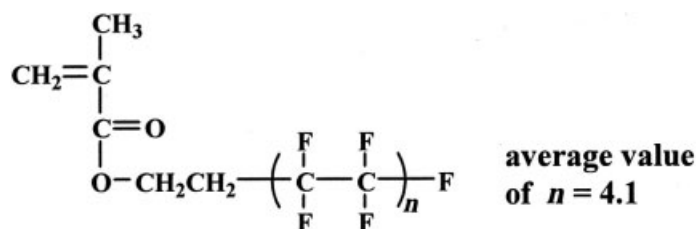


TABLE I
Acrylic Copolymers Used in Study

Designation	Feed composition (wt %)		Polymer composition ^a				Equiv. weight of polymer ^b	Reduced viscosity (dL/g)
	FMA	AA	wt %		mol %			
			FMA	AA	FMA	AA		
PFMAA20	80.0	20.0	91.1	8.9	58.2	41.8	816	0.98
PFMAA25	75.0	25.0	88.2	11.8	50.3	49.7	612	1.28
PFMAA30	70.0	30.0	86.3	13.7	45.9	54.1	524	1.39
PFMAA35	65.0	35.0	82.4	17.6	38.8	61.2	410	2.00

^a Determined by ¹H-NMR analysis.

^b Calculated from the polymer composition.



and acrylic acid (AA) can be effectively utilized in the preparation of IPMCs. It is also melt processable.

A compression-molded membrane of the copolymer was used to prepare the IPMC, and the performance of the IPMC is reported in this paper.

EXPERIMENTAL

FMA (Zonyl) and AA (Aldrich) were bulk copolymerized with 0.3 phr of 2,2'-azobisisobutyronitrile (Junsei) as a radical initiator at 60°C under a nitrogen atmosphere. The product was washed with methanol after crushing to remove residual monomer. The monomer compositions in the feed and the sample designation codes are provided in Table I.

An acrylic copolymer membrane was obtained by compression molding of the copolymer powder at 150°C. The thickness of the membrane used in this study was 0.16 mm, except when the effect of the membrane thickness was examined.

An IPMC with platinum electrodes plated on both faces was prepared by using the chemical plating method, which consisted of the ion exchange of H⁺ in the acrylic copolymer membrane with the cationic platinum complex followed by a reduction process in an aqueous solution of reducing agent.^{8,9} The compression-molded membrane was washed with deionized water and swelled in 25°C water for 2 days. The swollen membrane was immersed in an aqueous about 10⁻² M solution of tetraammineplatinum(II) chloride hydrate [Pt(NH₃)₄Cl₂ · xH₂O, Aldrich] for 3 h at 50°C to exchange the platinum complex cation. The impregnated cationic complex was reduced with an

aqueous 5 wt % solution of sodium borohydride (NaBH₄, Aldrich) at 40–60°C. The ion exchange and reduction processes were repeated up to 4 times to make thick platinum layers on the membrane.

The counteraction of carboxylate groups in the IPMC was converted to Li⁺, Na⁺, Ca²⁺, and (CH₃)₄N⁺ ions by soaking the IPMC in aqueous solutions of corresponding chloride salts for 48 h at room temperature and then rinsing with deionized water.³

To analyze the acrylic copolymer composition, the acrylic copolymers were dissolved in trifluoroacetic acid, and the ¹H-NMR spectra were recorded at room temperature with a Varian Plus 300-MHz NMR spectrometer.

The reduced viscosity was measured with an Ostwald viscometer at 30°C with a 0.5 g/dL acrylic copolymer solution in a mixed solvent of dimethylformamide (DMF)/1,3-bis(trifluoromethyl)benzene (50/50 v/v).

The tensile properties were measured by a tensile tester (Instron 4411) at room temperature with a cross-head speed of 10 mm/min. The compression-molded microtensile specimen had dimensions of 30 × 10 × 0.2 mm (length/width/thickness) and was swelled before measurement in 25°C water for 2 days.

