithium bis(trifluoromethanesulfonyl)imide (Li[TFSI]), of which the chemical structures are shown in Fig. 1. ILs used were 1-ethlyl-3-methyl-imidazolium tetrafluoroborate (EMI[BF_4]) and 1-ethlyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (EMI[TFSI]), of which the chemical structures are shown in Fig. 1. Li[BF_4] and Li[TFSI] were from Kishida Chemical, Co. Ltd., which were used as received. EMI[BF_4] and EMI[TFSI] were from Fluka and Merck, Co. Ltd., which were used as received. Other reagents were used as received from Carbon Nanotechnologies Inc. (high-purity HiPco™ SWCNTs), Arkema Chemicals Inc. (poly(vinylidene fluoride-*co*-hexafluoropropylene (PVdF(HFP)): Kynar Flex 2801), Aldrich (Methyl Pentanone (MP), Propylene Carbonate (PC)), Kishida Chemical Co. Ltd. (Dimethylacetamide) (DMAc).

2.2. Preparation of the actuator film [9]

The configuration of our bucky-gel actuator is illustrated in Fig. 1. Typically, the polymer-supported bucky-gel electrode layer composed of 19.6 wt% of SWCNTs, 2.2 wt% of Li[BF_4], 46.9 wt% of EMI[BF_4] and 31.3 wt% of PVdF(HFP) was prepared as followed. The mixture of 50 mg of SWCNTs, 5.68 mg (0.06 mmol) of Li[BF_4], 120 mg (0.6 mmol) of EMI[BF_4] and 80 mg of PVdF(HFP) in 9 ml DMAc was dispersed in ultrasonic bath for more than 5 h. Then, a gelatinous mixture composed of SWCNTs, Li[BF_4], EMI[BF_4] and PVdF (HFP) in DMAc was obtained. In the case of Li[TFSI], the casting solution was obtained by mixing 0.6 mmol of EMI[TFSI] 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 × 2.5 cm^2) and evaporating the solvent, finally, the solvents removed *in vacuo*. at 80 °C, perfectly. The thickness of the obtained electrode film was 70–80 μm. The gel electrolyte layer were fabricated by casting 0.5 ml of the solutions composed of Li salts (Li[BF_4]; 0.1 mmol/9.47 mg), IL (EMI[BF_4]; 1 mmol/200 mg) and PVdF(HFP) (200 mg) in a mixed solution composed of 6 ml of MP and 500 mg of PC in the Teflon mold (an area of 2.5 × 2.5 cm^2) and evaporating the solvent, the solvents removed *in vacuo*. at 80 °C, perfectly. The thickness of the obtained gel electrolyte film was 20–30 μm. In the case of Li[TFSI], the gel electrolyte layer were fabricated by casting 0.5 ml of the solutions composed of Li salts (Li[TFSI]; 0.1 mmol), IL (EMI[TFSI]; 1 mmol) and PVdF(HFP) (200 mg) in a mixed solution composed of 6 ml of MP and 500 mg of PC in the Teflon mold (an area of 2.5 × 2.5 cm^2) and evaporating the solvent, finally, the solvents removed *in vacuo*. at 80 °C, perfectly. An actuator film was fabricated by hot-pressing the electrode and electrolyte layers which have the same internal IL (70 °C, 120 N, 60 s). 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.

2.3. Displacement measurement [11]

The actuator experiments were conducted by the applied triangle voltages to a 10 × 1 mm^2 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 any position along the actuator: there is no distortion of the cross-sections:

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

where L is the free length and d is the thickness of the actuator strip [13].

