Carbon nanoparticle composite actuators

Midori Kato, Masayoshi Ishibashi
Hitachi, Ltd., Central Research Laboratory, 1-280 Higashi-koigakubo, Kokubunji,
Tokyo, 185-8601, Japan
e-mail : midori.kato.ch@hitachi.com

Abstract. We have developed a new type of electroactive polymer actuator film that is made of composite materials consisting of carbon nanoparticles and binder polymers. The actuator film can operate in two modes of actuation, the “charge accumulation mode,” or the “self-heating mode.” The former operates in an electrolyte solution when the voltage is applied against a counter electrode due to the charge accumulated on the electric double layer formed at the surface of the carbon nanoparticles. The latter operates in air owing to the thermal expansion caused by Joule heating. The actuator film is easily fabricated using casting or printing methods.

1. Introduction
Interest in actuator systems that convert electrical energy into mechanical energy for a wide range of applications is increasing. Electroactive polymers (EAPs) are promising materials for light, flexible, noiseless actuators [1]. The EAPs are materials that deform by themselves on application of the electrical signal. Furthermore, since they are based on an organic material, they allow for ease of processing compared with conventional actuator materials such as shape-memory alloys and piezoceramics. Thus, EAPs are expected to be used to compose actuators that can be easily tailored to the appropriate form. Actuators can be built in minute sizes for incorporation into small devices such as micropumps and valves [2], and some actuators have even been microfabricated by means of photolithography [3].

Among the EAPs, polymers that show electrochemomechanical deformation can operate with low voltages. In particular, EAPs based on non-Faradaic processes, such as ionic polymer-metal composites (IPMC) [4] and carbon nanotubes [5, 6], have a stable cycle life. They generally operate in solution, and thus, there have been efforts to operate them in air using ionic liquid [7,8].

In this paper we describe a new type of EAP actuator that uses composite materials consisting of conductive nanoparticles and polymers. The composite materials have an advantage in that we can use various types of materials compared with other EAP actuators. We typically used low-cost and lightweight carbon nanoparticles as the conductive particles, and solid electrolyte polymers as the polymers. Using these composite materials, we successively developed actuators operating in two modes of actuation. One operates in an electrolyte solution, and the other operates in air. We refer to the former as “charge accumulation mode” and the latter as “self-heating mode.” The actuator features of these two modes will be introduced.
2. Experimental

2.1. Material
The actuator film material we used here was a composite material of carbon nanoparticles (CNP) and a binding polymer. The composite material was prepared as follows. The CNPs (Ketjen Black, Lion) were dispersed into Nafion® 5% solution (Nafion® 117, Wako). The mixed solution was sonicated for homogeneity, and then the aggregated CNPs were removed by centrifugal separation. The composite films were obtained by casting. The supernatant solution was cast onto a clean glass substrate. The solvent was allowed to evaporate at 70°C, and the composite film was formed on the glass substrate. The free-standing composite film was easily peeled off from the substrate while immersing it in water. The films had thicknesses from 15 to 200 μm, which could be controlled by the amount of solution cast onto the substrate. When we measured the actuator properties of the actuator films, we usually used 200-μm-thick films cut into rectangular shapes with a width and length of about 2 and 7 mm, respectively. The amounts of Nafion® solution and CNPs were determined so that the resultant composite film included up to 30 % CNPs by weight.

2.2. Experimental details
Figure 1 shows the experimental set-up used to measure the actuation properties of our actuator films. Figure 1(a) and 1(b) are the set-up for the charge accumulation mode and self-heating mode, respectively.

For the charge accumulation mode, the actuation experiment was performed in an electrochemical cell filled with an aqueous electrolyte, with an Ag/AgCl reference electrode, and, a Pt wire counter electrode. A NaCl aqueous solution was used for the electrolyte solution. An actuator film was held by a Pt electrode and was used as the working electrode. One end of the film was fixed at the bottom of the cell, and the other was held by an upper holder that was connected to a balance weight to stretch the film. The balance weight was equivalent to the weight of the upper holder, thus, no further stress was applied to the actuator film. Depending on the electrochemical potential applied to the actuator film versus the reference, the film will expand or contract. The position of the end of the film was monitored with a CCD camera with microscope optics or with a laser displacement sensor (HL-C105B-BK, SUNX) while the potential was applied by a potentiostat (HA-151, Hokuto Denko) controlled by a personal computer.