The surface and cross section of dried IPMC were observed with a scanning electron microscopy (SEM) JEOL JSM820 microscope after sputtering with gold. To attain the cross section of dried IPMC, the IPMC was cryogenically fractured in liquid nitrogen.

The water uptake of the membrane or the IPMC was defined by eq. (1), where W_{wet} is the weight of the sample after storing in deionized water at 25°C for

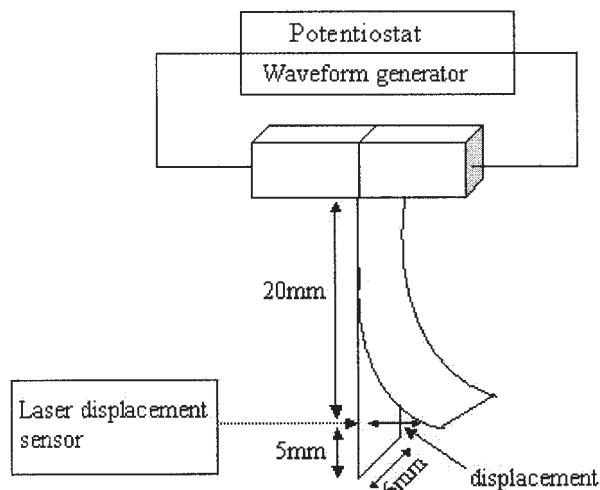


Figure 1 A schematic of the displacement measuring system.

48 h and W_{dry} is the weight of the sample after drying in a vacuum at 80°C for 48 h.³

water uptake (g water/100 g dry sample)

$$= \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

The experimental setup for the measurement of the bending deformation is shown in Figure 1. The IPMC film was cut into a ribbon with a width of 6 mm. One end of the ribbon was fixed with a clamp and the other end was kept free to bend horizontally by applied voltage. The effective length of the IPMC was 25 mm, and the displacement at the point of 5 mm from the free end was observed with a laser displacement meter. To actuate the IPMC, a ± 5 - or ± 9 -V step function voltage with an alternating cycle 0.2-Hz was applied between the platinum electrodes through the membrane.^{3,4} The displacement was measured after several training cycles for reproducibility.

RESULTS AND DISCUSSION

Properties of membrane and IPMC

The stress-strain curves of the wet acrylic copolymer membranes used in this study are shown in Figure 2. The tensile properties were measured and are summarized in Table II. The table shows that the wet acrylic copolymers were tender and became softer when the hydrophilic AA content in the copolymer was increased. The water uptake of the membrane into the hydrophilic domain of AA seemed to be a major cause of this softening (see Table III).

We observed that the membrane swelled and the water uptake increased during the chemical plating

process, as can be seen in Table III. This showed that the morphology of the hydrophilic domain changed and the hydrophilicity increased when the $-\text{COOH}$ group changed to the ionic $-\text{COO}^- \text{Na}^+$ group during the chemical plating process. It was reported that divalent Ca^{2+} formed a salt bridge ($\text{COO}^- - \text{Ca}^{2+} - \text{OOC}^-$) with considerable dehydration and contraction of the polyanionic polyacrylate molecules, an effect not observed for the monovalent Na^+ ion.¹⁰ This explained the smaller water uptake of the IPMC with divalent Ca^{2+} in Table III compared with those with monovalent Li^+ or Na^+ ions. In contrast, a weakly bound hydrophobic cation [$(\text{CH}_3)_4\text{N}^+$] seemed to allow an easy expansion of the macromolecular coil with a significant water uptake increase, which is demonstrated in Table III.¹⁰ We also observed that the IPMC became too soft to handle by excessive water uptake when the counteraction was exchanged with more the hydrophobic tetrabutylammonium ion. The larger charge density and hydration enthalpy of Li^+ compared with Na^+ seemed to be a cause of the larger water uptake (see Table III), as other researchers observed with Nafion.^{1,11,12}

