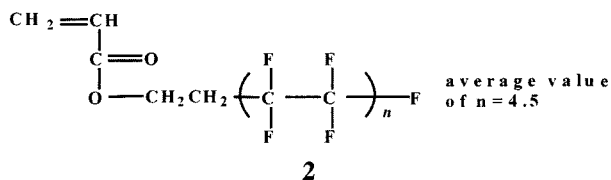


and AA can be easily polymerized and cast from a solution with many degrees of freedom in molecular and shape designs.



Experimental

Preparation of Copolymer Membrane. Fluoroalkyl acrylate (FA, Zonyl TA-N, Du Pont) and acrylic acid (AA, Aldrich) were bulk copolymerized with 0.3 phr of 2,2'-azobisisobutyronitrile (AIBN, Junsei) as a radical initiator, at 60°C under nitrogen atmosphere. The product was washed with methanol and acetone after crushing to remove residual monomers. The monomer compositions in the feed and the sample designation codes are shown in Table I. The acrylic copolymer membrane was cast from the copolymer solution in the mixed solvent of *N,N*-dimethylformamide (DMF, Aldrich)/1,3-bis(trifluoromethyl)benzene (Fluorochem) (50/50 by volume) at 80°C for 24 hrs on a Teflon plate. The membrane, whose thickness was about 0.2 mm, was further dried under vacuum at 110°C for 24 hrs.

Preparation of IPMC. The ionomeric polymer-metal composite (IPMC), having platinum electrodes plated on both faces, was prepared by a chemical plating method, which consisted of an ion-exchange of H⁺ in the acrylic copolymer membrane with cationic platinum complex followed by a reduction process in an aqueous solution of reducing agent.^{10,12} That is, the cast membrane was washed with deionized water and swelled in boiling water. The swollen membrane was immersed in the aqueous ca. 10⁻² M solution of tetraammine platinum(II) chloride hydrate, Pt(NH₃)₄ · xH₂O (Aldrich) for 3 hrs at 50°C to exchange platinum cation. The impregnated cationic complex was reduced with 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.

Characterization of Acrylic Copolymer and IPMC. To analyze the acrylic copolymer composition, the acrylic copolymers were dissolved in trifluoroacetic acid, and the proton nuclear magnetic resonance (¹H-NMR) spectra were recorded at room temperature with Varian Plus 300 MHz NMR spectrometer.

Reduced viscosity was measured with an Ostwald viscometer at 30°C with 0.5g/dL acrylic copolymer solution in the mixed solvent of DMF/1,3-bis(trifluoromethyl)benzene (50/50 by volume).

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

The water uptake of the membrane or IPMC was defined by the following Eq.(1), where W_{wet} is the weight of sample after storing in deionized water at 25°C for 48 hr and W_{dry} is the weight of sample after drying in vacuum at 80°C for 48 hrs.⁴

$$\text{Water uptake (g-water/100 g-dry sample)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

Differential scanning calorimetry (DSC) was carried out with a DSC 2910 of TA Instrument at a heating rate of 10°C/min from -40°C.

Measurement of the Bending of IPMC. The experimental setup for the measurement of bending deformation is shown in Figure 1. The IPMC film with a thickness of about 0.2 mm was cut into a ribbon with a width of 6 mm. A clamp fixed the one end of ribbon and the other end was kept free to bend horizontally by applied voltage. The effective length of IPMC was 25 mm, and the displacement at the point of 5 mm from the free end was observed by a laser displacement meter. To actuate the IPMC 3 V, 5 V, 9 V, or 1 Hz step voltage of ± 9 V was applied between the platinum electrodes through the membrane.^{4,13} The displacement was measured after several training cycles for reproducibility.