For the self-heating mode, voltage was applied to both ends of the actuator film (fig. 1(b)). The film expanded when the voltage was applied. To measure the deformation, the same set up as in the charge accumulation mode was used.

All analog data were converted to digital data by an A/D converter and were collected by a personal computer.

Morphology analyses were done using a Hitachi S800 scanning electron microscope (SEM).
3. Results and discussion

3.1. Composite material
An SEM image of the CNP composite film is shown in figure 2. The diameter of the carbon nanoparticles, Ketjen Black, was about 40 nm, however, many of the particles shown in the figure had larger diameters than 40 nm, and most of the particles were not separated from each other. This indicates that the Nafion® covered the carbon nanoparticles and bonded them to each other. The carbon nanoparticles were closely packed, yielding a maximum electrical conductivity of 3 S/m.

3.2. Charge accumulation mode
Figure 3 plots the electrical response and actuator response of the CNP composite actuator in the charge accumulation mode. The actuator film expanded when negative potential was applied to the actuator against the reference electrode. Because the actuator is presumed to isometrically expand or contract, we measured the strain of the longitudinal direction of the shaped actuator film. On applying
the voltage to the actuator, the actuator maintained the deformation even though the current decreased to almost zero. This means that this actuator requires little energy to maintain the deformation.

We can also see that while a constant electrical potential was applied, the measured current decayed exponentially. Furthermore, we observed no clear peaks due to electrochemical reactions such as reduction and oxidation in a cyclic voltammogram when the applied potential was between -0.8 V and +1.2 V vs Ag/AgCl (figure 4). This cyclic voltammogram shows a rectangular shape that indicates the electric double layer capacitor properties of the CNP composite actuator. These findings indicate that the CNP composite actuator is not a Faradaic actuator such as a conducting polymer actuator.

| Input voltage (V vs Ag/AgCl) | Current (mA) | Strain (%) |
|-----------------------------|--------------|------------|
| 0.0                         | 5            | 0.3        |
| 0.8                         | 0            | 0.2        |
| -0.8                        | 0            | 0.0        |

Figure 3. Input voltage, current, and strain of the CNP composite actuator in charge accumulation mode operating in 1 M NaCl aqueous solution.

Figure 4. Cyclic voltammogram from -0.8 to 1.2 V (vs Ag/AgCl). The scan rate is 5 mVs⁻¹.

The relationship between the amount of charge accumulated on the electric double layer calculated from figure 4 and the strain of the actuator film is shown in figure 5. The strain of the actuator film increases with the accumulated negative charge on the CNP composite actuator. This suggests that the actuation mechanism of the CNP composite actuator is related to the accumulated charge. Thus, we call this mode “charge accumulation mode.” The accumulable charge of the CNP composite actuator film is large, because the volumetric capacitance of this CNP composite actuator is as large as 20 F/cm³, which is comparative to the electric double layer capacitor. This is attributed to the extremely large specific surface area of the Ketjen Black carbon nanoparticles, which are components of the CNP composite film.

Similar non-Faradaic actuators, i.e, carbon nanotube actuators, have been reported [5, 6]. However, the carbon nanotube actuator shows a parabolic dependence of strain, whereas a parabolic minimum was not observed in the dependence of our actuator shown in figure 5. We consider that this is because of the limitation of the input voltage. The difference between the carbon nanotube actuator and our actuator, and the details of actuation mechanism are now under investigation.

The maximum generated stress of the CNP composite actuator was approximately 4 MPa. This value is lower than that of the carbon nanotube actuators. The generated stress of self-deforming actuator film depends on the Young’s modulus of the film. The CNP composite actuator needs an ion conductive polymer, such as Nafion®, as a binder, because the CNPs themselves cannot form a self-standing film while the carbon nanotube forms an actuator sheet by entangling each other without any binder polymer. Therefore, the Young’s modulus of the CNP composite film is lower than the carbon nanotube sheet. The maximum stress of the CNP composite actuator, however, can be varied by choosing a binder polymer and by changing the CNP content.
3.3. **Self-heating mode**

The principle of the actuation in the self-heating mode can be explained as follows. When the electric voltage is applied between both ends of the actuator film, the current flows through the actuator film, thus, Joule heat is generated. The CNP composite actuator has relatively high electrical conductivity because it includes conductive CNPs. Therefore, application of low voltages can generate large Joule heat. The electric conductivity of the CNP composite material can be optimized by the content of the CNP in the composite material. This heat raises the temperature of the actuator film itself, thus, the film expands because of the thermal expansion. Then the film contracts to the initial size when the current is turned off. We use this repeatable expansion and contraction as an actuation of the CNP composite actuator.