It was not easy to attain a normal IPMC with the membrane prepared by casting the acrylic copolymer solution in DMF/1,3-bis(trifluoromethyl)benzene (50/50 v/v) mixed solvent. The upper part of the cast membrane swelled too much to produce a stable deposition of the platinum layer during the chemical plating process, and the swollen upper part was easily separated from the relatively less swollen lower part. This showed that there was a heterogeneity in the acrylic copolymer composition, because the unreacted monomer in the batch was depleted in the FMA monomer that previously participated in the forma-

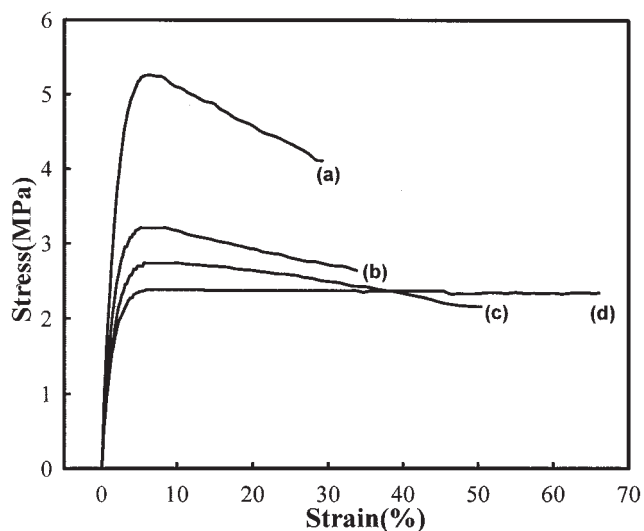


Figure 2 Stress-strain curves of wet acrylic copolymer membranes: (a) PFMAA20, (b) PFMAA25, (c) PFMAA30, and (d) PFMAA35.

TABLE II
Tensile Properties of Wet Acrylic Copolymer Membrane

Sample	Tensile modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
PFMAA20	0.91	5.26	3.90	30
PFMAA25	0.63	3.12	2.61	34
PFMAA30	0.49	2.73	2.30	51
PFMAA35	0.41	2.38	2.51	66

tion of the copolymer because of its high reactivity. Compared to the upper part, the lower part of the cast membrane seemed to contain acrylic copolymers with less amounts of AA, whose solubility in the solvent was lower and precipitated preferentially during the casting.

Morphology of IPMC

Figure 3 represents the morphology of the cross section and surface of the IPMC observed by SEM. In Figure 3(a) we can see that a deep layer of about 3 μm was developed from the surface where platinum was deposited. The surface of the IPMC showed islands separated by cracks. This showed that water swelling and contraction by drying generated these islands when the resulting strains exceeded the tensile strength of the thin platinum layer.¹

Response to electric stimulus

Figures 4 and 5 show the respective initial current and displacement responses of the IPMC for a period of 100 s just after an application of 5 or 9 V. Figure 4 shows that the current through the IPMC sharply increased as soon as the voltage was applied and then decreased exponentially. The maximum value of the initial current increased according to the order PFMAA20 < PFMAA25 < PFMAA30. However, the maximum value of PFMAA35 was smaller compared with that of PFMAA30. The initial displacement shown in Figure 5(b) also shows the same order of

magnitude. However, PFMAA30 and PFMAA35 showed a slow relaxation toward the neutral position.

