Ionic Polymer−Metal Composite Actuators Obtained from Radiation-Grafted Cation- and Anion-Exchange Membranes

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ABSTRACT: Two series of ionic polymer−metal composites (IPMCs), one cationic and one anionic, are designed and prepared from radiation-grafted ion-exchange membranes. Through examination of the properties of the membranes synthesized from the two grafting monomers and the two base polymers, acrylic acid-grafted poly(vinylidene fluoride-co-hexafluoropropylene) and quarternized 4-vinylpyridine-grafted poly-(ethylene-co-tetrafluoroethylene) with the appropriate amount of ionic groups are employed for the fabrication of cation and anion IPMCs, respectively. The bending displacement of the cation IPMC is comparable to Nafion-based IPMC under direct- and alternating-current voltage, but back-relaxation is not observed. The actuation performance of the anion IPMC is highly improved over those reported earlier in the literature for the other anion IPMCs.

KEYWORDS: ionic polymer−metal composite, actuator, electroactive polymer, ion-exchange membrane, radiation grafting
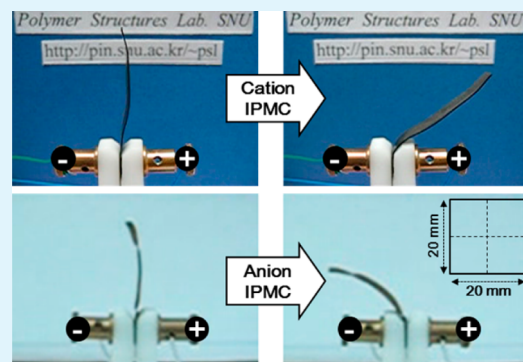
1. INTRODUCTION

Ionic polymer−metal composites (IPMCs), a kind of electroactive polymer, have considerable potential as actuators and sensors because of a large bending strain and a prompt response at a low applied voltage.[1−4] An IPMC contains an ion-exchange membrane as a transport medium for mobile ions, which is sandwiched between two metal electrodes.[3,5] Because the ion-exchange membrane in most IPMCs reported has been limited to a few commercial products like Nafion and Flemion,[6−9] the majority of research on IPMCs has been focused on assessing the effects of other components such as mobile ions,[7−10] solvents,[11,12] and metal electrodes[13,14] on the actuation performance of the IPMCs. Because one of the most important factors that determine the characteristics of IPMCs is, however, an ion-exchange membrane itself, developing a novel ion-exchange membrane with improved properties can be a natural approach to reinforce the actuation performance of IPMCs.[4,6] In recent years, efforts have been made to employ various ion-exchange polymers in the preparation of IPMCs: The polymers include aromatic backbone polymers, copolymers, and polymer blends.[15−19] Despite some progress being achieved, the preparation of large and uniform membranes, which are necessary for high-performance IPMCs, appears problematic. This is because the polymers are solution-cast to membranes. It is thus desirable to develop a facile, reproducible, and scalable method that produces ion-exchange membranes for IPMCs with tailored properties. We have demonstrated that radiation grafting can be an effective route to addressing this issue.[20]

Radiation grafting has been utilized to obtain ion-exchange membranes and is composed of the following steps.[21,22] First, radicals are created on a base polymer by irradiation. Second, monomers are reacted with the radicals thus graft-polymerized onto the base polymer. The last step, which is functionalization of the grafted polymers in order for them to offer ionic groups, can be added as an option. Radiation grafting is a simple and cost-effective route for the preparation of ion-exchange membranes with a large area.[23,24] Because the amount of ionic groups in radiation-grafted ion-exchange membranes can also be regulated by varying the grafting conditions, the properties of the resulting membranes can be easily controlled. Furthermore, radiation-grafted ion-exchange membranes have diverse ionic groups, either cationic or anionic, by selecting grafting monomers including styrene,[25−27] acrylic acid,[28,29] and 4-vinylpyridine.[30,31] Employing radiation grafting in the preparation of ion-exchange membranes for IPMCs thus appears to be advantageous and promising to develop IPMCs with designed and enhanced actuation performance.

