IONIC POLYMER-METAL COMPOSITES

Fast-moving bimorph actuator based on electrochemically treated millimeter-long carbon nanotube electrodes and ionic liquid gel

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The development is described of an electromechanical bimorph actuator composed of ionic liquid gel sandwiched by electrochemically treated millimeter-long single-walled carbon nanotubes (SG-SWNT). Electrochemical doping of the SG-SWNT and electrochemical polymerization of polypyrrole on the surface of the SG-SWNT improved the performance of a previously reported actuator using non-treated SG-SWNTs. The conductivity of the SG-SWNT sheets treated at the anodic potential (doped) was found to be three times larger than that of the original film. The generated strain of the actuator prepared from the doped SG-SWNT sheets was increased compared to that prepared from non-doped sample. Moreover, the generated strain of the actuator from the doped SG-SWNT sheets swelled with ionic liquid (IL) was increased to twice that without ILs. The electropolymerization of pyrrole on the surface of the SG-SWNT sheet was carried out. The conductivity of the SG-SWNT was seven times larger after the electropolymerization. The generated strain of the SG-SWNT actuator prepared from the SG-SWNT sheets with electropolymerization was twice as large as that without the electropolymerization at low frequency. At higher frequency, both actuators provide almost the same performance. Both actuators exhibit mechanical resonance at about 100 Hz.

Keywords: carbon nanotube; polypyrrole; electrochemical doping; ionic liquid; bimorph actuator

1. Introduction

Ionic polymer–metal composites (IPMCs), which are composed of ionic gel polymer plated with metal electrodes, are one of the most promising electroactive (EAP) materials for artificial muscle-like actuators [1,2]. The ionic gel polymers usually used are Nafion™ or Flemion™ with water as solvent. On applying a voltage, the counter cation moves to the cathode side with associated water dragging, which results in a pressure gradient for the ionic gel polymer [3,4]. An established method of electrode plating on the ionic polymer is chemical plating with platinum or gold electrodes [5–7]. Recently, electrode plating methods for nanoparticles of other metals, metal oxides or carbons including several physical technologies such as their printing or pressing have been developed [8–12]. The science
and technology of ionic gel polymers has also been developed: ionic liquids have been used as a solvent for the IPMCs in order to enable operation in air [8,13–15].

In previous papers [16–18], we have reported a dry actuator that can be fabricated simply by layer-by-layer casting using ‘bucky gel’ [19], a gelatinous room-temperature ionic liquid (IL) containing single-walled carbon nanotubes (SWNTs). Our actuator (the bucky-gel actuator) has a bimorph configuration with a polymer-supported internal ionic liquid electrolyte layer sandwiched by polymer-supported ‘bucky gel’ layer (bucky-gel electrode layer), which allows large and long-lived operation in air at low applied voltage. We have also reported a second-generation SWNT actuator composed of polymer-free nanotube electrodes, which showed a much better performance than reported ‘dry’ EAP actuators including our first-generation design [20–22], by using millimeter-long ‘super-growth’ carbon nanotubes (SG-SWNTs), produced by a water-assisted modified CVD method [23]. The SG-SWNTs, which associate together tightly with ionic liquids, afford a free-standing sheet with superb conductivity. By combining the SG-SWNT sheet with an electrolyte layer, we fabricated an actuator strip with a bimorph configuration (SG-SWNT actuator). We proposed that our actuator exhibits a bending response due to the dimensional changes of both electrode layers, which are driven by the transfer of ions to the dispersed SWNT electrode layers. The bucky-gel actuator or the SG-SWNT actuator is considered to be a kind of IPMC actuator.