Table I. Acrylic Copolymers Used in This Study

| Designation | Feed Composition (wt%) | | Polymer Composition ^a | | | | Equivalent Weight of Polymer ^b | Reduced Viscosity (dL/g) |
|-------------|------------------------|------|----------------------------------|------|--------|------|---|--------------------------|
| | FA | AA | Weight % | | Mole % | | | |
| | | | FA | AA | FA | AA | | |
| PFAA20 | 80.0 | 20.0 | 93.0 | 7.0 | 62.8 | 37.2 | 1030 | 0.76 |
| PFAA25 | 75.0 | 25.0 | 89.4 | 10.6 | 51.7 | 48.3 | 680 | 1.29 |
| PFAA30 | 70.0 | 30.0 | 86.9 | 13.1 | 45.5 | 54.5 | 550 | 1.11 |
| PFAA35 | 65.0 | 35.0 | 83.7 | 16.3 | 39.0 | 61.0 | 440 | 1.12 |

^aDetermined by ¹H-NMR analysis. ^bCalculated from polymer composition.

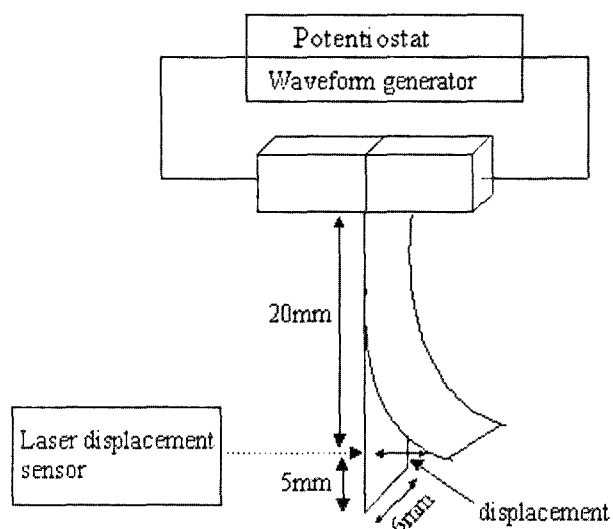


Figure 1. A schematic of displacement measuring system.

Results and Discussion

The morphologies of IPMC observed by SEM are shown in Figure 2. In Figure 2(a), we can see that an overlayer of platinum was deposited with a thickness of about $6\ \mu\text{m}$. Figure 2(b) shows that the surface overlayer appeared fractured, displaying discrete islands of platinum deposition between $5\sim 10\ \mu\text{m}$ across, as previously reported for an IPMC of perfluorinated ionomer membrane, such as Nafion.¹

The actuation mechanism of IPMC is generally explained as follows. When an IPMC subjects a voltage across the thickness, the cation moves from anode to cathode by an applied electric field, and this ionic migration induces an electro-osmotic drag of water. Therefore, the cathode side swells and anode side contracts, and the IPMC bends to the anode side.^{1,10,13} So, the uptake of water is an important variable in the actuation of IPMC. Table II shows that the uptake of water in both membrane and IPMC increased when the content of hydrophilic AA in acrylic copolymer was increased as can be expected. During the chemical plating process, we observed that the membrane swelled and the water uptake increased. This swelling was more evident at a high AA content as can be seen in Table II. This seemed to be due to the morphology change of the hydrophilic domain induced by a change of the $-\text{COOH}$ group to the $-\text{COO}^-\text{Na}^+$ group, because $-\text{COO}^-\text{Na}^+$ is much polar than $-\text{COOH}$.

We divided the water in the membrane into two different water states, as suggested by Y. Abe *et al.*,⁴ freezing water and nonfreezing water. The freezing water is that which showed melting endothermic on heating in DSC, because it existed freely or was weakly bounded. Whereas, the nonfreezing water was that which did not show melting endothermic, probably due to a strong interaction with the carboxylate

