NOTES

Bending of Polyelectrolyte Membrane–Platinum Composites by Electric Stimuli I.
Response Characteristics to Various Waveforms

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Recently, considerable attention has been paid to the deformation of polymer gels in response to environmental changes.[1] The deformation has potential applications for muscle-like actuators, such as that driven by electric stimuli since it can be controlled easily.[1] However, for using polymer gels as electrically driven actuators, there are some disadvantages, *i.e.*, slow response and high voltage that causes water electrolysis.

Previous papers[2-4] reported that low voltage which does not cause water electrolysis between platinum electrodes on both sides of perfluorosulfonic ion-exchange membrane gives a quick bent of the film in aqueous solution. The electrically driven composite has a lot of features, such as soft operation, easy minitaturization, fast response, long life to work and low driving voltage. However, the characteristics of bending response to various factors and mechanisms of bending still remain unclear. In this paper, bending response to several electric stimuli was studied. The aim of the paper is to represent the bending response as a function of current. By using the function, bending response to any electric stimuli is capable of being estimated. Phenomenological modeling is the first step to a theoretical understanding of bending response, and a mechanism of bending considered from the model is proposed.

EXPERIMENTAL

Preparation of the Composites

After surface roughening by dry-brasting, both sides of a film of perfluorosulfonic acid (Nafion® 117 by E. I. DuPont de Nemours and Co.) were chemically plated with platinum.[5] Platinum ammine complex cation adsorbed in the film was reduced by sodium boron hydride in outer solution. The amount of platinum on the surface of the membrane was about $3\,mg\,cm^{-2}$. The thickness of polymer electrolyte membrane is $185\,\mu m$ as received and $210\,\mu m$ in the wet state. Equivalent weight is 1100 and water uptake is $0.37\,g\ H_2O/g$ dry membrane.[6]

Measurement

Figure 1 shows the measurement system. The plated film was cut into a ribbon with a width of 1 mm and length of 15 mm. The ribbon was supported vertically in various aqueous solutions and displacement of the free end (10 mm from the fixed point) of the ribbon was measured by a laser displacement meter (KEYENCE LC-2100/LC-2220). In consideration of refraction of light, the value measured
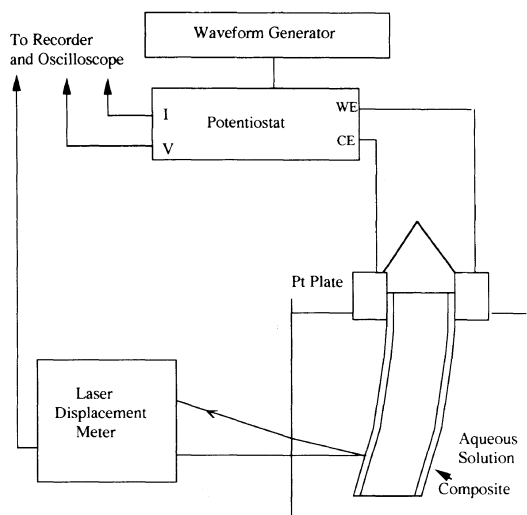
Figure 1. Layout of apparatus.

by laser displacement meter multiplied by 1.47 gives the compensated value for the refractive index.[2] The measured value in this paper is the compensated value. A voltage was measured with reference to the CE electrode and the sign of current flow from WE to CE electrode was a positive. All measured values were digitally sampled and recorded by Digital oscilloscope (Hitachi Denshi Ltd., VC-9145) and Digital recorder (Yokogawa Electric Co., ORM1200). The waveform generator and potentiostat/galvanostat used were an AG-1200 (Yokogawa Electric Co.) and HA-501G (Hokuto Denko Co.), respectively. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Figures 2—4 show displacement and current response driven by step or sweep voltage in aqueous mixed solution consisting of 0.1 M Na_2SO_4 and 10 mM H_2SO_4. The dotted lines in Figures 2—4 represent the displacement response curve calculated by the method as mentioned later. The current is the capacitive one in this voltage range, which does not cause water electrolysis.