The purpose of this paper is to describe the development of the SG-SWNT actuator using electrochemically treated single-walled carbon nanotubes, i.e. electrochemical doping of the SWNT and electrochemical polymerization of polypyrrole on the surface of the SWNT, in order to improve the performance of the actuator. It is well known that a single-walled carbon nanotube is a mixture of metallic and semiconducting nanotubes [24]. Hence, electrochemical doping of semiconducting nanotubes is considered to provide an increase in the capacitance and the conductance of the total SWNT film, which results in the increase in the generated stress of the actuation of the bucky gel actuator prepared from the SWNTs [25–27]. On the other hand, polypyrrole (PPy) is known to be an actuator material that has a large strain and low-voltage drive [28–31]. However, strain rates of PPy-based actuators are limited by high resistance of PPy on dedoped state [32]. Hence, the electrochemical polymerization of polypyrrole on the surface of the SWNT was expected to enable development of a low-voltage driven actuator that exhibits fast and large strain. In this paper, the the preparation is described of SG-SWNT actuators using electrochemically treated SWNTs and there actuation performance is discussed.

2. Experimental

2.1. Materials

‘Super-growth’ single-walled carbon nanotubes (SG-SWNTs), which were synthesized by water-assisted chemical vapor deposition (‘super-growth’) method, were obtained from Nanotube Research Center, AIST. Other reagents were used as-received from Fluka (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI)), Sigma Aldrich Co. (propylene carbonate (PC) and methyl isobutyl ketone (MIBK)), Arkema Chemicals Inc. (poly(vinylidene fluoride-co-hexafluoropropylene; Kynar Flex 2801®), Kishida Chemicals Co. (N,N-dimethylacetamide (DMAc)) and Wako Pure Chemical Industries Co. Ltd. (pyrrole (Py), tetraethylammonium bis(trifluoromethanesulfonyl)imide (TEATFSI), tetraethylammonium tetrafluoroborate (TEABF4), lithium tetrafluoroborate (LiBF4), lithium hexafluorophosphate (LiPF6), lithium trifluoromethanesulfonate
(LiCF₃SO₃), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(pentafluoroethanesulfonyl)imide (LiPFSI), tetrabutylammonium trifluoromethanesulfonate (TBACF₃SO₃), methyl benzoate (MB) and dimethyl phthalate (DP)).

2.2. Preparation of SG-SWNT sheets

As a typical example for the fabrication of the SG-SWNT sheets, a suspension of SG-SWNTs in dimethylacetamide (DMAc, 3 mL) was sonicated for 10 min using a horn-type ultrasonic probe (a Nissei model US-50 ultrasonic generator, 28 kHz, 50 W), whereupon it turned to a gel. It can be speculated that the gelatinous structure was formed by the entanglement of dispersed long SG-SWNTs. The gelatinous material thus obtained was diluted with DMAc (6 mL), and then an aliquot (1 mL) was cast on a Teflon mold (10 mm × 25 mm) preheated at 50°C. After being allowed to stand at room temperature for 1 day, the resultant cast sheet was dried under a reduced pressure at 80°C for 3 days. The SG-SWNT sheet without IL (EMITFSI) prepared as outlined above was used for electrochemical treatments, as described in Sections 2.3 and 2.4. Its thickness was 10 µm.

In order to swell the SG-SWNT sheet with EMITFSI, after drying, a portion (1 mL) of mixture of EMITFSI (30 mg) in DMAc (9 mL) was cast on the SG-SWNT sheet in the mold, which was heated at 50°C and allowed to dry the solvent for 1 day. Then, the electrode film was dried to remove the trace solvent (DMAc) under reduced pressure at 80°C for 3 days, thus affording a SG-SWNT sheet with EMITFSI, the thickness of which was 17 µm.

2.3. Electrochemical doping for SG-SWNT sheets

The electrochemical doping of the SG-SWNT sheets was carried out by using cyclic voltammetry in PC solutions containing 1 mol L⁻¹ salt at room temperature in a three-electrode cell system (see Figure 1) using a Ag/AgCl wire as a reference electrode, a Ni plate as a counter electrode and the SG-SWNT sheet as a working electrode from −1.25 V to 0.75 V against the reference electrode. The salts used are summarized in Table 2.