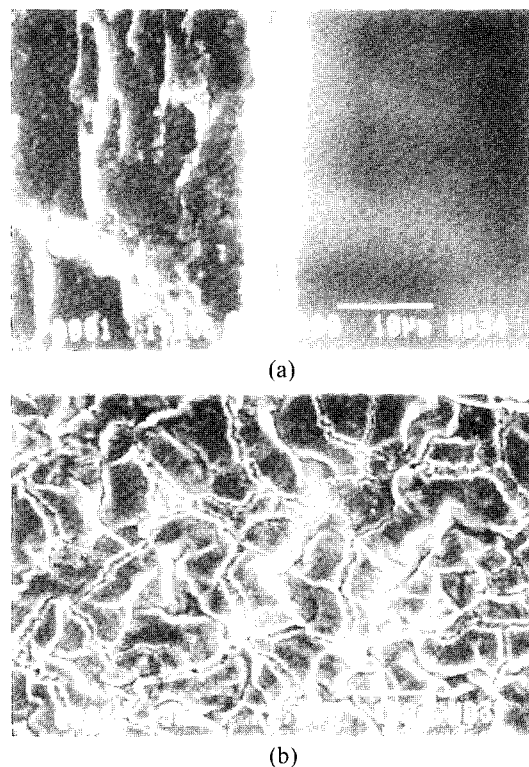


Figure 2. Scanning electron micrographs of (a) the cross-section and (b) the surface of the IPMC from PFAA25.

Table II. Water Uptake of Membrane and IPMC

| Sample | Water Uptake(g-water/100 g-dry sample) | | | |
|--------|--|----------|-------|-------|
| | Membrane | | | IPMC |
| | Nonfreezing | Freezing | Total | Total |
| PFAA20 | 6.0 | 0.0 | 6.0 | 20.5 |
| PFAA25 | 14.9 | 0.1 | 15.0 | 103.2 |
| PFAA30 | 24.0 | 1.2 | 25.2 | 138.4 |
| PFAA35 | 26.4 | 5.7 | 32.1 | 168.5 |

group or counter cation. The fractions of freezing water and nonfreezing water in the membrane were calculated from Eqs. (2), (3), and (4);

$$\text{Fraction of freezing water} = \frac{\beta}{\alpha \times \gamma} \quad (2)$$

$$\text{Fraction of nonfreezing water} = 1 - \text{fraction of freezing water} \quad (3)$$

where α and β are the values of melting enthalpy (J/g-sample) observed around 0°C with deionized water and the wet membrane, respectively, and γ is the water content of the wet membrane, which was calculated from Eq. (4).

$$\text{Water content} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \quad (4)$$

As the hydrophilic AA content in acrylic polymer membrane is increased, Table II shows that the increase of total water uptake is more evident than the decrease of equivalent weight in Table I, and that the fraction of freezing water increased together with total water uptake. These results showed that the concentration of ionic site in hydrophilic domain was diluted by the large water uptake, and this raised the fraction of free or weakly-bounded water.

Figure 3 shows the profiles of the initial current and displacement responses of PFAA25 for a period of 50 sec just after an application of 3, 5, or 9 V. We can see in Figure 3 that the current through the IPMC sharply increased as soon as the voltage was applied and then decreased exponentially. Higher applied voltages induced a higher current.^{1,10,13} When the applied voltage was 9 V, the IPMC reached the maximum displacement toward the anode within 5 sec. However, the displacements show a slow increase when 3 or 5 V were applied across the IPMC. This shows that there was a time lag for the deformation to occur after current flow, because the deformation was induced by internal stress in the IPMC, and this internal stress was caused by electroosmotic drag of water accompanied with cation migration.^{1,10,13}

Figure 4 shows the variation of current and displacement responses according to the hydrophilic AA content in a acrylic copolymer. We can see in Figure 4 that both the current and deformation decreased as the content of AA in the acrylic copolymer increased. Table II shows that the water uptake of IPMC increased remarkably as the hydrophilic AA content was increased, and this may cause the dilution

