

An Approximate Description of Strain-Voltage Relationships for SWNTs/Conducting Polymer Composite Actuator

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ABSTRACT

An approximate relationship of the strain and applied potential was derived for SWNTs and conductive polymer composite actuator. During the deriving process, we used an electrochemical system to model the electromechanical actuation of the composite film. This relationship can give us a direct understanding to the actuation of a nanoactuator.

1. INTRODUCTION

The development of an innovative actuator consisting of single wall carbon nanotubes (SWNTs) and conducting polymers (CPs) have been investigated for possible applications to the actuation of MEMS devices since last few years. In this new nano-composite 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 polymer films. Additionally, carbon nanotubes have high electrical conductivity, which can increase the charging-discharging rate and improve the electrode performance of CP films. SWNTs also exhibit strains due to

electrochemical redox at low bias voltage (non-Faradic electrochemical charging) [1], which is enough for the actuation of MEMS devices. The relationships between the strain and the applied potential for are developed for in this paper.

2. VOLTAGE AND STRAIN

If the nanotube fibers of the composite actuator is well-distributed, then we can consider that there are similarities between the electromechanical properties of the SWNT actuator and pure CPs [2]. During the electrochemical process of the composite actuator typical parameters used in actuator such as the diffusion coefficient and pseudocapacitor, etc. are formed, even though they would be changed remarkably because of the existence of the SWNTs. The development procedure is based on the model that was presented by Madden, J. D. *et al.* [3]. However, the big difference is

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that we replace the PPy(polypyrrole) film by the composites film of CNT-CPs. The valid logics behind the choice of ref. [3] approach is that it synthesizes the mechanisms of electrical to mechanical energy transduction responsible for actuation, rather than the effects of CNT on CPs.

As in the discussion of [3], the composite actuator has a cell structure. The electrolyte acts as a resistance, R_e , and the interface between the polymer and the electrolyte is a capacitance, C_{dl} . Current passing through the cell must traverse the electrolyte. Current charges the double layer capacitance, which in turn may be discharged by diffusion. So we can express this electrochemical process by following equations:

$$I_{(t)} = I_c(t) + I_D(t) \quad (1)$$

$$U(t) = I(t)R_e + \frac{1}{C_{dl}} \int I_c(t)dt \quad (2)$$

$$I_D(t) = -F \cdot A \cdot D_C \cdot \frac{dc}{dx}(x,t)|_{x=0} \quad (3)$$

$$I_c(t) = F \cdot A \cdot \delta \cdot \frac{dc}{dt}(x,t)|_{x=0} \quad (4)$$

where D_C is the coefficient of ionic diffusion in the composites. Note that this diffusion coefficient is different from that of the pure polymer electrode because of the participation of the SWNTs. δ is the double layer separation.

After transforming to Laplace domain and solution, the admittance of the system is obtained (in the Laplace domain):

$$Y(s) = \frac{\delta + \sqrt{\frac{D_C}{s}} \cdot \tanh\left(\frac{a}{2} \cdot \sqrt{\frac{s}{D_C}}\right)}{\left[\delta + \sqrt{\frac{D_C}{s}} \cdot \tanh\left(\frac{a}{2} \cdot \sqrt{\frac{s}{D_C}}\right)\right] \cdot R_e + \frac{\delta}{C_{dl}s}} \quad (5)$$

There are four parameters to be determined: C_{dl} , D_C , δ ,

and R_e .

It is well known that the electrical behavior of an ion-insertion electrode in a liquid electrolyte can be equivalent to be so-called Randles circuit [4], shown in Fig. 1. In this circuit, R_e refers to the solution resistance, C_{dl} to the double layer capacitance, R_e to the charge transfer resistance for the redox reaction, Z_W to the ion diffusion in the solution near the film/electrolyte interface, C_f to the film capacitance and R_f to the film resistance. The electronic resistance of the film, R_{fe} , should also be added in series with R_e because it is not significant compared with the R_e value.

