

Electrochemical Behavior of a New Type of Perfluorinated Carboxylate Membrane/Platinum Composite

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ABSTRACT: A new type of ionomeric polymer-metal composite (IPMC) based on various compositions of perfluoroalkylacrylate-acryl acid copolymer with different types of counter cation has been synthesized by a radical copolymerization of fluoroalkylacrylate (FA) and acrylic acid (AA). Swelling behavior of the membranes was studied in deionized water as well as in aqueous single salt solutions (LiCl and NaCl). Swell of membrane increased with the increase in ionic content of the copolymer. Swell in deionized water was much higher than in aqueous single salt solution. To examine its performance as a new electroactive polymer, actuation force and displacement responses to DC and step

voltage across the IPMC were measured. Results indicated that membranes prepared from 75/25 (FA/AA) (FA25) gave an adequate flexibility and proper hydrated state, allowing easy deflection toward the applied voltage. Surface morphology measurements (atomic force microscopy and scanning electron microscopy) showed that platinum particles are predominantly located at the surfaces. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2687–2693, 2006

Key words: metal-polymer complexes; perfluorinated carboxylate membrane; sensor; counter cation; swell ratio

INTRODUCTION

A large number of studies have been made on the shape deformations of polymers in response to environmental changes including the application of an electric field or light wave, and changes in temperature or in fluid composition.^{1–5} In particular, polymers that deform in response to an electric signal are highly preferable for actuators, since these are easy to operate.⁶

Ionic polymer-metal composites (IPMCs) are highly active sensors and actuators, which show very large deformation in the presence of low applied voltage and exhibit low impedance. They operate best in a humid environment and can be made as self-contained encapsulated actuators to operate in dry environments as well. They have been modeled as both capacitive and resistive element actuators, which behave like biological muscles and provide an attractive means of actuation as artificial muscles for biomechanics and biomimetics applications.⁷

Typical artificial IPMC is composed of a perfluoro-sulfonic acid ion-exchange membrane (Nafion), which was developed by Dupont in the early 1970s.⁸ An IPMC consisting of thin membrane that is plated with platinum on both sides undergoes large bending deformation when an electric field is applied across its thickness.⁹ The Nafion membrane has excellent ionic

conductivity because the ionic groups located at the end of side chain can position itself in its preferred orientation to create hydrophilic nanochannels. Because of these characteristics, almost all the recent studies about IPMCs use Nafion or similar materials such as Flemion as matrix.¹⁰

However, most of the commercially available Nafion membranes have a typical thickness of approximately 0.1–0.3 mm; they are not melt-processable, and involves high costs as well.⁸ So, some alternative matrix material has to be considered. In this regard, polymer membranes containing ionic groups have been considered.^{11–13} Also, perfluorinated carboxylic acid can be used as polymer electrolyte instead of sulfonic acid. Carboxylic acid membranes with higher ion-exchange capacity than sulfonic acid have also become available.¹⁴

In this work, we synthesized copolymers from fluoroalkylacrylate (FA) and acrylic acid (AA) at various compositions, which subsequently were used as new membranes for IPMC. Effects of counter cation type as well as ionic group content on actuation responses to DC and step voltage have been studied. In addition, swell and surface morphology have also been measured to interpret the actuation behavior.

EXPERIMENTAL

Materials

Extra pure grade of fluoroalkylacrylate (FA; ZONYL TA-N, Dupont), acrylic acid (AA; Aldrich), and 2,2'-

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TABLE I
Formulation of Perfluorocarboxylic Copolymers

Designation	Feed composition (wt %)		Copolymer composition ^a				Equivalent weight of polymer ^b
	FA	AA	Weight %		Mole %		
			FA	AA	FA	AA	
FA20	80.0	20.0	93.0	7.0	62.8	37.2	1030
FA25	75.0	25.0	89.4	10.6	51.7	48.3	680
FA30	70.0	30.0	86.9	13.1	45.5	54.5	550
FA35	65.0	35.0	83.7	16.3	39.0	61.0	440

^a Determined by ¹H NMR analysis.