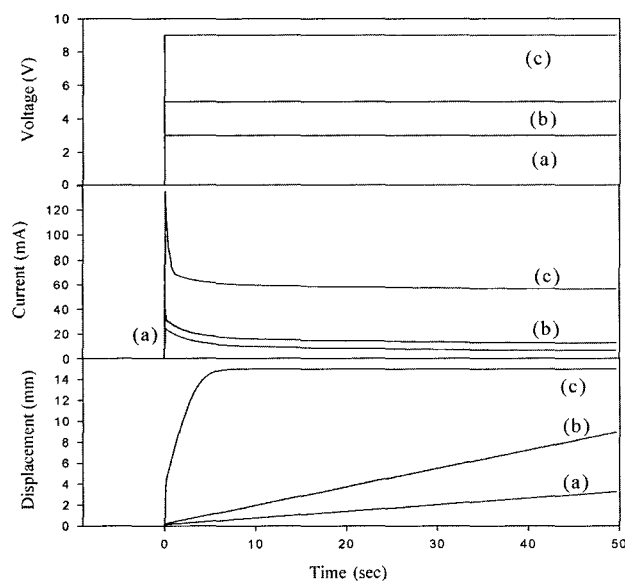


Figure 3. Initial current and displacement responses of IPMC from PFAA25 by the applied voltage of (a) 3 V, (b) 5 V, and (c) 9 V.

of ion concentrations in IPMC at the hydrophilic domain. That seems to be a cause of the reduced current at high AA content. We observed that the matrix of IPMC was partially damaged when swelled too much by a large uptake of water at high AA content. This may be another cause of current reduction at high AA content. In the continued study carried out by our laboratory, with the IPMC based on the copolymers of fluoroalkyl methacrylate (Zonyl TM of Du Pont) and 2-acrylamido-2-methyl-1-propanesulfonic acid (SA), we observed that the current and displacement showed a first increase and a second decrease as the content of sulfonate ionic site was increased.¹⁴ The AA or SA segment raises the cation contents in the IPMCs that can move with water by the applied voltage, however, these results of our laboratory on electroactive acrylic IPMCs showed that the increased anion content by AA or SA segment in the polymer chain could inhibit the migration of cation through the polymer matrix together with water. So, they suggest that there may exist an optimum hydrophobic-hydrophilic balance of polymer matrix for the best actuation by the applied voltage.

PFAA20 did not show any significant current flow and deformation with the an applied voltage up to 10 V. This suggested that the content of hydrophilic AA in PFAA20 was not sufficient to form a hydrophilic nano-channel for ionic flow. The frequently-used perfluorinated ionomer membrane with sulfonic group had an equivalent weight of around 1,100 g polymer per equivalent of ionic group.^{4,6,7,13} Whereas those with the carboxylic group had a value around 600 g,¹⁰ and this value was similar to those of the acrylic copolymer used in this study as can be seen in Table I. This

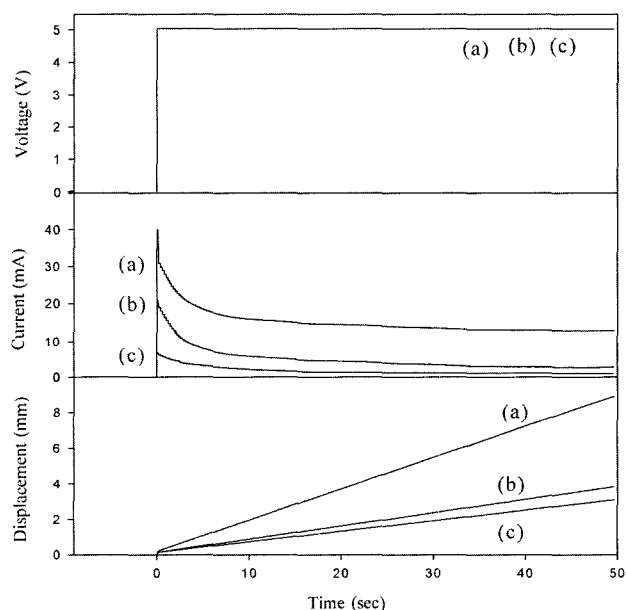


Figure 4. Initial current and displacement responses of IPMC from (a) PFAA25, (b) PFAA30, and (c) PFAA35 by the applied voltage of 5 V.