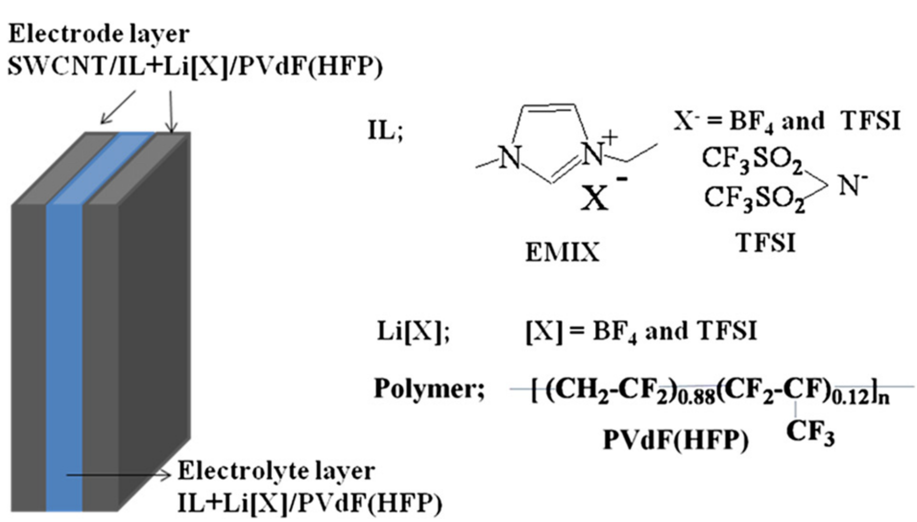

Fig. 1. Configurations of a polymer-supported SWCNT-IL gel actuator, and molecular structures of ionic liquids, Li salts and a polymer used.

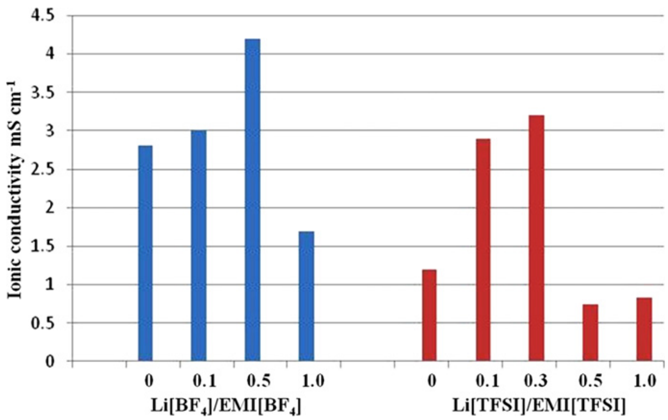

Fig. 2. The ionic conductivities of gel electrolyte layers with various molar ratios of Li[BF_4]/EMI[BF_4] and Li[TFSI]/EMI[TFSI]. (The data of Li[BF_4]/EMI[BF_4] = 0 and Li[TFSI]/EMI[TFSI] = 0 were quoted from ref. [9]).

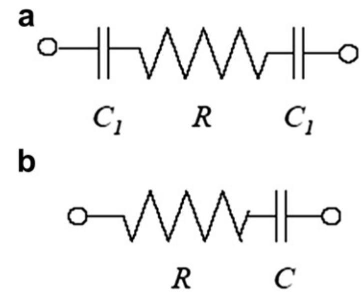

Fig. 4. Equivalent circuit model of the bucky-gel actuator. (a) The model composed of the two double-layer capacitance C_1 and the ionic resistance R. (b) The model in which the double-layer capacitance is represented by $C = C_1/2$.

2.4. Characterization of the electrode, electrolyte and actuator film

The double-layer capacitance of the polymer-supported bucky-gel electrode (φ7 mm) was estimated by cyclic voltammogram (CV), which was measured by two-electrode configuration using a Hokuto Denko Model HSV-100. The conductivity of the gel electrolyte layer was measured by impedance measurement, which was measured by Solatron 1250 Impedance Analyzer.