In order to swell the electrochemically doped SG-SWNT sheet with EMITFSI, the SG-SWNT sheet was immersed in an acetone solution of EMITFSI for 30 min, then the solvent evaporated completely.

2.4. Electrochemical polymerization of polypyrrole on SG-SWNT sheets

With a platinum plate, both sides of which was coated by SG-SWNT films, electropolymerization of pyrrole was carried out at 0°C in MB/DP mixed solution containing 0.25 mol L⁻¹ Py and 0.2 mol L⁻¹ LiTFSI. Alternatively, it was carried out at −10°C in MB solution containing 0.2 mol L⁻¹ Py and 0.25 mol L⁻¹ TBACF₃SO₃. After electropolymerization, the obtained films were unfixed from the platinum plate by peeling tape, rinsed with acetone and then dried to remove trace solvent under reduced pressure at 80°C for 3 days. Electropolymerization was carried out at 0.2 mA cm⁻² current densities and a reaction time of 2 h.

In order to swell the electropolymerized SG-SWNT sheet with EMITFSI, the SG-SWNT sheet was immersed in an acetone solution of EMITFSI for 30 min, then the solvent evaporated completely.
Figure 1. Photographs of the electrode holder made from Teflon™ for three-electrode systems. This holder is used by immersing it in an electrolyte solution. (A) The SG-SWNT film as a working electrode, (B) a Ag/AgCl wire as a reference electrode and (C) a Ni plate as a counter electrode. (a) Parts of the electrode holder. (b) The electrode holder after assembly.

2.5. Preparation of actuator films

A mixture of EMITFSI (300 mg), PVdF-HFP (300 mg), PC (750 mg) and MIBK (9 mL) was stirred overnight at 80°C. Then, a portion of the resulting gelatinous mixture was cast on an aluminum mold (25 mm × 25 mm) preheated at 35°C for 2 h and heated at 80°C for 4 h. Then, the electrolyte film was dried under a reduced pressure at 80°C for 3 days, affording a soft film (of thickness 17.5 µm).

Electrolyte film, with dimensions 15 mm × 2 mm width, was sandwiched by 11 mm × 1.5 mm-wide electrode films, and placed between hot-press plates of a screw-type small hot-pressing apparatus, heated at 70°C for 3 min, and then pressed (80 N) for 3 min at the same temperature, to accomplish conjugation of the three layers. Finally, actuator strips were trimmed to 10 × 1 mm² size.

2.6. Measurements of the properties of the SG-SWNT sheets

Thicknesses of the SG-SWNT sheets were measured using a micrometer (Mitutoyo Co.). Electrical conductivities of the SG-SWNT sheets were evaluated by a 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 by a Hokuto Denko model HA-151 Potentiostat/Galvanostat with a Yokogawa Electric model FC 200 waveform generator. Young’s moduli and breaking strengths of the nanotube sheets were evaluated from the stress–strain curves obtained for 2 × 7 mm² wide films (15–20 µm in thickness) using a SEIKO Instruments model TMA/SS 6000 thermal stress–strain measurement instrument.
2.7. **Displacement measurements**

Displacement measurements were conducted by square-wave voltages to a $10 \times 1$ mm$^2$ sized actuator strip clipped by two gold disk electrodes (see Figure 2a); 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), where strain $\varepsilon$ generated in the electrode layer was estimated by the following equation:

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

where $d$, $\delta$ and $L$ are the thickness, displacement and free length of the actuator strip, respectively.

