

論文

다발/매트로 구성된 탄소나노튜브 복합재 액츄에이터의 거동특성 및 응용연구

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Electromechanical Behaviors and Application of Carbon Nanotube Composite Actuators Consisting of Bundles and Mats

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ABSTRACT

The relationship between strain and applied potential was derived for composite actuators consisting of single-wall carbon nanotubes (SWNTs) and conductive polymers (CPs). During deriving the relationship, an electrochemical ionic approach is utilized to formulate the electromechanical actuation of the composite film actuator. This relationship can give us a direct understanding of the actuation of a nanoactuator. The results show that the well-aligned SWNTs composite actuator can give good actuation responses and high actuating forces available. The actuation is found to be affected by both SWNTs and CPs components and the actuation of SWNTs component has two kinds of influences on that of the CPs component: reinforcement at the positive voltage and abatement at the negative voltage. Optimizations of SWNTs-CPs composite actuator may be achieved by using well-aligned nanotubes as well as choosing suitable electrolyte and input voltage range.

초 록

단일벽 탄소나노튜브와 전기전도성 폴리머로 구성된 복합재 액츄에이터의 변형율-전압간의 관계식이 유도되었으며, 얇은 복합재 필름 형태의 액츄에이터의 전기기계적인 작동을 수식화하기 위해서 전기화학적 이온 접근법을 사용하였다. 이 방법은 액츄에이터의 작동에 대한 이해를 쉽게 할 수 있다. 실험결과와 계산결과는 잘 일치한다. 이상적으로 잘 배열된 단일벽 탄소나노튜브 액츄에이터는 좋은 반응특성과 작동력을 나타내었다. 작동변위는 나노튜브와 기지인 폴리머의 영향을 받으며, 단일벽 탄소나노튜브는 양의 전압에서는 기지를 보강하며 음의 전압에서는 기지를 수축하게 하는 영향을 미친다. 나노튜브의 배열을 곧게 하고, 적절한 전해질과 전압을 선택하면 액츄에이터의 성능을 최적화시킬 수 있다.

Key Words : 복합재 액츄에이터(Composite Actuator), 전기전도성 폴리머(Conducting Polymer), 전기기계적 성질(Electromechanical Properties), 탄소나노튜브(Carbon Nanotube)

1. Introduction

Many efforts to develop an innovative actuator which consists of SWNTs and conducting polymer have been made for last several years for its possible application to operate MEMS devices or small insect-like robots. In this

nanocomposite film actuator, the SWNTs electrodes exhibit a unique pore structure and high efficiency of specific surface areas, which can be considered as the surface-area-enhancing component in composite films. Therefore, the composite pseudocapacitance is increased remarkably. This large capacitance suggests that the composite film can be used for

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local energy storage as well as actuation. Carbon nanotubes have high electrical conductivity that can increase the charging-discharging rate and improve the electrodic performance of CPs (conducting polymers) films. SWNTs also exhibit strains due to electrochemical redox at low bias voltage (non-Faradic electrochemical charging) [1], which is enough for actuating MEMS devices. In addition, SWNTs show very high Young's modulus so that they can function as reinforcing fibers to the CPs matrix in the composite actuator. As a result, it is possible to make a SWNTs/CPs composite actuator that can show both high actuation strain and high available stress. SWNTs can also improve the life cycle of the actuators. In order to develop a SWNTs/CPs actuator, it is important to derive the relationships between strain and applied potential for predicting its behavior.

2. Voltage-Strain Relationships

A typical SWNTs/CPs composite actuator consists of a unit cell structure. When the potential difference is applied, a double layer capacitor is formed at electrolyte/composite film interface, and at the same time it is discharged by the ions diffusion. The ions diffused into the composite film are then neutralized by the charges within the film. Based on the method that was suggested by Madden *et al.*[2] to the polypyrrole actuator, the actuator's admittance transfer function, $Y(s)$, can be obtained, which combines the effects of diffusion, capacitance and electrolyte resistance as;

$$Y(s) = \frac{\delta + \sqrt{\frac{D_c}{s}} \cdot \tanh\left(\frac{d}{2} \cdot \sqrt{\frac{s}{D_c}}\right)}{\left[\delta + \sqrt{\frac{D_c}{s}} \cdot \tanh\left(\frac{d}{2} \cdot \sqrt{\frac{s}{D_c}}\right)\right] \cdot R_e + \frac{\delta}{C_{dl}s}} \quad (1)$$

where R_e is the resistance of electrolyte, D_c the coefficient of ionic diffusion in the film, C_{dl} the double layer capacitance, δ the double layer separation, and d is the thickness of the composite film. Note that the diffusion coefficient is different from that of pure polymer electrode due to SWNTs. In fact, each carbon nanotube acts as an electrode so that ions need not travel a long distance [3]. In this model, the polymer resistance is assumed to be negligible compared to the electrolyte resistance.