3. Results and discussion

Fig. 2 shows the ionic conductivity κ (=(thickness/(R × Area)) against Li salt/IL. The ionic conductivity of the gel electrolyte layer depended on the molar ratio of Li salt/IL. Furthermore, the ionic conductivities of the gel electrolyte layers with the molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5, and Li[TFSI]/EMI[TFSI] = 0.1 and 0.3 were higher than those containing only EMI[BF_4] and only EMI[TFSI], respectively. This result is considered to attribute that the van der Waals volume of Li cation is smaller than that of [EMI] cation. However, the ionic conductivities of the gel electrolyte layers with the molar ratios of Li[BF_4]/EMI[BF_4] = 1.0 and Li[TFSI]/EMI[TFSI] = 0.5 and 1.0 are lower than those containing only EMI[BF_4] and only EMI[TFSI], respectively. These results are considered that the ionic conductivity of the gel electrolyte depends on other factors (e.g. the diffusion coefficient of the gel electrolyte).

It is well-known that the SWCNTs have extraordinary mechanical [14] and electrochemical [15,16] properties. Due to these properties, SWCNTs are promising materials for electrochemical actuators based on the double-layer electrostatic mechanism [17]. In this respect, the bucky-gels are soft composite materials of SWCNTs in imidazolium ion-based ILs, where the heavily entangled nanotube bundles are exfoliated by the cation-π interaction on the SWCNT surfaces to give much finer bundles [18]. Hence, the bucky-gel electrode layer prepared by the ultrasonic dispersion method has large electric double-layer capacitance, which gives the large actuation. Moreover, we pay attention to the electrode for high-energy density device, such as an electrochemical capacitor using Li salt/IL. It is expected that double-layer capacitance of the polymer-supported bucky-gel electrode containing Li salt/IL is larger than that containing only IL.

In order to confirm this, we measured the cyclic voltammetry of the two-electrode configuration composed of PVdF(HFP)/Li salt/IL gel sandwiched by the two same polymer-supported bucky-gel electrodes. Fig. 3 shows the cyclic voltammogram of the cell system composed of Li salt/IL electrolyte sandwiched by two bucky-gel electrode layers with a molar ratio of Li[BF_4]/EMI[BF_4] = 1.0 (the applied triangle voltage: ±0.5 V, sweep rate = 1 mV s^{-1}). Basically, CV shows the capacitive wave at this sweep rate. The CVs with other molar ratios of Li[BF_4]/EMI[BF_4] and Li[TFSI]/EMI[TFSI] (the applied triangle voltage: ±0.5 V, sweep rate = 1 mV s^{-1}) show the capacitive wave, basically.

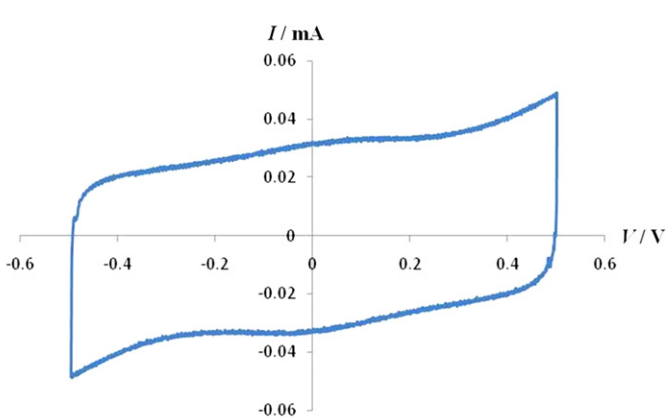

Fig. 3. The Cyclic voltammogram of the cell system composed of Li[BF_4]/EMI[BF_4] electrolyte sandwiched by two bucky-gel electrode layers with molar ratio of Li[BF_4]/EMI[BF_4] = 1.0 (the applied triangle voltage: ±0.5 V, Sweep rate = 1 mV s^{-1}).