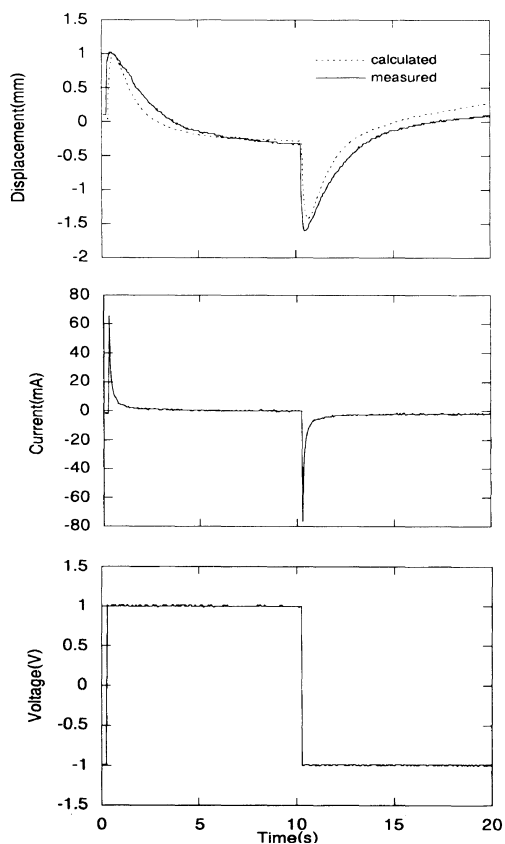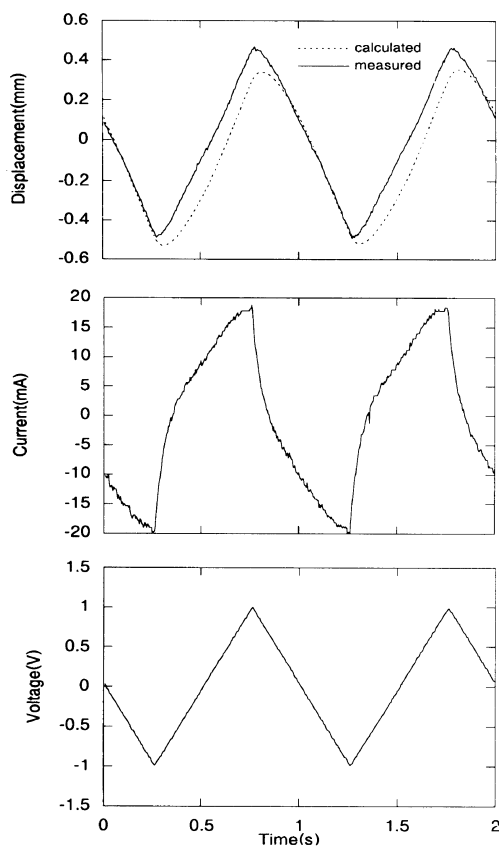In the case of step voltage, the composite

Figure 2. Displacement and current response driven by step voltage. The composite was immersed in a mixed solution consisting of 0.1 M Na_2SO_4 and 10 mM H_2SO_4.

quickly bends to the anode side and bends back to the cathode side gradually as shown in Figure 2. The displacement reached a peak value within 100 ms.[3,4] Triangular wave voltage of high sweep rate ($4V s^{-1}$) gave displacement proportional to the voltage as shown in Figure 3. In the case of triangular wave voltage of low sweep rate ($400 mV s^{-1}$), the displacement waveform appeared similar to the current waveform rather than the voltage (Figure 4).

Figure 5 shows displacement and voltage response driven by square wave current in the same aqueous solution. The voltage varies gradually as the constant current charges or discharges electrodes. The displacement response $d(t)$ can be experimentally represented
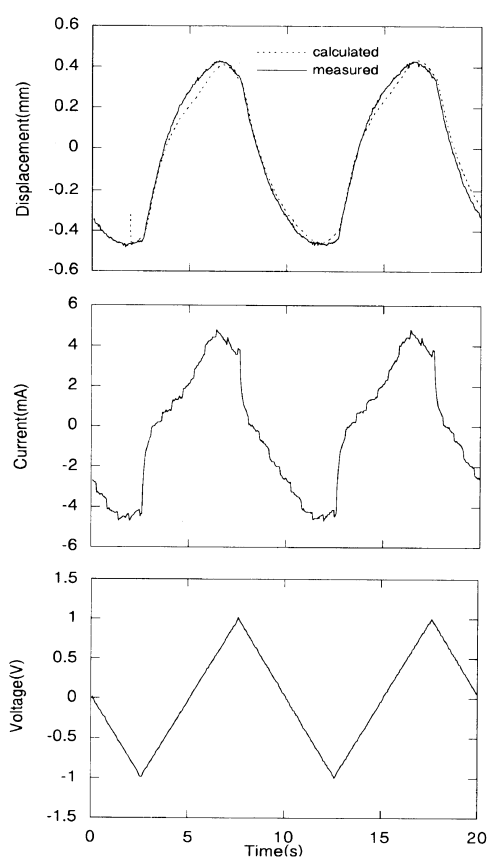
Figure 3. Displacement and current response driven by triangular voltage. The composite was immersed in a mixed solution consisting of $0.1\,M$ Na_2SO_4 and $10\,mM$ H_2SO_4. Sweep rate, $4\,V\,s^{-1}$.