^b Calculated from copolymer composition.

azobisisobutyronitrile (AIBN, Junsei) were used as received. To prepare IPMC, tetraamineplatinum(II) chloride hydrate (Aldrich) (platinum powder) and sodium borohydride (Aldrich) were used as reduction agent for platinum. 1,3-bis(trifluoromethyl)benzene (Fluorochem) and dimethylformamide (DMF, Aldrich) were used as a casting solvent. Acetone and methanol were used for recrystallization of synthesized resin. For counter cation, lithium chloride (Aldrich) and sodium chloride (Aldrich) were used as received.

Synthesis of random copolymer membrane

New perfluorocarboxylic acid membrane was prepared by radical copolymerization of FA and AA with AIBN as initiator. Copolymerization reactions were conducted in a Pyrex vial under nitrogen atmosphere at 60°C. To remove any residual monomers, the copolymers were recrystallized in methanol and acetone. Then, this copolymer was dissolved in the cosolvent of dimethylformamide/1,3-bis(trifluoromethyl)benzene (50%/50%). Membranes for the IPMC were prepared by casting the solution on a Teflon plate at 80°C for 24 h. The remaining solvent was removed at 110°C under vacuum for the next 24 h. Formulations to prepare the copolymers are shown in Table I. In the table, number following FA is the AA composition in feed. For example, FA25 is a copolymer prepared from a feed ratio of 75/25 (FA/AA) by weight.

Analysis of copolymer structure

To analyze the copolymer composition, samples were dissolved in trifluoroacetic acid and the ¹H NMR spectra were recorded at room temperature. NMR spectra were recorded with Varian Unity Plus 300 MHz spectrometer in trifluoroacetic acid using tetramethylsilane (TMS) as internal standard.

Preparation of IPMC

The IPMC having platinum electrodes plated on both faces was prepared by a chemical plating method. An

ion-exchange of H⁺ in the acrylic copolymer membrane with cationic platinum complex was followed by a reduction process in an aqueous solution of reducing agent.³ The procedure is as follows. After washing the surface in deionized water, the membrane was swelled in boiled water. The swollen membrane was immersed in 2 mg Pt/mL aqueous solution using tetraamineplatinum(II) chloride hydrate to exchange ions of platinum with H⁺ of membrane for 3 h at 50°C. Then, after rinsing the membrane with water, 30 cm² of membrane was transferred to 180 mL of water at 50°C, with stirring. The impregnated cationic complex was reduced with 5 wt % aqueous solution of sodium borohydride every 30 min for 5 times. Black layer of fine Pt particles deposited only on the surface of the membrane.

The counter cation of membrane was converted to monometal ions by soaking the composite in an aqueous single salt solution for about 48 h at room temperature and then rinsed with water. The salts used were LiCl and NaCl. The concentrations of all solutions were adjusted to 1N with deionized water.

Displacement measurement

The composite was vertically suspended in air and top of the composite was fixed. To actuate the composite, a laser displacement sensor with a controller was used. The IPMC film with a thickness of about 0.2 mm was cut into ribbon of 2 × 3 cm². One end was clamped, while the other end was subject to bend horizontally by applied voltage. An 8 V DC or 1 Hz step voltage of ±8 V was applied to the platinum electrodes separated by the membrane. The initial displacement of the stripe fixed at one end was measured during the first 5 s to compare the initial deflection. At the same time, maximum actuation force was measured.

Water content and differential scanning calorimetry measurements

Water content, i.e. the amount of water absorbed by IPMC, was measured by immersing a film in water.