![Figure 2](image)

**Figure 2.** (a) Schematic drawing of the actuator composed of the electrochemically treated SG-SWNT sheets sandwiching ionic liquid gel layer. L: free length; $\delta$: displacement. (b) Electric current and displacement curve in response to the square-wave voltage of $\pm 2$ V with a frequency of 0.1 Hz.
3. Results and discussion

3.1. Actuation of SG-SWNT actuator

In previous papers [20–22], we have reported SG-SWNT actuators composed of the SG-SWNT sheets containing an ionic liquid sandwiched an ionic liquid gel electrolyte layer. Figure 2 shows a schematic view of the configuration of the SG-SWNT actuator, together with the electric current and displacement response curves for SG-SWNT electrode sheets containing an ionic liquid (EMITFSI) driven by $\pm 2\ V$ square-wave voltage at a frequency of 0.1 Hz. The actuators respond on the anode side when the square-voltage changes. The electric current curves are basically of exponentially form. The actuation responses reported in this paper showed the same behavior, qualitatively. In this paper, in order to analyze the displacement response in detail, we estimated a generated strain from the peak-to-peak value of the displacement measured, as shown in Figure 2, by using Equation (1) and discuss its dependence on the frequency of the applied square wave voltage.

3.2. Effect of electrochemical doping

Figure 3 shows the cyclic voltammogram of the SG-SWNT film in 1M TEABF$_4$ PC solution. We found that an anodic wave is observed from 0 V to 0.75 V and a cathodic wave is observed from –0.5 V to –1.25 V. The electric conductivities of the SG-SWNT sheets at each potential, as measured by the four-probe DC current method, are summarized in Table 1. The conductivity of the SG-SWNT films treated at the anodic potential is three times larger than that of original film. However, the conductivity of the SG-SWNT films treated at cathodic potential has almost the same value as, or is lower than, that of the original film. These waves are considered to be attributed to the electrochemical doping of the semiconducting type of SWNTs. In consideration of the dependence of the conductivity of SG-SWNT, the semiconducting SWNTs are p-type semiconductors. Hence,
Table 1. Electric conductivity of the SG-SWNT sheet doped electrochemically in 1M TEABF₄ PC solution in three-electrode cell system using a Ag/AgCl wire as a reference electrode, a Ni plate as a counter electrode and the SG-SWNT sheet as a working electrode from −1.25 V to 0.75 V against the reference electrode at a sweep rate of 1 mV s⁻¹.

| Electrode potential, E (V), vs. AgAgCl | Conductivity (S cm⁻¹) |
|---------------------------------------|-----------------------|
| +0.75                                 | 267.0                 |
| +0.50                                 | 129.0                 |
| +0.25                                 | 50.7                  |
| 0                                     | 45.9                  |
| −0.25                                 | 40.7                  |
| −0.50                                 | 66.9                  |
| −0.75                                 | 78.4                  |
| −1.00                                 | 93.7                  |
| −1.25                                 | 48.3                  |

the electrochemical doping might take place at anodic potential, and de-doping might take place at cathodic potential in the cyclic voltammogram shown in Figure 3.

Kimizuka et al. [25,26] reported electrochemical doping of SG-SWNT film electrodes prepared from SG-SWNT forests in the same three-electrode system as our system. They found that the SG-SWNT film system exhibited a butterfly-shaped cyclic voltammogram and V-shaped conductivity plot against electrode potentials. According to Kimizuka et al., this shows that the SG-SWNTs behave as both p-type and n-type semiconductors. The reason for this discrepancy still remains unclear. The structure of both carbon nanotube films must be completely different. This may be the reason for the difference. However, it was also reported that chemical doping of dispersed SWNT electrodes for transparent conductive coatings was p-type [33,34]. Here, ‘doped’ is defined by electrochemically treated at +0.75 V vs. Ag/AgCl and ‘dedoped’ is defined by electrochemically treated at −1.25 V vs. Ag/AgCl. Table 2 summarizes the electrical conductivity of the SG-SWNT films doped electrochemically in various 1M electrolyte PC solutions. The electrical conductivity of doped and dedoped SG-SWNT films depends on the species of the doping ions.

Figure 4 shows the frequency dependence of the generated strain of the actuator film composed of the ionic gel layer sandwiched by two SG-SWNT films without ILs that were both doped (doped), doped and dedoped (doped/dedoped), both dedoped(dedoped) in TEATFSI PC solution, together with using the original SG-SWNT films (non-doped). As shown in Figure 4, the strains of ‘doped’ and ‘doped/dedoped’ actuators are larger than those of ‘dedoped’ and ‘non-doped’ actuators. The electrochemically doping gives the increases in the conductivity and capacitance of the SG-SWNT film, which result in the increase in the strain.