In order to keep the highest electrical to mechanical conversion efficiency, the period of applied potential is usually slower than the time constant for diffusion to produce such ideal behavior, because in this regime much of the transferred electrical energy is recoverable. The admittance of system becomes [4]

$$Y(s) = s \cdot C_{dl} \left(\frac{a}{2\delta} + 1 \right) \quad (2)$$

where a is a polypyrrole electrode thickness and provided that the frequency of the applied voltage, $f \ll D_c / a^2$ and $f \ll 1 / 2\pi R_e C_{dl}$

From the morphology of CPs coated with SWNT nanocomposite [3,5], we can notice that, among all of the ions which diffuse into the composite, some of them are neutralized by the charges adhering to CPs chain and the others are neutralized by the charges in the SWNTs, just as shown in Fig. 1. Therefore, for each CPs-SWNTs unit cell, it can be considered as other form of an electrochemical actuator, where the SWNTs act as the electrode and the ions required are transmitted by the coated CPs from the electrolyte. At this time, the conductive polymer can be considered as a solid electrolyte.

At the lower injection level, the relative change of the length $\Delta\gamma$ can be described by a following equation [6]:

$$\Delta\gamma = \left(\frac{\alpha}{Kd} \right) \cdot \left(\frac{2\sqrt{3}\beta}{\alpha} \mp q \cdot \sin 3\phi \right) \cdot \delta_n \quad (3)$$

where q is the remainder of $(N-M)/3$ for (N, M) tube, N and M are the chiral vector index, ϕ is the chiral angle and δ_n is the doping level. The representative numerical values of α/Kd and β/α are 0.2 and 0.1, respectively. The \mp signs correspond to electron and hole doping, respectively. In fact, even though the SWNTs electrode contacts with the electrolyte directly, the doping level is low, just as mentioned [7], at $\approx 1 \text{ Volt}$ applied potential and its value amounts to $\delta_n \approx 0.005e^-/C\text{-atom}$.

Because SWNTs bundles are involved in the double layer charging only on their external surfaces, the diffusion-limiting effects can be neglected. Therefore, for this ideal double layer capacitor we can get [8]:

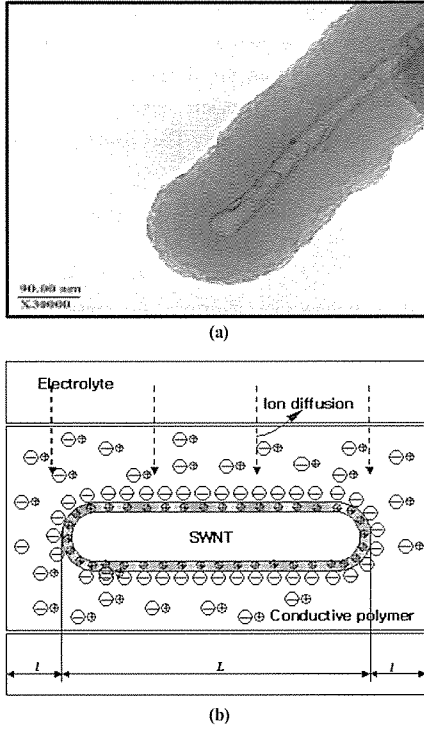


Fig. 1 (a) The morphology of a SWNT coated with Polypyrrole nanocomposite [3] (b) the ionic distribution.

$$\Delta\delta_n = M_c \cdot C_g \cdot \Delta V / F \quad (4)$$

where M_c is the atomic weight of carbon, C_g is specific capacitance, $\Delta V = V - V_o$ is the potential difference between applied and initial potentials, and F is the Faraday constant. For each single SWNTs/CPs composite actuator as shown Fig. 1(a), the change of a length can be expressed as

$$\varepsilon_n = \Delta\gamma = 0.2 \times (0.1 \times 2\sqrt{3} \mp q_i \cdot \sin 3\phi_i) \frac{M_c \cdot C_g}{F} V \quad (5)$$