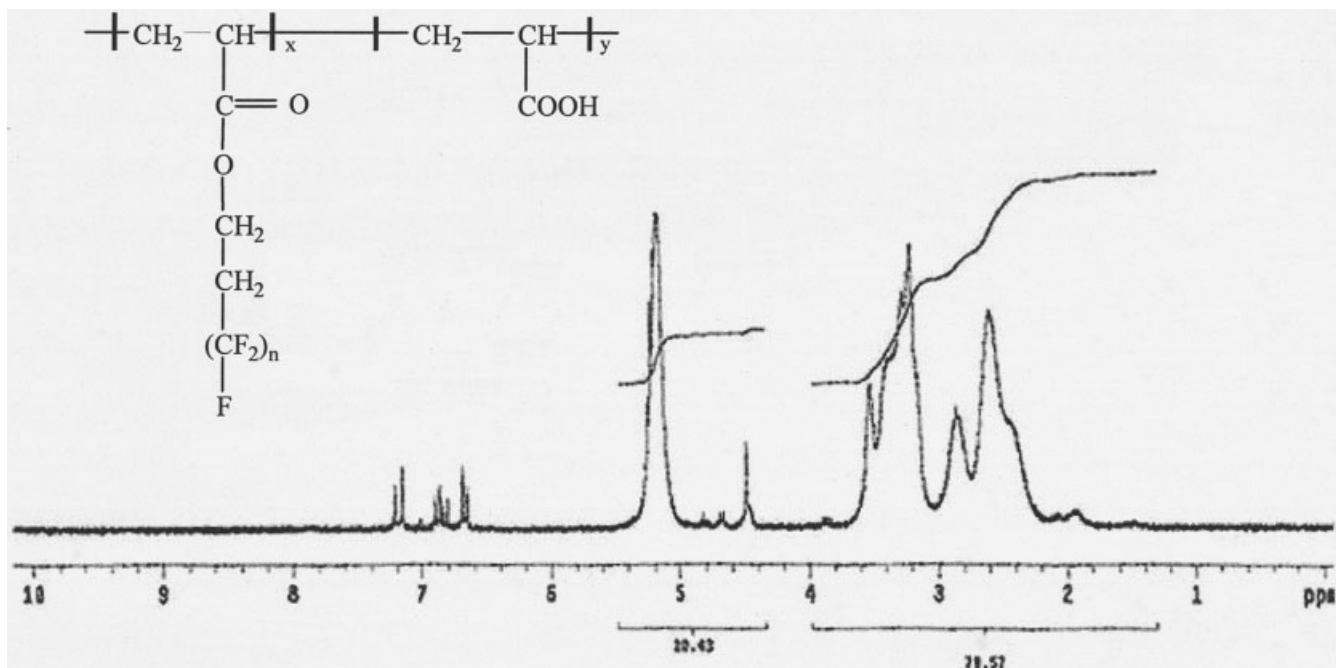


Figure 1 ^1H NMR spectra of perfluorocarboxylic acid copolymer.

The water content was calculated by the following equation

$$\text{Water content (wt \%)} = \frac{W - W_0}{W_0} \times 100$$

where, W_0 is the weight of dried film and W is the wet film immersed in room temperature for 48 h.

For DSC (Seiko DSC 220) measurements, 1 mg of deionized water and 4 mg of the fully hydrated membrane were put in an aluminum pan. DSC measurements were done from -30 to $+30^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.

Surface morphology

Platinum deposited on the surface and the cross section of membrane was visualized using a scanning electron microscopy (SEM, JEOL JSM-820) attached with an energy dispersive X-ray microanalysis (EDX). To obtain the cross section of dried IPMC, sample was cryogenically fractured in liquid nitrogen and sputtered with gold before viewing. The surface morphology of the manufactured IPMC was characterized by an atomic force microscopy (AFM, Digital Instruments Nanoscope III-a).

RESULTS AND DISCUSSION

Preparation and characterizations

The purification and formation of copolymer can be assured by the absence of double bond ($\text{CH}_2=\text{CH}$)

about $5.86\text{--}6.49$ ppm (Fig. 1). Proton of carboxyl group appears at $10\text{--}12$ ppm. The composition of copolymer was obtained from methylene closed CF_2 and the remaining proton about $3.8\text{--}4.3$ and $2\text{--}4$ ppm, respectively. In this spectrum, proton of methylene closed fluorine atom was shifted down to $3.8\text{--}4.3$ ppm due to electro negativity of fluorine. It is also seen that peak of proton about $2\text{--}4$ ppm is broad because of polymerization.

Copolymer composition has been quantitatively calculated by NMR spectra and the results are shown in Table I. As the AA content in feed is increased from 20 to 35%, AA content in copolymer is increased from 7 to 16% by weight. The lower content of AA in copolymer than in feed is due to the lower reactivity of AA than perfluoroalkylacrylate in radical copolymerization.