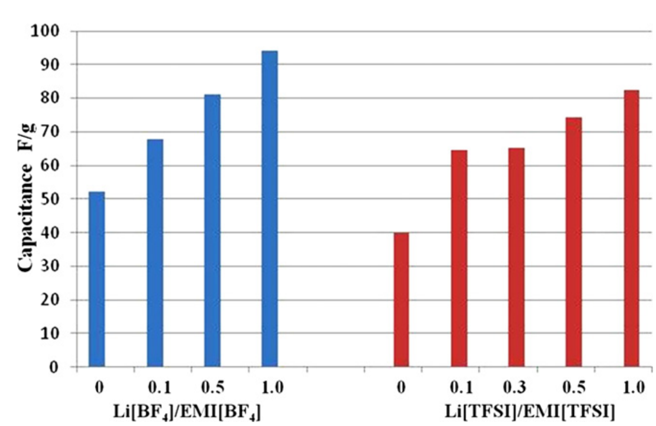

Fig. 5. The gravimetric capacitance C_{SWCNT} of the SWCNT in the polymer-supported SWCNT-IL gel electrode with various ratios of Li[BF_4]/EMI[BF_4] and Li[TFSI]/EMI[TFSI] (the applied triangle voltage: ±0.5 V, Sweep rate = 1 mV s^{-1}). (The data of Li[BF_4]/EMI[BF_4] = 0 and Li[TFSI]/EMI[TFSI] = 0 were quoted from ref. [9]).

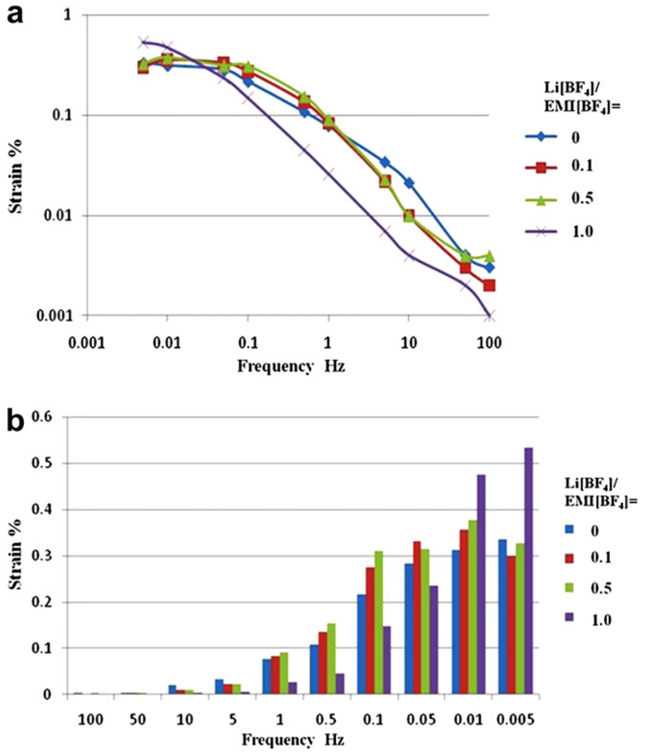

Fig. 6. The strain calculated from the peak-to-peak value of the displacement of the polymer-supported SWCNT-IL gel actuator with various ratios of Li[BF_4]/EMI[BF_4] at the frequency of the applied triangle voltage (±2 V).

In previous paper, we developed a simple equivalent circuit model [6]. The bucky-gel actuator as shown in Fig. 1 is modeled by the equivalent circuit model composed of the double-layer capacitance between the SWCNT and the electrolyte layer, C_1 and the resistance, R which is correspond to the ionic gel electrolyte layer as shown in Fig. 4a. The equivalent circuit shown in Fig. 4a is simplified to that shown in Fig. 4b, where the capacitance C_1 is replaced by the capacitance $C = C_1/2$.