In the AC response of a Randles circuit (Fig.2), the high frequency semicircle is attributed to charge

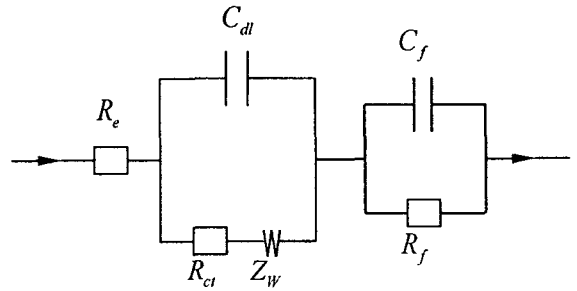


Figure 1. Generally equivalent circuit for an electrochemical system

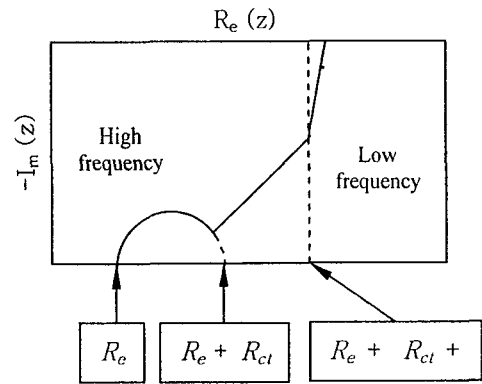


Figure 2. Typical complex AC impedance spectrum (Nyquist plot) of the circuit shown in figure 1.

transfer reactions, while the low frequency tail is associated with diffusion processes. R_e and R_{ct} can be directly determined ($Z' \sim R_e$ for $f \rightarrow \infty$ and R_{ct} is

determined from the widths of the Z'/Z' -semicircles (Fig.2)). So R_L can be easily determined, while C_{dl} can be calculated at its maximum using eq. (7), the diffusion coefficients, D_C , can generally be extracted from the low frequency EIS data using eq. (8), and the limiting capacity, C_L , can be determined from the slope of a plot of imaginary component of impedance (Z'') at low frequency (ω)(Fig .3) using eq. (9).

$$R_T = R_e + R_{ct} + R_L \quad (6)$$

$$C_{dl} = \frac{1}{2\pi\omega_{max}} R_{ct} \quad (7)$$

$$C_L \times R_L = \frac{a^2}{3D} \quad (8)$$

$$\frac{d(-z'')}{d(\omega^{-1})} = \frac{1}{C_L} \quad (9)$$

The double layer separation, δ , can be approximately related to C_{dl} by assuming a parallel plate capacitor, whose area, A , is the size of the interfacial region, the dielectric constant is that of the solvent. So the expression of admittance has been

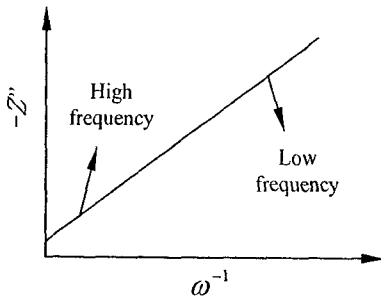


Figure 3. Z'' vs ω^{-1} plot of the electrochemical system

explicit.

$$\delta = \frac{k \cdot \epsilon_0 \cdot A}{C_{dl}} \quad (10)$$

Experiments show that strain, ϵ , is proportional to the density of charge, ρ , transferred over a range of strains of about 0.5 %:

$$\epsilon = \frac{\sigma}{E} + \alpha \cdot \rho \quad (11)$$

where σ is the applied stress and E is the elastic modulus [5]. The strain to charge ratio, α , is typically in the range of $\pm 1-3 \times 10^{-10} m^3 \cdot C^{-1}$ [3]. For a given polymer volume, V_f , and without any applied stress, the relationship between current and strain is then:

$$\epsilon_p = \frac{\alpha I}{V_f} = \frac{\alpha \cdot U \cdot Y}{V_f} \quad (12)$$

If we know the SCNTs' weight fraction, W_n , the CNTs' equivalent density, ρ_c and the polymer's density, ρ_p , the polymer's volume fraction V_n can be determined by

$$V_n = \frac{w_n \cdot \rho_p}{w_n \cdot \rho_p + (1 - w_n) \rho_p} \quad (13)$$

So, the equivalent volume of conductive polymer is

$$V_f = a \cdot A \cdot V_n \quad (14)$$

Then the strain caused by conductive polymer's electromechanical actuation has been determined. In

fact, in order to keep the highest electrical to mechanical conversion efficiency, we usually apply the ac whose period is slower than the time constant for diffusion produces such ideal behavior, because in this regime much of the transferred electrical energy is recoverable.