Typical surface morphology of the IPMC is given for FA25 (Fig. 2) where the black layers of fine platinum particles are deposited only on the surface of the membrane. It seems that the platinum particles are not uniformly distributed along the membrane thickness and they are predominantly located at the surface. Platinum layer is buried $3\ \mu\text{m}$ deep into IPMC membrane. EDX measurement again shows that platinum particles are distributed at the interfaces (Fig. 3). It is concluded that surfaces are covered with three-dimensionally networked dispersed metals, which are separated by crack.

Another fine tool to characterize the surface morphology of the IPMC is AFM.¹⁵ Its ability to directly image the surface of the IPMC can provide detailed

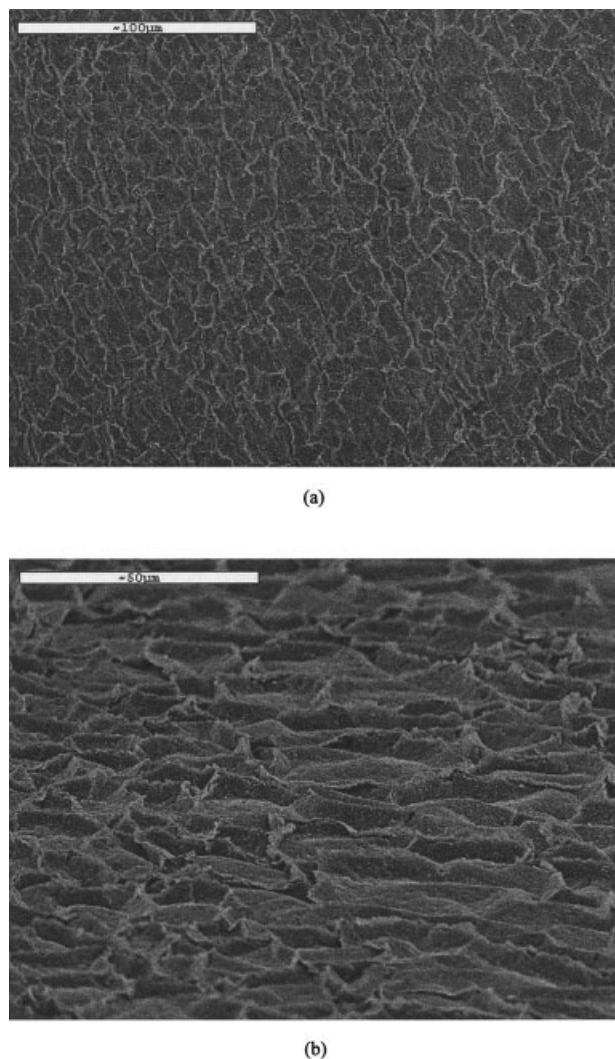


Figure 2 SEM image of FA25 surface at 1000 \times (a) and 2000 \times (b).

information, with the resolution of a few nanometers. AFM images of pure membrane and IPMC are given in Figure 4. It is seen that platinum particles are partially dense and show cohesive shape. The height of pure membrane (a) is about 450 nm and that of the IPMC (b) about 500 nm. The difference of about 50 nm should be the layer of platinum. SEM shows that the layer of the platinum was 3 μm thick, but it turned out that actual layer thickness is about 50 nm on surface and the rest is imbedded in IPMC.

Bending deformations

Figure 5 shows displacement response to DC (a) and step voltage (b) according to the content of Li^+ . Among three of the ion contents being tested, FA25 shows by far the highest bending displacement for both types of electric field. On the contrary, H^+ is virtually insensitive to the field regardless of its con-

tent. It is noted that flapping displacement is small and nearly symmetric for FA20.

Regarding the operation principle of IPMC with perfluorocarboxylic acid membrane, hydrophilic spherical cluster are connected with narrow ionic channels.¹⁶ The clusters and the channels make ion-water network in the membrane. Ion flux and electro-osmotic drag flow of water form the charged current through the narrow hydrophilic channels in the perfluorinated resin. The electro-osmotic flow of water makes resin near the cathode wet and resin near the anode dry. This difference of water content in the membrane swells or shrinks the membrane near the electrodes. The swollen cathode and shrunk anode deflect the composite to anode.¹⁷ Therefore, the existence of water is essential to actuate IPMC. In our experiment, FA20 and FA30 series did not give notable bending deformation. With insufficient water IPMC does not operate, while with too much water, free water that does not make ion-water network provides resistance to ionic current. It seems that FA25 contains proper amount of water, and hence, effect of counter ion type has been studied at this particular composition.