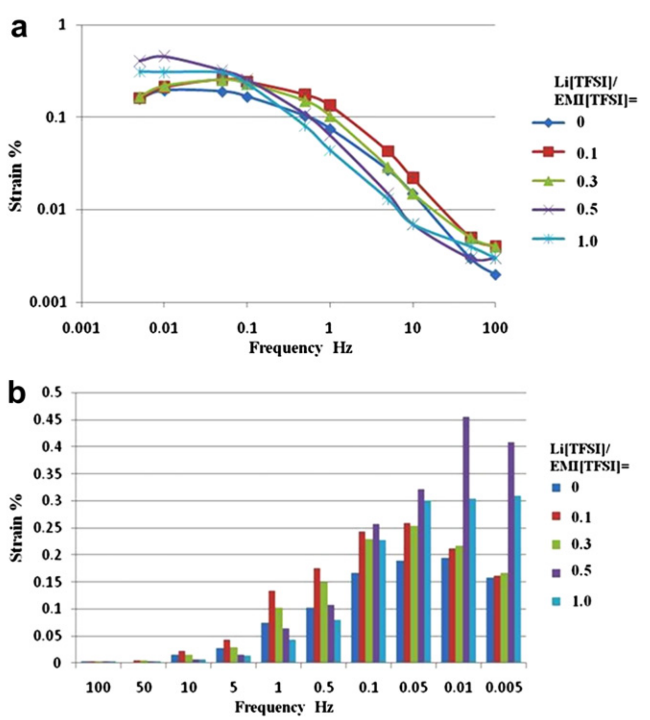

Fig. 7. The strain calculated from the peak-to-peak value of the displacement of the polymer-supported SWCNT-IL gel actuator with various ratios of Li[TFSI]/EMI[TFSI] at the frequency of the applied triangle voltage (±2 V).

Fig. 5 shows the double-layer capacitance C (the gravimetric capacitance of the SWCNT, $C_{SWCNT} = C_1$/(the weight of SWCNT) × 2) of the polymer-supported bucky-gel electrode containing Li salt/IL. At a slow sweep rate 1 mV s^{-1}, we found large capacitance value 68–96 F/g in the case of the Li[BF_4]/EMI[BF_4] and 65–82 F/g in the case of the Li[TFSI]/EMI[TFSI]. The double-layer capacitance depends on the ratio of Li salt/IL in the electrode layer. It is found that the double-layer capacitance of the gel electrode layer containing Li salt/IL is larger than that containing only IL, and that Li salt produces the large electrochemical capacitor.

Fig. 6 shows the generated strains of the polymer-supported bucky-gel electrodes of the actuators containing Li[BF_4]/EMI[BF_4] on the frequency of the applied triangle voltage (±2 V). As shown in Fig. 6a, the generated strains depend on the measuring frequency. For low frequencies (0.05–0.005 Hz) of the applied triangle voltage, it is considered that the SWCNTs dispersed in the electrode layer is fully charged. On the contrary, for higher frequencies, it is considered that there is not enough time for the dispersed SWCNTs to be fully charged [6]. As shown in Fig. 6b, for high frequencies (0.5–0.1 Hz), the generated strains of the actuators with molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5 are larger than that containing only EMI[BF_4]. This result is considered to be attributed that the ionic conductivities of the gel electrolyte layers with molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5 are higher than that containing only EMI[BF_4]. In addition to that, for low frequencies (0.01–0.005 Hz), the generated strain of the actuator with molar ratio of Li[BF_4]/EMI[BF_4] = 1.0 is larger than that containing only EMI[BF_4]. This result is considered that the large capacitance gives the very large generated strain. While, at a slow sweep rate 1 mV s^{-1}, the double-layer capacitances of the bucky-gel electrode with molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5 are larger than that containing only EMI[BF_4], however, for low frequencies (0.01–0.005 Hz), the generated strains of the actuators with the molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5 are about the same as that containing only EMI[BF_4]. These results may be considered to be attributed to other factors (e.g. young's modulus).