The preparation of anion-exchange membranes, in particular, is critical in diversification of the motion of IPMCs. The IPMCs containing anion-exchange membranes (anion IPMCs) bend in the opposite direction to conventional IPMCs obtained from cation-exchange membranes (cation IPMCs). Combining these two types of IPMCs with mobile ions of anions and cations allows assembled IPMCs to exhibit even complex motions,[32] while common IPMCs bend only in one direction. However, few reports regarding anion IPMCs at this point in time exist.[33,34] The actuation performance of those anion IPMCs

was significantly inferior to that of cation IPMCs because the properties of anion-exchange membranes in the former were insufficient compared to those of cation-exchange membranes in the latter.[33,34] Because radiation grafting can produce anion-exchange membranes with properties comparable to those of cation-exchange membranes, the actuation performance of anion IPMCs can be improved by employing radiation-grafted anion-exchange membranes.

Herein, we report novel IPMC actuators obtained from radiation-grafted cation- and anion-exchange membranes. The preparation of cation- and anion-exchange membranes with precisely controlled properties is pursued via a γ-ray-induced grafting method. Fluoropolymers are employed as base polymers. Cationic and anionic groups, carboxyl and quaternary ammonium groups, are grafted onto the fluoropolymer films. The properties of the resulting membranes are controllable by regulating grafting conditions. The IPMCs comprising the membranes are expected to exhibit advanced actuation performance compared to conventional IPMCs.

2. RESULTS AND DISCUSSION

Figure 1 describes the schematic for the radiation-grafting process in this study. In virtue of the high radiation
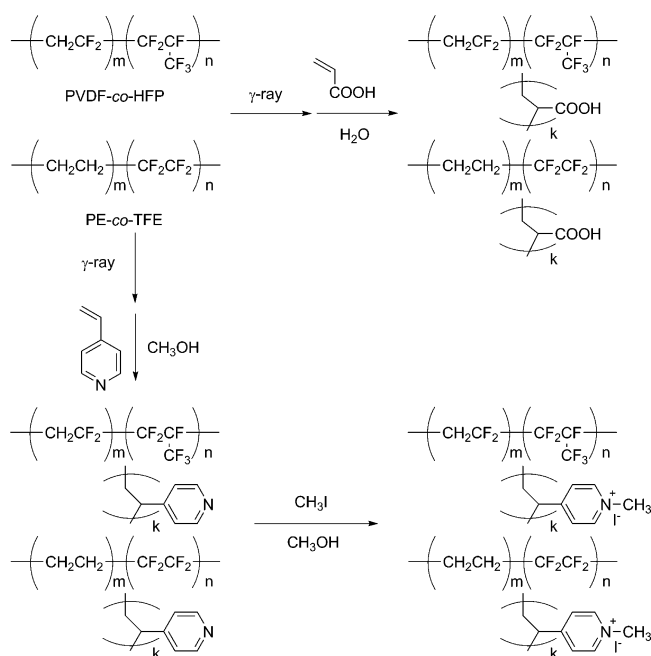
Figure 1. Scheme for radiation grafting of acrylic acid and quaternized 4-vinylpyridine onto fluoropolymers.

resistance,[22,35] fluoropolymers including poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) and poly(ethylene-co-tetrafluoroethylene) (PE-co-TFE) are selected as the base polymers. Acrylic acid and 4-vinylpyridine are grafted onto fluoropolymer films, resulting in the preparation of poly(acrylic acid) (PAA)- and poly(4-vinylpyridine) (P4VP)-grafted membranes, respectively. Because the grafted polymers, PAA and P4VP, are insoluble in their monomers, a solvent for swelling is necessary to enable the monomers to diffuse through the entire irradiated films. Water and methanol are adequate as solvents for grafting acrylic acid[28,29] and 4-vinylpyridine,[30,31] respectively. While the grafted acrylic acid group itself is a cation-exchange group, the vinylpyridine group needs to be

modified to become an anion-exchange group. Methyl iodide was employed to convert P4VP-grafted membranes to poly(quaternized 4-vinylpyridine) (PQ4VP)-grafted membranes containing anion-exchange groups.

In general, the amount of ionic groups in ion-exchange membranes directly affects the membrane properties such as water uptake, ion-exchange capacity (IEC), and ionic conductivity. Because the degree of grafting (DOG) determines the amount of ionic groups in ion-exchange membranes prepared via radiation grafting, the DOG needs to be precisely controlled to acquire the membranes with desired properties.[21] The DOG can be adjusted by varying the grafting conditions such as the radiation dose, monomer concentration, and reaction time. In this study, the radiation dose for base polymers was fixed to 50 kGy with an irradiation rate of 7.0 kGy h^{-1}. Instead, the effect of the other conditions on the DOG was investigated.