As described previously, at the low frequency the electrode behavior is capacitive and the effective capacitance is given by [2]

$$C_{eff} = C_d \left(\frac{a}{2\delta} + 1 \right) \quad (6)$$

It was known that for the ions entering into the film, two ionic trapping sites are in the film, one is the double layer and the other is the bulk of the film [9]. Now we can describe this electrochemical system as an equivalent circuit shown in Fig. 2, where C_p and C_c are the pseudo-capacitance of CPs and SWNT in the film, respectively. This equivalent circuit is identical to Randel modified equivalent circuit at low frequency [10]. The limit capacitance of the film is consisted of three components: the double layer capacitance, the CPs and the SWNTs pseudocapacitance. So, we can express the potential drop of the composite film as

$$V(s) = U(s) - I(s) \cdot R_e = U(s) \cdot [1 - Y(s)R_e] \quad (7)$$

where $V(s)$ is the potential drop of the composite film, $U(s)$ is the applied voltage to the composite film, R_e is the resistance of the electrolyte, and s is a variable in frequency domain.

Then, the equivalent applied potential to a single SWNT/CP unit nanoactuator is V , and the average strain of SWNTs in the composite film is

$$\varepsilon_r(s) = 0.2 \times (0.1 \times 2\sqrt{3} \mp K) \frac{M_c \cdot C_g}{F} \cdot U(s) \cdot [1 - Y(s)R_e] \quad (8)$$

where $K = \frac{\sum_{i=1}^n q_i \cdot \sin \phi_i}{n}$ indicates the whole semiconducting or metallic property of the SWNTs component in the composite film. Experiments show that at low frequencies the strain and voltage of CPs may be related as [2]

$$\varepsilon_r(s) = \alpha \cdot \rho(s) + \frac{\sigma(s)}{S(s)} \quad (9)$$

where ρ refers to charge density, σ an applied stress and S stiffness.

We assume that in the Fig. 1, $L \gg l$. At this time, for CPs the effects of stress along SWNTs aligned direction caused by SWNTs actuations may be ignored. So, for the aligned SWNTs composite film without any applied stress, the strain caused by CPs in aligned direction can be expressed as [2]

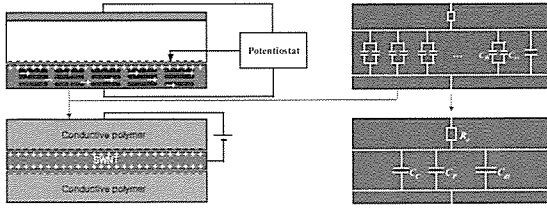


Fig. 2 Equivalent electrical circuit of the SWNTs/CPs composite actuator electrochemical system at low frequency.

$$\varepsilon_p = \frac{\alpha I}{sV_f} = \frac{\alpha \cdot U \cdot Y}{sV_f} \quad (10)$$

where α is an empirically derived constant of proportionality referred to as the ratio of strain to charge and V_f is the volume of the composite film. In the composite film, SWNTs not only have their own actuation but also reinforce the polymer matrix. So if we know the SWNTs weight fraction, w_c , the SWNTs equivalent density, ρ_c and the polymer density, ρ_p , the polymer volume fraction, V_p , can be determined by the rule of mixture,

$$V_p = 1 - \frac{w_c \cdot \rho_p}{w_c \cdot \rho_p + (1 - w_c) \rho_c} \quad (11)$$

And the equivalent Young's modulus of the composite film under $L \gg l$ is determined by

$$E_r = E_p V_p + E_c (1 - V_p) \quad (12)$$

where E_p and E_c are Young's moduli of conductive polymer and SWNTs, respectively.

Then, the combined strain of the composite actuator can be expressed as

$$\begin{aligned} \varepsilon_r(s) = & \{ [a_1 \cdot \frac{\alpha}{s \cdot V_f} \cdot s \cdot C_{dl} \cdot (\frac{d}{2\delta} + 1) \cdot \\ & + a_2 \cdot \frac{0.2 \times (0.1 \times 2\sqrt{3} \mp K) \cdot M_c \cdot C_G}{F} \cdot \\ & [1 - s \cdot C_{dl} \cdot (\frac{d}{2\delta} + 1) \cdot R_e] \} \cdot U(s) \end{aligned} \quad (13)$$