Then, we further studied the actuator prepared from the doped SG-SWNT with ILs. Figure 5 shows the frequency dependence of the generated strain of the actuator composed of the SG-SWNT films sandwiching an EMITFSI gel film driven by ±2 V square-wave

Table 2. Electric conductivity (S cm⁻¹) of the SG-SWNT sheet doped electrochemically in 1M various electrolyte PC solutions. Other conditions are the same as for Table 1.

| Electrode potential | TEATFSI | TEABF₄ | LiBF₄ | LiPF₆ | LiCF₃SO₃ | LiTFSI | LiPFSI |
|---------------------|---------|--------|------|------|----------|--------|--------|
| −1.25 V vs. AgAgCl  | 86.39   | 48.3   | 80.49| 20.54| 62.47    | 155.14 | 135.11 |
| Non-doped           | 94.22   | 80.64  | 119.76| 133.97| 121.80   | 104.82 | 119.13 |
| +0.75 V vs. AgAgCl  | 462.10  | 267.00 | 181.98| 190.83| 120.27   | 297.22 | 208.67 |
Figure 4. Dependence of the generated strain of the induced charge of the SG-SWNT sheets sandwiching an EMITFSI electrolyte gel film layer driven by ±2 V square-wave voltages of different frequencies.

Figure 5. Frequency dependence of the generated strain of the actuator composed of the SG-SWNT sheets sandwiching an EMITFSI gel film driven by ±2 V square-wave voltages of different frequencies. The SG-SWNT sheets used were electrochemically doped in various electrolyte solutions, electrochemically doped in TEATFSI solution following immersion in EMITFSI solution and untreated.

voltages of different frequencies. The SG-SWNT films used were those electrochemically doped in various electrolyte solutions, electrochemically doped in TEATFSI solution swelled with EMITFSI and without doping and EMITFSI. As a result of swelling with EMITFSI, the strain of the doped SG-SWNT actuator was twice as large as that without EMITFSI. This is considered to be due to the increase in the ion transfer in the electrode. In conclusion, the doping makes the increase in the capacitance and the conductance of the SG-SWNT sheet electrode and the swelling with IL enables an increase in the ion transfer in the SG-SWNT sheet, which results in the increase in the generated strain of the SG-SWNT actuator.

3.3. Effect of electopolymerization of polypyrrole

As previously shown, the generated strain of the SG-SWNT actuator can be improved by the increase in the conductivity and the capacitance of the SG-SWNTs in the electrodes. Here, we report the improvement of the generated strain of the SG-SWNT actuator by an electopolymerization of the polypyrrole on the surface of the SG-SWNT electrode. Spinks et al. reported the improvement of the conductivity of the SWNTs by an
electropolymerization of PPys [35]. While, it is well known that PPys are typical redox conjugated polymers that have large capacitance originating from redox reactions [36]. Hence, by the electropolymerization of PPys, the capacitance and conductivity of the SG-SWNT sheets were expected to be much increased.

As mentioned in the introduction, it is well known that polypyrrole is an actuator material that has a large strain and low-voltage drive [28–31]. However, strain rates of PPy-based actuators are limited by high resistance of PPys in the dedoped state [32]. Hence, the purpose of this study was to fabricate a solid-state low-voltage driven actuator that exhibits fast and large strain by sandwiching an ionic liquid gel film by PPy/SWNT composite films. In order to fabricate solid state actuator using a PPy, it was reported that there is a serious problem involving delamination between PPy electrodes and gel electrolyte layer [37]. Therefore, the electropolymerization of PPy was carried out on the one surface of the SG-SWNT sheet electrode, as described in Section 2.4. There was no delamination observed between the electropolymerized PPy and the SG-SWNT sheet. Then, after the prepared SG-SWNT/PPy electrode films were immersed in IL solution overnight and the solvent evaporated, we prepared the actuator film by hot-pressing the PPy/SWNT films sandwiching the ionic gel electrolyte layer with contacting the SG-SWNT.