Figure 6 shows displacement of FA25 according to various types of counter cation. As expected, displacement response to DC shows a monotonous increase with time, whereas response to step voltage is periodic. Among three of the different counter cations, Li^+ gives predominantly high deformation. In contrast, H^+ is virtually insensitive to the applied electric field.

Bending deformation in IPMC strip is driven by the migration of counter cations forming clusters with water molecules. Therefore, effect of counter cation should be based on its ability to form cluster with water. Following Xie and Okada, hydrated cation molecules pump loosely bounded or peripheral water molecules toward the cathode.¹⁶ It seems that Li^+

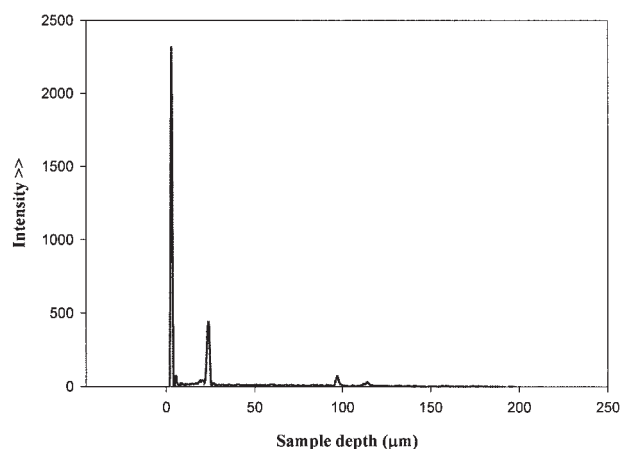
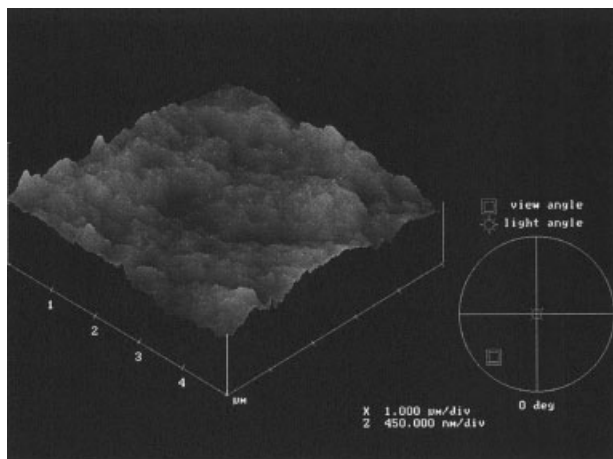
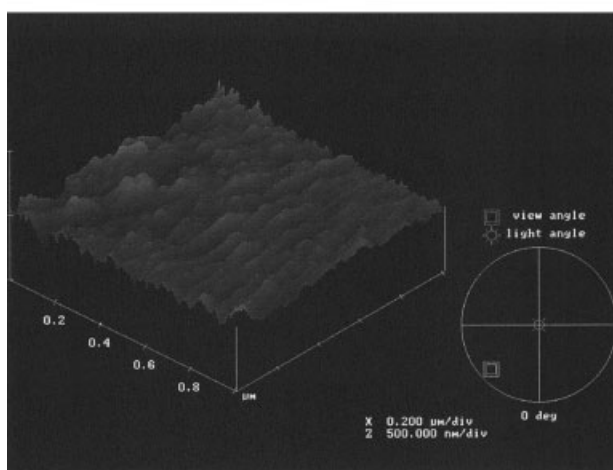


Figure 3 Distribution of Pt particles in IPMC interface by EDX.



(a)



(b)

Figure 4 Three-dimensional AFM image of pure membrane (a) and IPMC (b) for FA25.

effectively forms clusters with water to come up with the greatest bending displacement.