Figure 6 shows the electrical response and the actuator response of the CNP composite actuator in the self-heating mode. Because of the hygroscopicity of the binder polymer Nafion®, the CNP composite actuator expanded depending on the ambient humidity when voltage was not applied. Thus, we always applied 6 V in order to avoid the humidity effect. As shown in the figure, applying 14 V can provide a strain as large as about 3%. This large deformation can be achieved because the binder polymer Nafion® has a large coefficient of thermal expansion (CTE). We can obtain a larger actuation by replacing Nafion® with a polymer with a larger CTE.

As shown in figure 6, a constant current is needed to maintain the deformation in the self-heating mode. The actuator works as an ohmic resistance so that the constant current flows in a steady state when a constant voltage is applied. The amount of the deformation is determined according to the balance of the electrically applied thermal energy and the radiated thermal energy.

Compared to the CNP composite actuator in the charge accumulation mode, one of the advantages of the actuator in the self-heating mode is that the actuator can work in air, which means that a wider range of applications is possible. Another advantage is the wide choice of polymers. For the charge accumulation mode, the polymer needs to be a polymer electrolyte. On the contrary, for the self-heating mode, one can choose various kinds of polymers if the carbon nanoparticles can be dispersed in the polymer. In this study we used Nafion® as the binder polymer for the actuator in the self-heating mode to compare with the actuator in the charge accumulation mode under the same conditions. It is possible to select a polymer that has a larger thermal expansion coefficient to provide an actuator with larger strain. If the right polymer is chosen, it is also possible to make an “actuator ink” to fabricate the actuators using a printing process. Using a suitable resin for screen printing as a binder polymer, we fabricated unimorph bending actuators as shown in figure 7. The actuator patterns were printed on a polyimide sheet by screen printing. The printing process can provide uniform and precise actuators and can be used in mass production fabrication process.
Figure 6. Input voltage, current, and strain of CNP composite actuator in self-heating mode operating in air.

Figure 7. Unimorph actuators fabricated using a printing process.

4. Conclusion
We have developed two actuation modes of a CNP composite actuator consisting of carbon nanoparticles and Nafion®. One is a charge accumulation mode that operates in electrolyte solution, and the other is a self-heating mode that operates in air. Both actuators are linear actuators that repeatedly expand and contract when voltage of several to a dozen volts is applied.

The charge accumulation mode has good energy consumption because it requires little energy to maintain the deformation. On the other hand, the self-heating mode is advantageous to the wide range of possible applications and also because of the unique feature that enables fabrication by printing process. In both actuation modes, the CNP composite material is good for making light and flexible actuators that are also low in cost and easy to fabricate.

References
[1] Bar-Cohen Y 2001 Electroactive Polymer [EAP] Actuators as Artificial Muscles (Washington: SPIE Press)
[2] Guo S, Nakamura T, Fukuda T, Oguro K 1997 IEEE International Conference on Robotics and Automation 1 266
[3] Jager E W H, Smela E, Inganas O 2000 Science 290 1540
[4] Asaka K, Oguro K 2000 J. Electroanal. Chem. 480 186
[5] Baughman R H, Cui C, Zakhidov A A , Iqbal Z, Barisci J N, Spinks G M, Wallace G G, Mazzoldi A, De Rossi D, Rinzler A G, Jaschinski O, Roth S, Kertesz M 1999 Science 284 1340
[6] Hughes M, Spinks G M 2005 Adv. Mater. 17 443
[7] Akle B J, Bennett M D, Leo D J 2006 Sensors and Actuators A 126 173
[8] Fukushima T, Asaka K, Kosaka A, Aida T 2005 Angew. Chem. Int. Ed. 44 2410