Figure 4. Displacement and current response driven by triangular voltage. The composite was immersed in a mixed solution consisting of $0.1\,M$ Na_2SO_4 and $10\,mM$ H_2SO_4. Sweep rate, $0.4\,V\,s^{-1}$.

as a function of time t as follows:

$$d(t) = c_1(1 - \exp(-(t - t_s)/\tau)) + c_2(t - t_s) + c_3 \tag{1}$$

where c_1, c_2, c_3 are constant values, t_s is the time when the sign of the square wave current changes, and τ is a time constant.

Preliminary experimental results show that displacement of different composites immersed in the same solution on application of the same voltage linearly depends on admittance of the composite. Therefore, displacement should be represented as a function of current rather than voltage, since the relation between displacement and current is simpler than that between displacement and voltage. Hence, on the basis

of the experimental results mentioned above, bending response is represented as a function of current flow between two electrodes, and a simple model is proposed for the bending of composites.

To generalize eq 1, it is assumed that a superposition theorem can be applied to the relation between displacement response and current stimuli. The superposition theorem is that the response can be represented as a linearly additive function of stimuli history. The theorem can be applied to various phenomena and is called the "Curie-Hopkinson superposition theorem" in dielectrics[7a] and the "Boltzemann superposition theorem" in viscoelastic phenomena.[7b] By using the super-
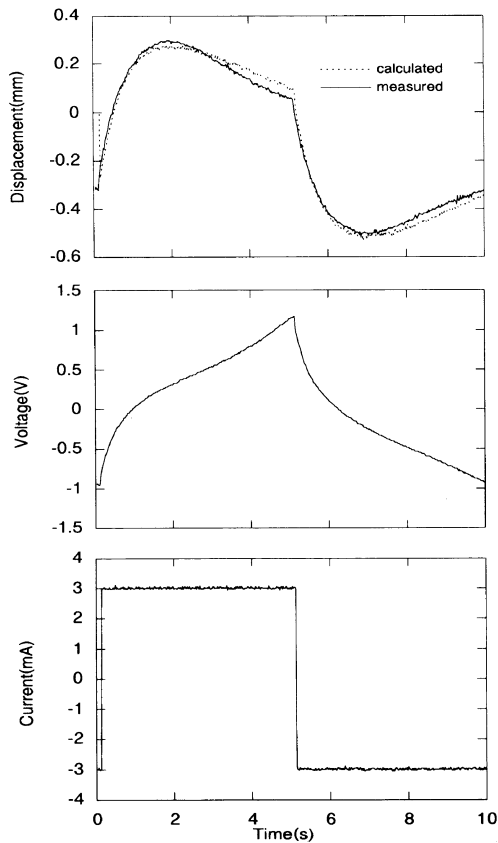
Figure 5. Displacement and voltage response driven by step current. The composite was immersed in a mixed solution consisting of 0.1 M Na_2SO_4 and 10 mM H_2SO_4.

position theorem, we obtain the following equation:

$$d(t) = \int_{-\infty}^{t} k_1 \exp(-(t-u)/\tau)i(u)\mathrm{d}u$$

$$+ \int_{-\infty}^{t} k_2 i(u)\mathrm{d}u \qquad (2)$$

where k_1, k_2 are displacements per unit charge and $i(u)$ is current at time u. For simplicity, k_1, k_2 are assumed to be constant.