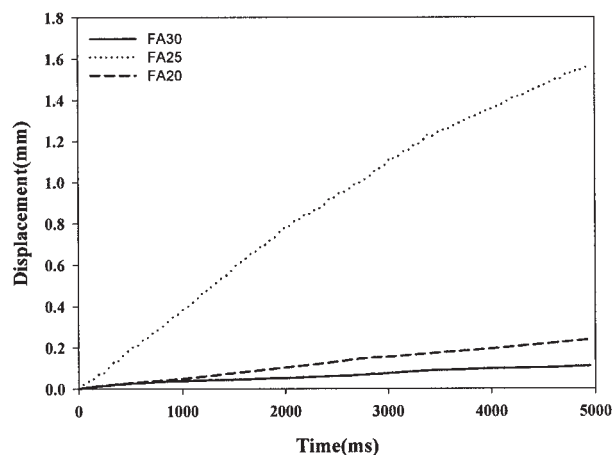
Figure 7 shows that maximum actuation force decreases with increasing ionic content presumably because of the increased film flexibility. It has already been shown that water swell increases with increasing ionic content due to the hydrophilic nature of ionic groups. However, increase of actuation force with decreasing ionic content should not be mixed up with increased bending displacement that increases with ionic content. That is, flexibility provides the film with less resistance to bend.

Figure 8 shows time dependent water swell of IPMC stripe as a function of ionic content (a) and type of solution (b). As expected, initial rate of water swell as well as equilibrium water swell increases with increasing amount of the ionic content because of the hydrophilic nature of ionic group. During the experiment, it

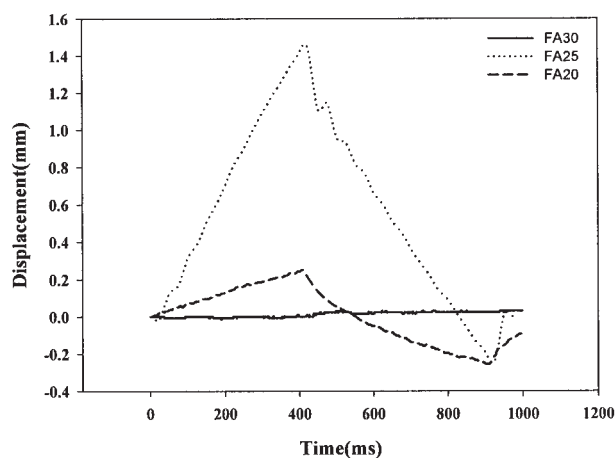
was found that swollen FA40 and FA50 were soft gel, which no longer can be used as an actuator. Only FA25-FA35 proved useful for actuator application.

Swell in deionized water is much greater than in aqueous single salt solution. As mentioned earlier, displacement in salt solution was much higher than in deionized water. It means that excessive amount of water taken up by the membrane impedes the transportation of hydrated ion clusters from anode to cathode upon applying the electric field across the thickness. Water uptake should also be related to the relative amount of bound water to free water as mentioned earlier.

The structure of water in the membranes having H^+ and monovalent metal ions was investigated by DSC measurements. Figure 9 shows melting endotherms of deionized water and water in hydrated pure mem-

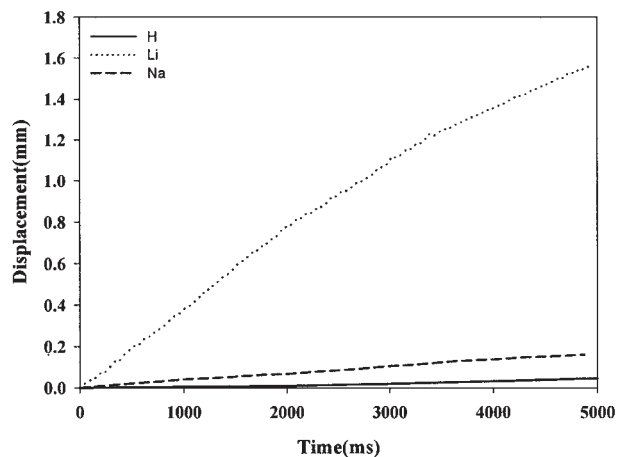


(a)