When an IPMC is subjected to a voltage across its thickness, the cation moves from anode to cathode by an applied electric field, and this ionic migration induces an electroosmotic drag of water. Therefore, the cathode side swells, the anode side contracts, and the IPMC bends to the anode side.^{1,4,8} This actuation mechanism suggested that the current and displacement increased when the ionic concentration in the IPMC was increased according to the order PFMAA20 < PFMAA25 < PFMAA30, as we observed. Nemat-Nasser and Li applied a step voltage to an IPMC in dry air and observed that the sample quickly bent toward the anode side, to a maximum position, and stayed there, showing little tendency toward immediately returning to its neutral position.¹¹ However, when the same step voltage was applied while the IPMC was immersed in water, the sample slowly relaxed backward toward its neutral initial position.¹¹ These results and our above experimental observations suggest that the effect of osmotic pressure, which might cause the reverse cation migration from cathode to anode, works more evidently when there is sufficient water in the IPMC. That is, the slow relaxations of PFMAA30 and PFMAA35 in Figure 5(b) and the reduced initial maximum current of PFMAA35 compared with PFMAA30 in Figure 4 seem to be the effect of osmotic pressure, which more evidently works at a high content of water in the IPMC. We observed that the matrix of IPMC was partially damaged and the deposition of platinum particles on the surface was

TABLE III
Water Uptake of Membrane and IPMC

Sample	Membrane	Water uptake (g water/100 g dry sample)				
		Before cation exchange	IPMC			
			After cation exchange			
			Li ⁺	Na ⁺	Ca ²⁺	(CH ₃) ₄ N ⁺
PFMAA20	12.3	49.1	—	—	—	—
PFMAA25	15.0	59.6	79.3	71.1	47.3	207.2
PFMAA30	16.4	66.4	—	—	—	—
PFMAA35	19.1	80.7	—	—	—	—

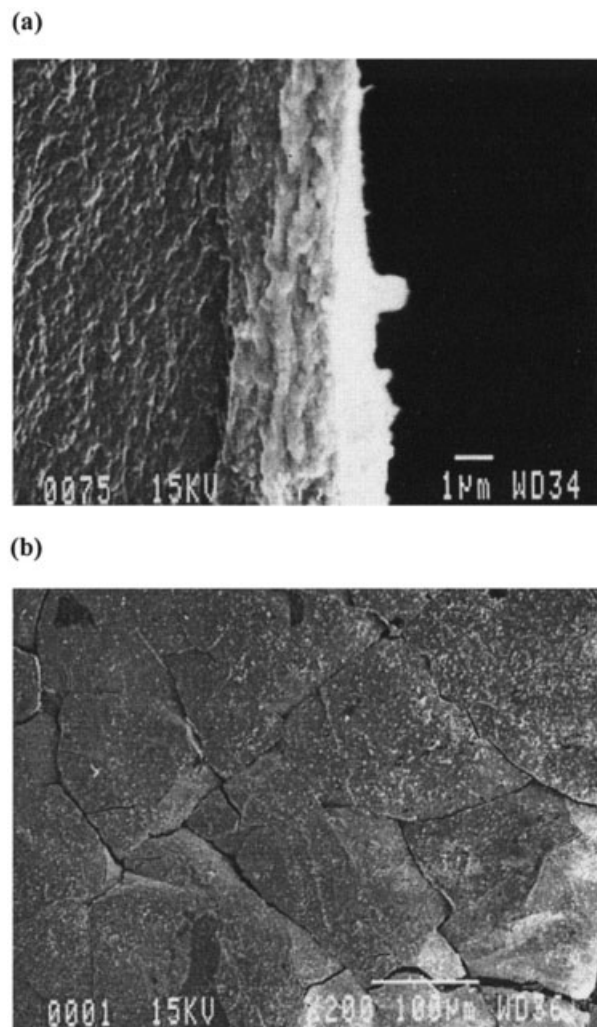


Figure 3 SEM photographs of IPMCs: (a) a cross section of PFMAA25 and (b) the surface of PFMAA25.

not dense enough when swollen too much by the large uptake of water at high AA content. This might be another cause of current reduction with high AA content.