Hara et al. [38,39] reported that the conductivity and mechanical properties greatly depend on the conditions of the electropolymerization, especially the species of the counter doping ions. In this paper, TBACF$_3$SO$_3$ and LiTFSI were used for electrolyte for the electropolymerization. In this case, CF$_3$SO$_3^-$ and TFSI$^-$ are counter doping anions for the electropolymerized PPy (PPyCF$_3$SO$_3$, PPyTFSI). The conductivity, Young’s modulus and thickness of the SG-SWNT sheet were increased by the electropolymerization as follows: SG-SWNT (79.96 S cm$^{-1}$, 0.84 GPa, 10 µm) < SG-SWNT/PPyCF$_3$SO$_3$ (236 S cm$^{-1}$, 1.72 GPa, 23 µm); SG-SWNT (86.28 S cm$^{-1}$, 0.84 GPa, 10 µm) < SG-SWNT/PPyTFSI: (587 S cm$^{-1}$, 3.15 GPa, 16 µm).

Figure 6 shows the frequency dependence of the generated strain of the SG-SWNT actuator electropolymerized with PPyCF$_3$SO$_3$ and PPyTFSI, and without electropolymerization. Every actuator was prepared from electrode sheets containing EMITFSI. From the figure, it can be seen that the generated strain of the SG-SWNT actuator with the electropolymerization was twice as large as that without electropolymerization at low frequency. However, at frequencies higher than 10 Hz, both data sets revealed almost the same values. At a frequency of 100 Hz, all data revealed resonance. The resonant

![Figure 6](image_url)

Figure 6. Frequency dependence of the generated strain of the actuator composed of the SG-SWNT sheets electropolymerized with PPy (counter anion: CF$_3$SO$_3$ or TFSI), or without electropolymerization, sandwiching an EMITFSI gel electrolyte layer driven by ±2 V square-wave voltage of different frequencies.
frequency of the SG-SWNT actuator with electropolymerization was higher than that without electropolymerization. This is due to the increase in the Young’s modulus by the electropolymerization. In conclusion, the electropolymerization enables an increase in the capacitance and the conductance of the SG-SWNT sheet electrode and the swelling with ILs facilitates an increase in the ion transfer in the SG-SWNT sheet, which results in the increase in the generated strain of the SG-SWNT actuator.

4. Conclusion

The preparation of SG-SWNT actuators using electrochemically treated SWNTs, i.e. electrochemical doping of the SG-SWNT and electrochemical polymerization of polypyrrole on the surface of the SG-SWNT, has been described and the actuation performance reported. The conductivity of the SG-SWNT sheets treated at the anodic potential (doped) was three times larger than that of the original film. The generated strain of the actuator prepared from the doped SG-SWNT sheets was increased compared with that of the non-doped sample. Moreover, the generated strain of the actuator from doped SG-SWNT sheets swelled with EMITFSI was twice as large as that without EMITFSI. Electropolymerization of pyrrole on the surface of the SG-SWNT sheet was carried out. The conductivity of the SG-SWNT was seven times larger as a result of the electropolymerization. The generated strain of the SG-SWNT actuator prepared from the SG-SWNT sheets with electropolymerization was twice as large as that without the electropolymerization at low frequency. At higher frequency, both actuators show almost the same performance. Both actuators exhibit mechanical resonance at about 100 Hz. In conclusion, the doping or electropolymerization of the SG-SWNT sheet enables an increase in the capacitance and the conductance of the SG-SWNT sheet electrode and swelling with ILs facilitates an increase in the ion transfer in the SG-SWNT sheet, which results in an increase in the generated strain of the SG-SWNT actuator.

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