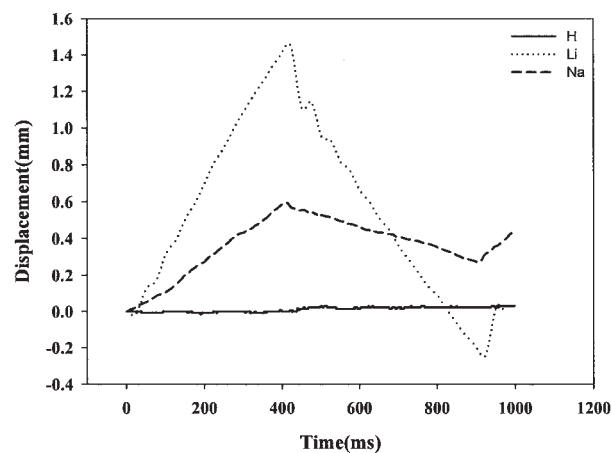


(b)

Figure 5 Displacement response of the composites versus Li^+ content to DC 8 V (a) and step voltage of ± 8 V (period, 900 ms) (b).



(a)



(b)

Figure 6 Displacement response of FA25 versus types of counter cation to DC 8 V (a) and step voltage of ± 8 V (period, 900 ms) (b).

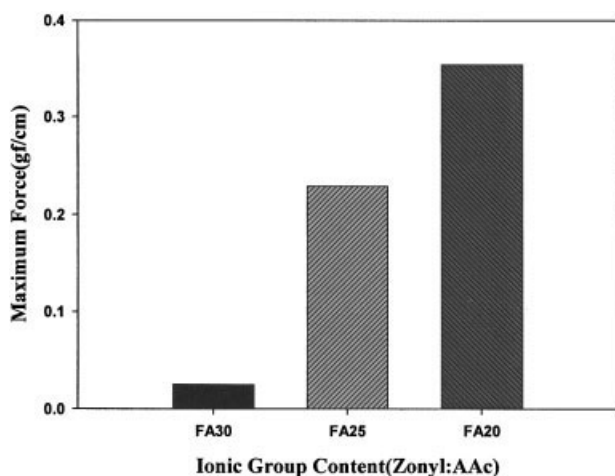
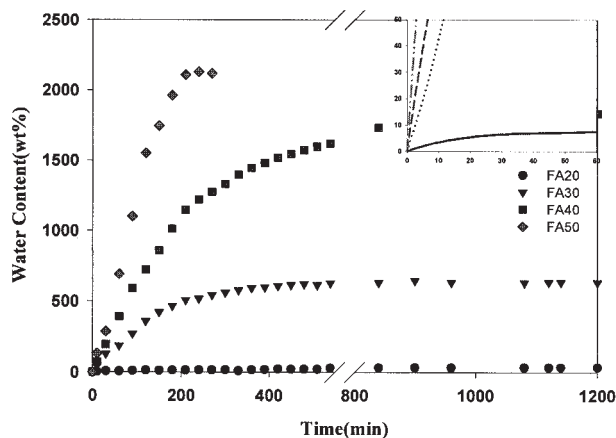
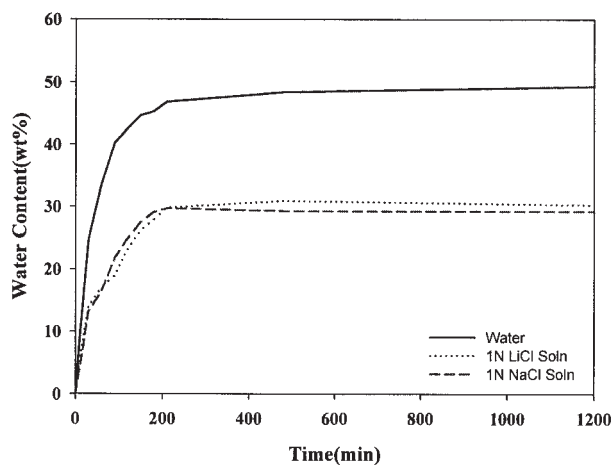


Figure 7 Actuation force of the composites with Li^+ at DC 8 V.