Figure 6 shows the response of displacement by a ± 5 -V step voltage repeatedly applied across the IPMC with a 0.2-Hz cycle, where we can see that the variation in the magnitudes of displacement observed for the PFMAA25 and PFMAA30 IPMCs are larger compared with those values for PFMAA20 or PFMAA35 IPMCs, as in Figure 5. In Figures 5 and 6 we can see that, when the applied voltage is 9 V, the displacement value of IPMC from PFMAA30 is larger compared with the value from PFMAA25. However, this order is reversed when the applied voltage is 5 V. This suggests that the effect of the osmotic pressure that drives the cation from the cathode to the anode becomes more evident at lower applied voltage as well as at high water content. Figure 6 shows that the displacement drifts by repeated cycles toward the direction of

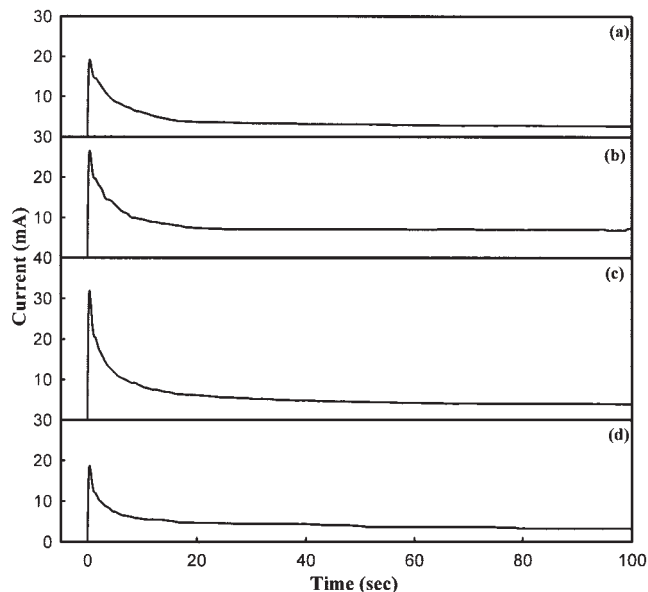


Figure 4 The initial current response of IPMCs from (a) PFMAA20, (b) PFMAA25, (c) PFMAA30, and (d) PFMAA35 with an applied voltage of 9 V.

the first deformation. This shows that the first migration of the cation and water is not fully recovered by the second reverse voltage, and this accumulates more with repeated cycles.

The membrane used in this study was compression molded to a thickness of 0.16 mm, except when the effects of the membrane thickness were examined. Figures 7 and 8 show the effect of the membrane

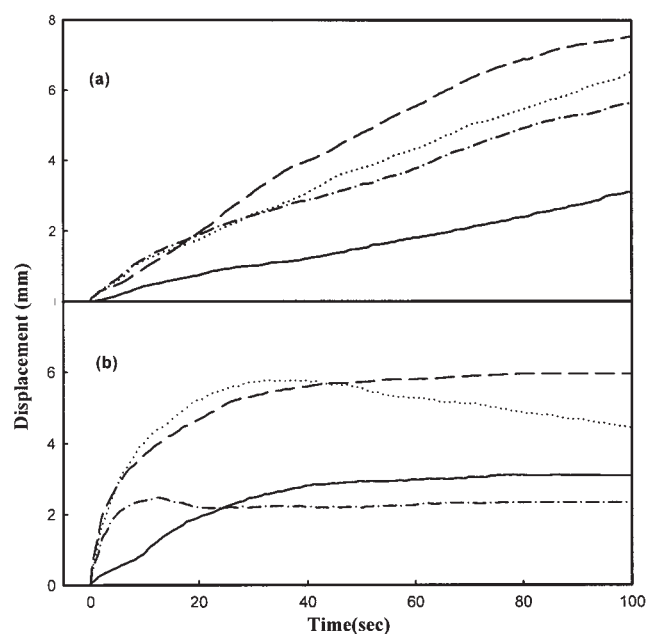


Figure 5 The displacement response of IPMCs with an applied voltage of (a) 5 and (b) 9 V: (—) PFMAA20, (---) PFMAA25, (···) PFMAA30, and (-·-) PFMAA35.