where $a_1 = \frac{E_c}{E_r} \cdot V_p$ and $a_2 = \frac{E_p}{E_r} (1 - V_p)$. Eq. (13) can be converted to a time domain by Lapalce transform,

$$\mathcal{E}_T(t) = \mathcal{L}^{-1} [\mathcal{E}_T(s)] \quad (14)$$

Here, the electrolyte resistance, R_e , and the thickness of the film, d , can be readily measured. The double layer capacitance, C_{dl} , and the specific capacitance of SWNTs, C_G , also can be measured, fit, or the accepted value can be used. The double layer separation, δ , can be approximately related to C_{dl} using Eq. (15). For the given SWNTs that is used to reinforce the composite film, K is a constant. And we can determine it by identifying the constant to that of pure SWNTs mat actuators. Then the strain of well-aligned SWNTs composite actuator is explicit.

$$\delta = \frac{k \cdot \varepsilon_0 \cdot A}{C_{dl}} \quad (15)$$

In this equation, k is a dielectric constant and ε_0 is the permittivity of a free space. The last three parameters (C_{dl} , C_G , K) can be determined by fitting the experimental data ε^* from a strain-voltage test by means of a chi-square estimation of the error, \aleph^2 :

$$\aleph^2 = \sum_{i=1}^n \left[\frac{\varepsilon(t_i, n) - \varepsilon^*(t_i)}{s^2(t_i)} \right]^2 \quad (16)$$

where, n is the vector of three parameters to be determined in order to minimize the error and s^2 is the data variance. Using the Nelder-Meads simplex method, which is an iterative direct search method implemented with Matlab, the values of three constants C_{dl} , C_G , K can be obtained.

3. Results and Discussion

Actually, the nanotubes in composite films are far away from well-aligned status so that the pore structure of the film may affect on the double layer capacitance and the equivalent

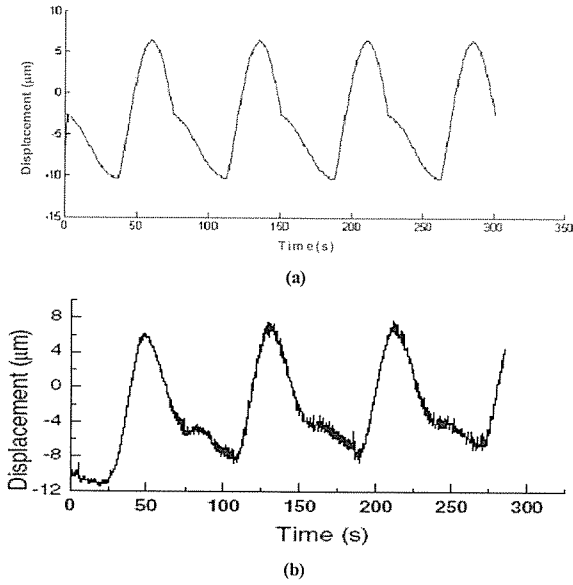


Fig. 3 (a) Displacement result from Eq. (13) and (b) experimental results [11] of a CNTs-PAN actuator.

Young's modulus of SWNTs is closer to a SWNTs mat (typical value is 0.9 MPa) rather than to SWNTs bundles (typical value is 640 MPa). As a result, the role of SWNTs is weakened and the CPs influence is strengthened.

Fig. 3 displays strains calculated from Eq. (13) under the applied voltage. The data were obtained from the experimental result [11] of the CNTs-PAN composite actuator. The composite film thickness, $d=0.169 \times 10^{-4} \text{ m}$, area $A=1.8 \times 10^{-5} \text{ m}^2$, $R_c=175 \text{ Ohm}$. The double layer capacitance $C_{dl}=0.2 \text{ A}$ is likely in the range of 0.1 A to 0.4 A [2], and the double layer thickness can be determined from C_{dl} , $\delta=2.37 \times 10^{-9} \text{ m}$ (determined from C_{dl}). The value of $K=-0.1562$ is obtained by relating Eq. (13) to the experiment data of pure SWNT actuator. $C_G=40 \text{ F/g}$, $M_c=12$, $F=9.64846 \times 10^4$, $E_c=10 \text{ GPa}$ and $E_p=0.9 \text{ GPa}$ are typical Young's moduli of SWNTs and polyaniline. Two results show that the calculated data are correlated very well with the experiment.