(a)



(b)

Figure 8 Time dependent swell of the composite versus ionic content in deionized water (a) and various solutions (FA25) (b).

brane. Deionized water shows a sharp melting peak at about 0°C , whereas membrane having Li^+ shows a broad one in the range of $-5\sim 10^\circ\text{C}$. However, it is small and mere a board shoulder around -5°C for H^+ . In this regard, Abe suggested that free water shows melting endotherm on heating but no endotherm for nonfreezing water due to the strong interactions between the carboxylate group and counter cation.⁶ It seems that Li^+ among the three types of ions gives strongest interior interactions with carboxylate anions of copolymers. In fact, this is well agreed with the greatest bending displacement of Li^+ , which was discussed with regard to Figure 6.

CONCLUSIONS

A new type of electroactive polymer based on perfluorinated carboxylate has been prepared with different

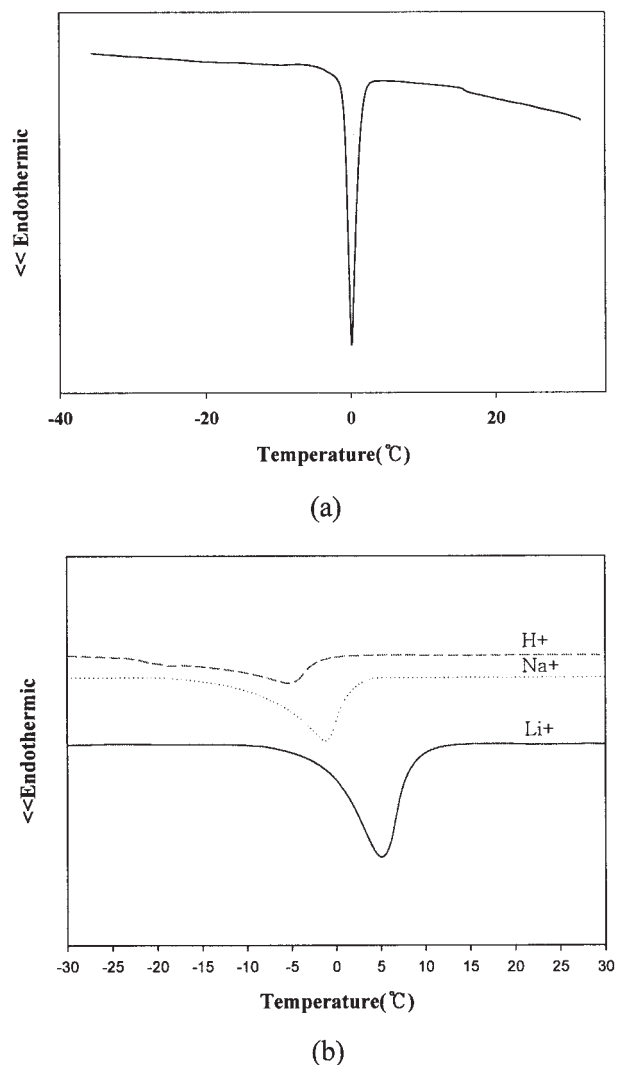


Figure 9 DSC melting endotherms of deionized water (a) and hydrated membrane of FA25 (b).

ionic contents and counter cation types, and tested for actuation performance and water swell. Both initial and equilibrium swell monotonically increased with the increase in ionic content due to the hydrophilic nature of ionic groups. Among three types of solution,

i.e., deionized water, NaCl, and LiCl solutions, the swelling behavior of the IPMC was most pronounced with water.

Regarding the effect of ionic content on bending, an optimum content seems to exist (FA25). Above the content, excessive free water impedes transportation of hydrated ion clusters, and below the content, IPMC does not properly operate.

Regarding types of counter ion, Li^+ gave the greatest displacement response to step voltage as well as to DC. It seems that Li^+ effectively forms clusters with water since content of water controls the flexibility of film.

Actuation force monotonically increased with the decrease in ionic content (FA20 > FA25 > FA30) due to the high rigidity of film containing less amount of water.

AFM and SEM measurements show that platinum particles are predominantly deposited on the surface of membrane, with the depth of about 50 nm.

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