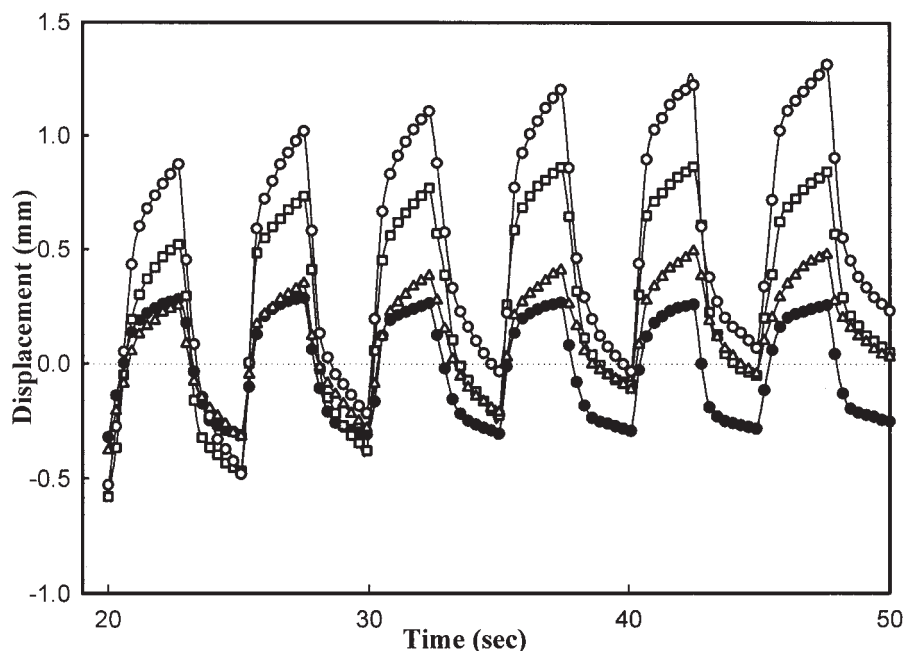


Figure 6 The displacement response of IPMCs with a ± 5 -V step voltage repeatedly applied with a 0.2-Hz cycle: (Δ) PFMAA20, (\circ) PFMAA25, (\square) PFMAA30, and (\bullet) PFMAA35.

thickness on the responses of the current and displacement to a ± 9 -V step voltage repeatedly applied across the IPMC with a 0.2-Hz cycle: the variation in the magnitudes of the current and displacement of IPMCs from the membrane with 0.16-mm thickness was the largest compared with those values of IPMCs from thinner or thicker membranes. In the thinner IPMC the amount of cation that can migrate from the anode to the cathode by applied voltage was less compared to the thicker IPMC. This seemed to cause reduced current and displacement of the IPMC from the 0.07 mm thick membrane compared with those values of the IPMC from the 0.16 mm thick membrane. The metal electrode of the IPMC had a dendritic structure that the deposited metal concentration decayed from the surface to the interior of the IPMC. The dendritic structure enlarged the interface area between the electrodes and the polymer electrolyte, causing an enhanced response to an electric stimulus.⁸ The interface area per unit volume of polymer electrolyte decreased as the thickness of the IPMC was increased. This might be a cause of the reduced current and displacement of the IPMC when the membrane thickness increased from 0.16 to 0.32 mm (Figs. 7, 8).

To examine the effect of the cation type on actuation, an IPMC prepared with a 0.16 mm thick membrane of PFMAA25 was treated with 1N LiCl, NaCl, CaCl₂, or (CH₃)₄N⁺Cl⁻ solution to exchange the cation of IPMC. Figure 9 shows the displacement driven by a ± 9 -V step voltage repeatedly applied with a 0.2-Hz cycle, where we see that the magnitude of the displacement variation has the order (CH₃)₄N⁺