As shown in Fig. 7a, the generated strains also depend on the measuring frequency. For low frequencies (0.1–0.005 Hz) of the applied triangle voltage, it is considered that the SWCNTs dispersed in the electrode layer is fully charged. On the contrary, for higher frequencies, it is considered that there is not enough time for the dispersed SWCNTs to be fully charged [6]. As shown in Fig. 7b, the generated strains of the actuators with molar ratios of Li[TFSI]/EMI[TFSI] = 0.1 (in the high frequency range; 10–0.5 Hz) and 0.3 (in the high frequency range; of 1–0.5 Hz) are larger than that of the actuator containing only EMI[TFSI]. This result is considered that the ionic conductivities of the gel electrolyte layers with molar ratios of Li[TFSI]/EMI[TFSI] = 0.1 and 0.3 are higher than that containing only EMI[TFSI]. For low frequencies (0.01–0.005 Hz), the generated strains of the actuators with molar ratios of Li[TFSI]/EMI[TFSI] = 0.5 and 1.0 are larger than that containing only EMI[TFSI]. It is considered that the large capacitance gives the very large generated strain. While, at a slow sweep rate 1 mV s^{-1}, the double-layer capacitances of the polymer-supported bucky-gel electrodes with the molar ratios of Li[TFSI]/EMI[TFSI] = 0.1 and 0.3 are larger than that containing only EMI[TFSI], however, for low frequencies (0.01–0.005 Hz), the generated strains of the actuators with molar ratios of Li[TFSI]/EMI[TFSI] = 0.1 and 0.3 are about the same as that containing only EMI[TFSI]. These results may be considered to be attributed to other factors (e.g. young's modulus).

4. Conclusion

In this study, the effects of Li salts (Li[BF_4] and Li[TFSI]) on the electrochemical and electromechanical properties of an actuator using a polymer-supported SWCNT − IL gel electrode were investigated. The ionic conductivity of the gel electrolyte layer depended on the ratio of Li[X]/IL. The ionic conductivities of the gel electrolyte layers with molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5, and Li[TFSI]/EMI[TFSI] = 0.1 and 0.3 were higher than those containing only EMI[BF_4] and only EMI[TFSI], respectively. At a slow sweep rate 1 mV s^{-1}, we found large capacitance value 68–96 F/g in the case of the Li[BF_4]/EMI[BF_4] and 65–82 F/g in the case of the Li[TFSI]/EMI[TFSI]. The double-layer capacitance depends on the ratio of Li[X]/IL in the electrode layer. For high frequencies (0.5–0.1 Hz), the generated strains of the polymer-supported bucky-gel electrodes of the actuators with molar ratios of Li[BF_4]/EMI[BF_4] = 0.1 and 0.5 are the quick response. In addition to that, for low frequencies (0.01–0.005 Hz), the generated strain of the actuator with molar ratio of Li[BF_4]/EMI[BF_4] = 1.0 is larger than that containing only EMI[BF_4]. Similarly, in the case of the actuator containing Li[TFSI]/EMI[TFSI], the generated strains with molar ratios of Li[TFSI]/EMI[TFSI] = 0.1 (in the high frequency range; 10–0.5 Hz) and 0.3 (in the high frequency range; 1–0.5 Hz) are quick response. For low frequencies (0.01–0.005 Hz), the generated strains of the actuator with molar ratios of Li[TFSI]/EMI[TFSI] = 0.5 and 1.0 are larger than that containing only EMI[TFSI].

Therefore, it is found the polymer-supported SWCNT − IL gel electrodes containing Li[BF_4]/EMI[BF_4] and Li[TFSI]/EMI[TFSI] are large capacitor. The actuator containing Li salt/IL performed much better than that containing only IL. It is considered that higher ionic conductivities of the gel electrolyte layers containing Li[BF_4]/EMI[BF_4] and Li[TFSI]/EMI[TFSI] produce the quick response actuators, and that the larger capacitance gives the large generated strain in the actuator. These results are considered to be opened a new and robust way for the development of actuators.

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