At this point, the admittance of system becomes

$$Y = j\omega \cdot C_{dl} \left(\frac{a}{2\delta} + 1 \right) \quad (15)$$

providing that frequency $f \ll \frac{D}{a^2}$, and $f \ll \frac{1}{2\pi R_c C_{dl}}$

In the next step, we need to determine the strain ε_c associated with the SWNTs. For SWNTs sheet or bundles actuators, it is not so straightforward to disentangle the quantum-mechanical and electrostatic effect [6]. Considering the high electrical conductivity and high redox current of the composite film, we use the following approximate modeling. Because the SWNTs bundles were coated within the conductive polymer, for every SWNTs bundles monomer, we can consider the conductive polymers coating them represent a solid electrolyte to provide a high charge concentration in the SWNT/electrolyte interface (double layer). Indeed, from the others' experiment result, we know during the electrochemical process, the redox current of SWNTs/CPs composites electrode was much higher than that of the pure CPs [7,8], so it can provide sufficient charge transfer to SWNTs.

In this solid electrolyte cell, the SWNTs actuator response can be described by a strain-voltage coefficient S_v , which is the ratio of change in actuator strain to the change in applied electrode potential [1].

$$S_v = \frac{C_G M \Delta L}{F L \Delta y} \quad (16)$$

Where $\frac{\Delta L}{L}$ is the fractional change in length

caused by a Δy change in the concentration of injected charge per monomer unit, C_G is the specific capacitance, M is the monomer molecular weight and F is the number of coulombs of charge in a mole of electrons (the Faraday constant). The strain-charge coefficient $(\frac{\Delta L}{L} / \Delta y)$ can be regard as $(\frac{\delta_{dc-c}}{d_{c-c} \cdot f_c})$, that is, the change in C-C bond length or in in-plane lattice constant (δ_{dc-c}) caused by the doping level f_c .

There is the following universal relationship between f_c and δ_{dc-c} [6,9]

$$\delta_{dc-c} = 0.157 f_c + 0.146 [f_c]^{\frac{3}{2}} + 0.236 f_c^2 \quad (17)$$

Notice that δ_{dc-c} is positive for donors and negative for acceptors. So the strain-charge coefficient can be expressed as a function to f_c

$$\frac{\delta_{dc-c}}{d_{c-c} f_c} = \frac{0.157 \pm 0.146 [f_c]^{\frac{1}{2}} + 0.236 f_c}{d_{c-c}} = \delta [f_c] \quad (18)$$

If the SWNTs were well purified, it would develop an ideal double layer capacitor behavior without any redox process [6]. And during the double layer forming process, the diffusion limited effect can be neglected, since the given ionic is much smaller than the distance between neighboring wall of SWNTs in a bundle [10].

For an ideal double-layer capacitor, we can express [11]

$$\Delta f_c = M_c \cdot C_G \cdot \Delta V / F \quad (19)$$

where M_c is the atomic weight of carbon, ΔV is the potential difference, and F is the Faraday constant. So we can obtain the following equation

$$s_v = \frac{d\varepsilon_c}{dV} = C_G \cdot \frac{M_c}{N} \cdot \delta[f_c] \quad (20)$$

The result of this equation is, then

$$\varepsilon_c = \frac{\beta}{d_{c-c}} (0.157V + \frac{2}{3} \cdot 0.146\beta^{\frac{1}{2}} \cdot |V|^{\frac{3}{2}} + \frac{1}{2} \cdot 0.236 \cdot \beta \cdot V^2) \quad (21)$$

where $\beta = C_G \cdot \frac{M_c}{F}$, and V in volt, d_{c-c} in nm.

As have been mentioned [4,12], at very low frequencies, the composites electrode behaves like a capacitor in series with a resistor, respectively, called C_L and R_L . As this time, the equivalent voltage V applied to the composites film is

$$V = I(t) \cdot R_L = U(t) \cdot Y \cdot R_L \quad (22)$$

We assume there are sufficient ions be transport to meet the ion requirements of both composite components, the total strain will be

$$\varepsilon_T = \varepsilon_C + \varepsilon_P \quad (23)$$

From eq. (23) we can find that during a voltage period, the SWNTs have two kinds of effect: reinforcement at positive voltage and abatement at negative voltage. This is identical to the experimental observations about CNT and polyaniline composite actuators [13]. But there are some discussions about this model, for example, even though the high redox current in the composite film, but it also very difficult to meet the ion requirements of both composite components. And it is not easy to determine the specific capacitance of the SWNTs that was embedded in the CPs.

3. CONCLUSIONS

The approximate strain-voltage relationships at

low operational frequency have been derived using an electrochemical cell modeling. During the derivation of equations, most of the effects of SWNTs on conductive polymers, such as the increase of the redox current and pseudocapacitance of the composite actuator, was included by the parameters of this electrochemical model, that are diffusion coefficient and the double layer capacitance. These parameters can be easily determined by experiments.

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