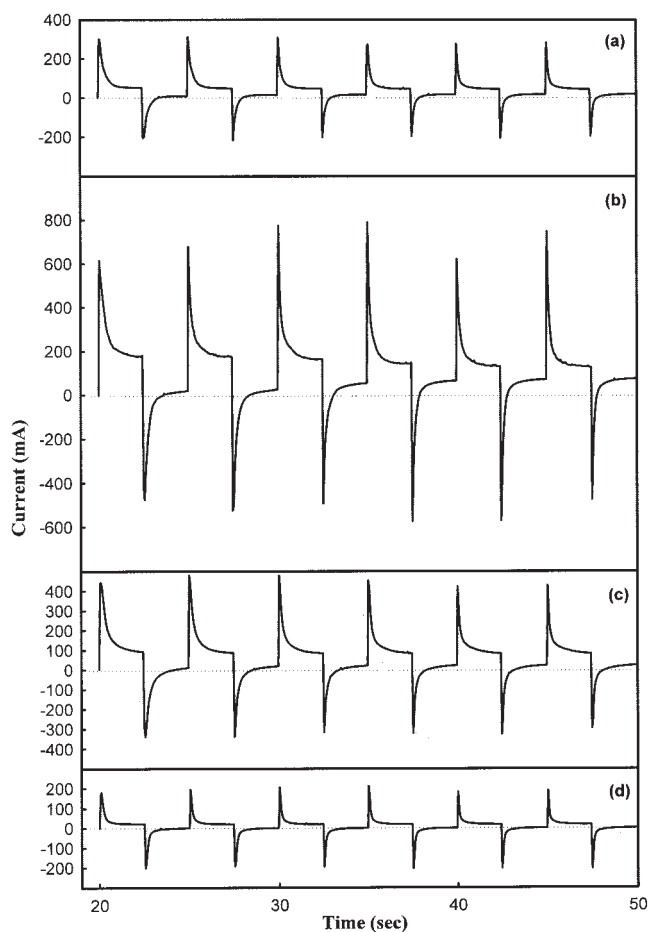


Figure 7 The current response of IPMCs from the PFMAA25 membrane with thicknesses of (a) 0.07, (b) 0.16, (c) 0.22, and (d) 0.32 mm by a ± 9 -V step voltage repeatedly applied with a 0.2-Hz cycle.

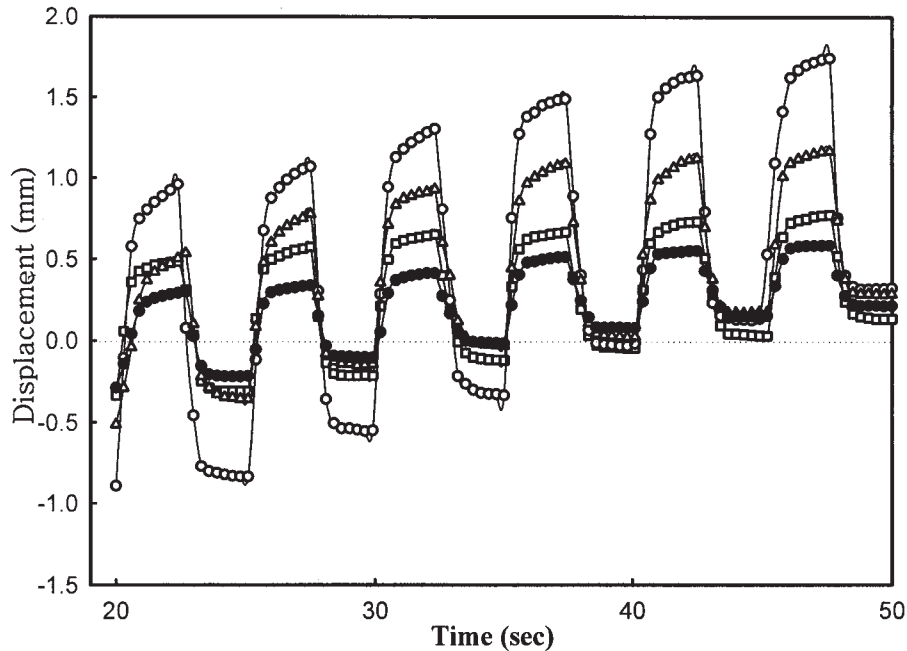


Figure 8 The displacement response of IPMCs from the PFMAA25 membrane with thicknesses of (\square) 0.07, (\circ) 0.16, (\triangle) 0.22, and (\bullet) 0.32 mm by a ± 9 V-step voltage repeatedly applied with a 0.2-Hz cycle.