Let us consider the case that current $i(u)$ is a square waveform whose period T is much longer than time constants τ. If time t_0 satisfies the condition: $T > t_0 \gg \tau$, and the square waveform current $i(u)$ switches from $-I$ to I at time 0, the integral constant $-\infty$ can be replaced

by $-t_0$ in eq 2, since the inequality:

$$\int_{-\infty}^{-t_0} k_1 \exp(-(t-u)/\tau)I\mathrm{d}u$$

$$\ll \int_{-t_0}^{t} k_1 \exp(-(t-u)/\tau)I\mathrm{d}u$$

is satisfied. Hence we obtain the following equation:

$$d(t) = -\int_{-t_0}^{0} k_1 \exp(-(t-u)/\tau)I\mathrm{d}u$$

$$- \int_{-t_0}^{0} k_2 I\mathrm{d}u$$

$$+ \int_{0}^{t} k_1 \exp(-(t-u)/\tau)I\mathrm{d}u$$

$$+ \int_{0}^{t} k_2 I\mathrm{d}u + d(-t_0)$$

$$= k_1 I\tau - 2k_1 I\tau \exp(-t/\tau) + k_2 It - k_2 It_0$$

$$+ d(-t_0)$$

$$= 2k_1 I\tau(1 - \exp(t/\tau)) + k_2 It + d(0) \qquad (3)$$

where $d(0)$ and $d(-t_0)$ are displacement at time 0 and $-t_0$, respectively, and $d(0)$ is represented as $d(0) = -k_1 I\tau - k_2 It_0 + d(-t_0)$. Equation 3 is in conformity with eq 1. By fitting the theoretical curve calculated by eq 3 to the measured curve, the parameters k_1, k_2, τ can be determined. The dotted line in Figure 5 shows the calculated curve.

To confirm the applicability of eq 2, the displacement response driven by step or sweep voltage (Figures 2—4) was calculated by using eq 2 from the parameters k_1, k_2 obtained by the step current measurement. Calculation was carried out by numerical computation, using the discrete form of eq 2 as follows:

$$d(nt_{\mathrm{samp}}) = \sum_{j=0}^{n} \left[k_1 \exp\{-t_{\mathrm{samp}}(n-j)/\tau\}i_j t_{\mathrm{samp}} \right.$$

$$\left. + k_2 i_j t_{\mathrm{samp}} \right] + d_{\mathrm{off}} \qquad (4)$$

$$(n = 1, 2, 3, 4, \cdots)$$

where t_{samp} is the sampling rate, i_j jth sampled value of current and d_{off} appropriate offset value of displacement. In the case of triangular waveform, d with which the condition $nt_{samp} > 3\tau$ is fulfilled is adopted as the steady state one, which can be compared with experimental results. The dotted lines in Figures 2—4 show the calculated curves, which are in good agreement with those measured.

Table I summarizes the parameter values obtained by square wave current measurement, together with those in aqueous solution of different H_2SO_4 concentrations. The results of voltage control measurements in aqueous solution of different H_2SO_4 concentrations can be simulated by the parameters in Table I, in the same manner as shown in Figures 2—4. The parameter k_1 is always positive, irrespective of pH, while the parameter k_2 depends on H_2SO_4 concentration markedly and is negative in acidic solution.

In the case of cation-exchange membrane, coupled with charging current, ion flux and electro-osmotic drag of water flow from the anode to the cathode.[8] It is therefore considered that the cathode side swells, the other side contracts, and the composite bends to the anode side. This process is accompanied by relaxation, i.e., water diffusion. The first term of eq 2 represents this situation.

Another mechanism of bending considered is as follows. It is considered that there is electric double layer at the interface between Pt electrode and polyelectrolyte membrane. Application of voltage between Pt electrode and polyelectrolyte membrane cause interfacial tension[9] and ion concentration in the layer to change. Change in ion concentration means change in osmotic pressure.[10] Application of voltage between two electrodes gives different interfacial tensions and osmotic pressures at each interface between the electrode and polyelectrolyte membrane. Bending stress is considered due to these differences. This mechanism is considered to have no relaxation process. The direction of bending stress de-

pends on various factors . The second term of eq 2 may be due to the stress.

The characteristics of bending response depends on pH and salt concentration in aqueous solution, element in electrode, process of plating, composition of the polymer, and and others. The effects of these factors are being studied and the results will be reported soon.

Table I. Parameter data[a]

H_2SO_4 Conc.	k_1	k_2	τ
mM	mC^{-1}	mC^{-1}	s
0	0.137	0.0631	0.79
5	0.211	−0.0163	0.75
10	0.179	−0.0236	0.67
20	0.170	−0.0396	0.73
30	0.148	−0.0382	0.72

[a] The composite was immersed in a mixed aqueous solution consisting of 0.1 M Na_2SO_4 and H_2SO_4 of different concentrations.

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