The maximum actuator strain and stress can be calculated based on the following equations;

$$\begin{aligned} \varepsilon_T(s)_{\max} = & \left\{ \left[\frac{\alpha}{s \cdot A \cdot d} \cdot s \cdot \left(\frac{d}{2\delta} + 1 \right) \cdot C_{dl} \cdot E_c \right. \right. \\ & \left. \left. + \frac{0.2 \times (0.1 \times 2\sqrt{3} \mp K) \cdot M_c \cdot C_G}{F} \right] \right. \\ & \left. [1 - s \cdot C_{dl} \cdot \left(\frac{d}{2\delta} + 1 \right) \cdot R_c] \cdot E_p \right\} \cdot \frac{V_p \cdot U(s)_{\max}}{E_p V_p + E_c (1 - V_p)} \quad (16) \end{aligned}$$

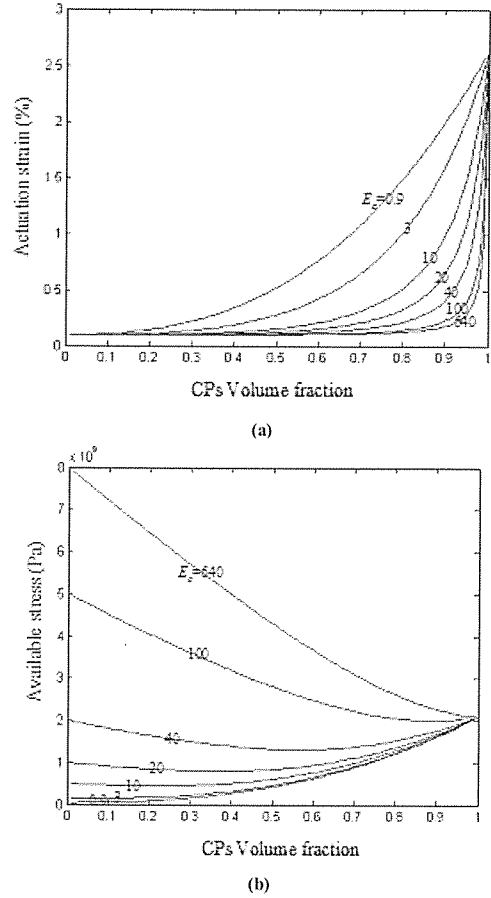


Fig. 4 (a) Actuation strains and (b) induced stresses.

$$\tau_{\max} = \varepsilon_{\max} \cdot E_T \quad (17)$$

As the CPs volume fraction in the film increases, the double layer capacitance of the composite film changes from the value of pure SWNTs bucky paper (0.4 F/m^2) actuator to pure CPs actuator (0.2 F/m^2). Consider that, C_{dl} fits to available experimental data for different CPs fractions. Then, the maximum of strain $\varepsilon_{T\max}$ and stress σ_{\max} of the composite actuator can be described as a function of a CPs volume fraction V_p such as Eqs. (16) and (17). Fig. 4 displays the actuation strains and induced stresses for various CPs volume fractions and equivalent Young's moduli of SWNTs based on the same parameters used for Fig. 3.

It is shown from Fig. 4 that the alignment of the SWNTs

affects on actuation of composite actuator remarkably. For the same CPs volume fraction, the well-aligned actuators have smaller strain as in Fig. 4(a), but larger induced stresses as in Fig. 4(b). However, well-aligned SWNTs composites need less SWNTs weight fraction under the same strain requirement. So the optimal SWNTs/CPs composite actuator may be achieved through well-aligned SWNTs in CPs matrix. Besides that, there are some other factors that affect the strain-voltage relationship of the actuator, such as the type of ions in the electrolyte, the conductivity of the film and the input voltage. Hence, we also can choose the suitable electrolyte, input voltage, etc. to improve the actuation strain of the composite actuator.

4. Conclusions

The strain-voltage relationships of a SWNTs/CPs composite actuator at a low frequency has been derived using an electrochemical unit cell model. Based on the relationship, the actuating strains and stresses of the actuator were obtained under various applied voltages. The actuation is found to be affected by SWNTs and CPs components. The actuation of the SWNTs has two different influences on that of the CPs reinforcement at a positive voltage and abatement at a negative voltage. Additionally, the SWNTs reinforcement plays an important role in a actuation response due to its high Young's modulus. The performance of the SWNTs/CPs actuator can be optimized based on well-aligned SWNT and choice of suitable electrolyte and applied voltage.

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