$< \text{Ca}^{2+} < \text{Na}^+ < \text{Li}^+$, according to the kind of cation. As described before, divalent Ca^{2+} binds to the carboxylate anion of a polymer chain more strongly compared to a monovalent Na^+ or Li^+ cation, with a consequent formation of salt bridges.¹⁰ This might be a cause of the reduced responses of the IPMC with Ca^{2+} to electric stimulus compared to those of IPMCs

containing the Na^+ or Li^+ ion. The relatively insensitive response of the IPMC with the $(\text{CH}_3)_4\text{N}^+$ cation compared with the IPMCs containing other cations seemed to be due to excessive swelling by a large water uptake, because this caused the dilution of the cation concentration in the IPMC, the sparse deposition of platinum particles on the surface, and the am-

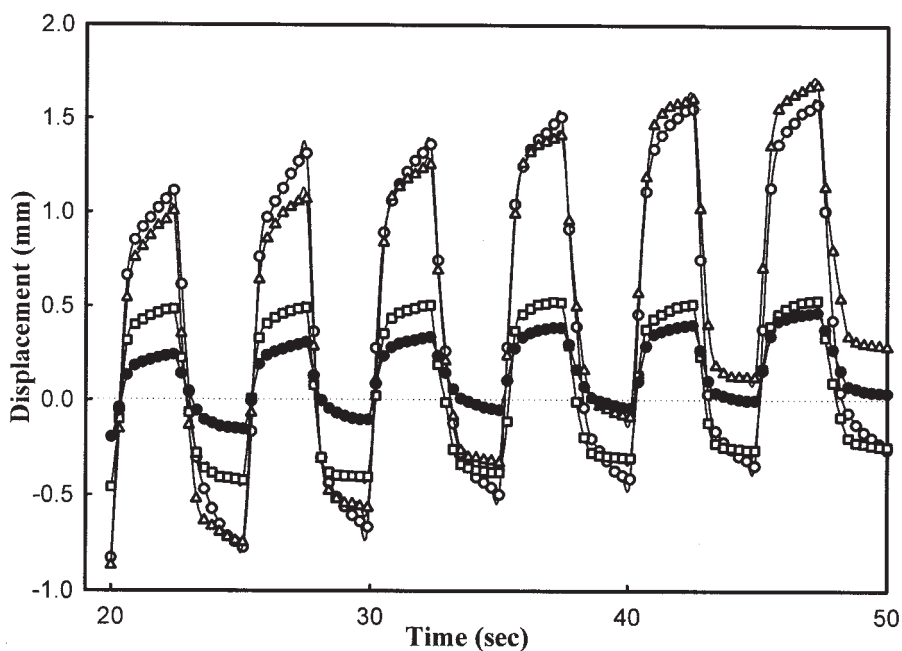


Figure 9 The displacement response of IPMCs from PFMAA25 membrane with (\circ) Li^+ , (\triangle) Na^+ , (\square) Ca^{2+} , or (\bullet) $(\text{CH}_3)_4\text{N}^+$ as a cation by a ± 9 -V step voltage repeatedly applied with a 0.2-Hz cycle.

plification of osmotic pressure effects for the reverse cation migration, as previously explained.

CONCLUSION

Our experimental results show that the ionic polymers used for the preparation of IPMCS should have a high content of ionic site for good performance. However, large water uptake accompanied by high ionic site content caused adverse effects in the actuation by an electric stimulus. That is, when the water uptake was excessive, the current or displacement was decreased by a dilution of the ionic site concentration, by a sparse deposition of platinum particles on the surface, and by an enlargement of the osmotic pressure effect causing a reverse cation migration.

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