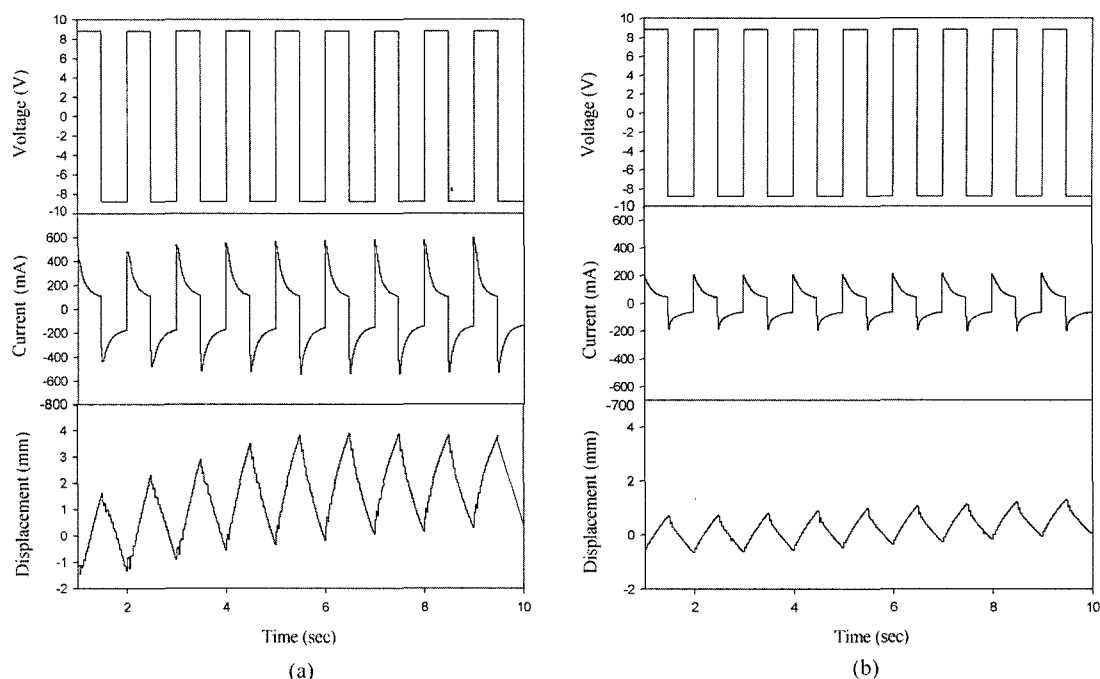


Figure 5. Current and displacement responses of IPMC from (a) PFAA25 and (b) PFAA30 by 1 Hz, ± 9 V step voltage repeatedly applied.

seemd to be due to the fact that perfluorocarboxylic acid membrane contained larger amounts of ionic site without any significant loss of mechanical strength, because the water sorption of the perfluorocarboxylic acid membrane was smaller than that of the perfluorosulfonic acid membrane with the same equivalent weight.^{6,10}

Figure 5 shows the responses of current and displacement by 1 Hz, ± 9 V step voltage repeatedly applied across IPMC. As in Figure 3 and Figure 4, here we can also observe the rapid increase of current followed by the decay and slow increase of displacement at every cycle. Figure 5 also shows that displacement drifts by repeated cycles toward the direction of first deformation. This shows that the first migration of cation and water is not fully recovered by the second reverse voltage, and that this accumulates more by repeated cycles. The magnitude of displacement decreased after a few minutes, because the water in the IPMC could subject to hydrolysis when the applied voltage was above 1.23 V.¹

Conclusions

We found that the acrylic copolymers of FA and AA, which were easily polymerized and cast from a solution, could be effectively utilized in the preparation of IPMC. The responses of the current and the displacement by applied voltage decreased after the first increase, as the content of AA in the copolymer was increased. The best performance of IPMC was observed when the AA content was 10.6 wt%.

Acknowledgments. This study was supported by a grant of the Korea Health 21 R&D Project, Ministry of Health & Welfare, Republic of Korea (02-PJ3-PG10-31402-0001).

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