During grafting of acrylic acid, the irradiated films were immersed in an aqueous solution with a monomer concentration of 50 vol % at 70 °C. Then, the DOG was observed at different reaction times from 2 to 5 h. Figure 2a shows that the DOG increases with the grafting time. It appears that monomers require a certain period of time to diffuse into the entire thickness of the base polymer films.[36] In the initial period of the grafting step, monomers are reacted onto only the surfaces of the films, whereas the middle interior region remains unreacted. For this reason, when the grafting time was shorter than 3 h, the membranes with even a considerable DOG had low ionic conductivity (Table 1), implying that the transport pathways for mobile ions are not yet constructed through the membranes. On the other hand, under a grafting time of over 5 h, the resulting membranes were wrinkled and had rough surfaces presumably because of excessive homopolymerization of acrylic acid, causing poor morphology of the metal electrodes for IPMCs. Accordingly, the optimum time for grafting acrylic acid seems to be around 4.5 h to construct the percolated paths for the mobile ions across the membranes as well as to obtain smooth surfaces of the membranes.

Both base polymers, PVDF-co-HFP and PE-co-TFE, were effective in achieving high DOG values of over 200% at a grafting time of 4.5 h. However, PE-co-TFE films exhibited a much higher DOG than the PVDF-co-HFP ones. This may originate from the differences in the chemical structures of the polymers and in the crystallinity of the films. It is known that the C−H bonds are more vulnerable to γ-rays than the C−F bonds.[22,35] Because PE-co-TFE contains more C−H bonds than PVDF-co-HFP does, the radical concentration generated by γ-ray irradiation in the former would be higher than that in the latter, leading to a high DOG for PE-co-TFE films. In addition, the crystallinity of the PE-co-TFE films (21.0%) is lower than that of the PVDF-co-HFP ones (27.4%).[20] Because the crystalline region in the films hinders the monomers from diffusing into the films,[36] the low crystallinity imparts high DOG values to the PE-co-TFE films.

Figure 2b shows the variation in DOG when monomer solutions of 4-vinylpyridine with different concentrations (30, 50, and 90 vol % in methanol) are applied at 60 °C for 16 h. The DOG for both base polymers increases with increasing monomer concentration. In comparison of the two base polymers, PE-co-TFE films have higher DOG values than PVDF-co-HFP films probably for the same reasons as that in the grafting of acrylic acid. Compared with acrylic acid, the DOG of 4-vinylpyridine is much lower, presumably owing to
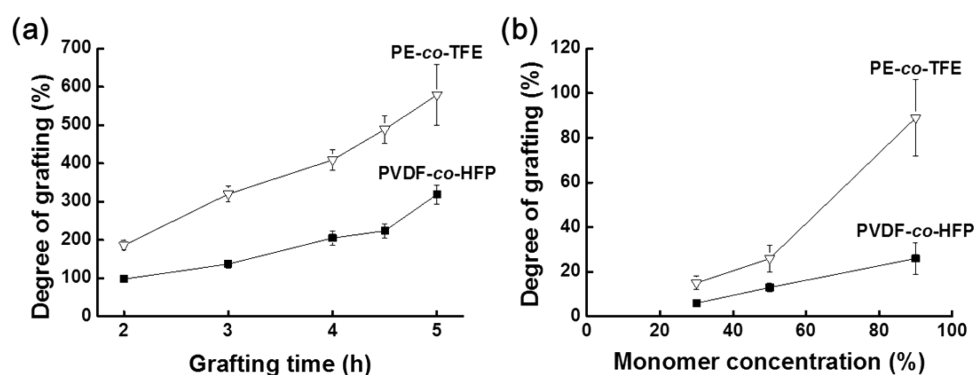
Figure 2. (a) DOG for acrylic acid as a function of the grafting time. Other conditions for grafting were as follows: radiation dose of 50 kGy, monomer concentration of 50 vol %, and reaction temperature of 70 °C. (b) DOG for 4-vinylpyridine as a function of the monomer concentration. Other conditions for grafting were as follows: radiation dose of 50 kGy, grafting time of 16 h, and reaction temperature of 60 °C. The thickness of all base polymer films was about 100 μm. Some error bars are not shown because they are smaller than the size of the data points.

Table 1. Properties of Radiation-Grafted Ion-Exchange Membranes

base polymer	grafted polymer	grafting time (h)	monomer concentration (vol %)	DOG (%)	water uptake (g g^{-1})	IEC (mequiv g^{-1})	ionic conductivity (mS cm^{-1})	IPMC denotation
PVDF-co-HFP	PAA	2	50	102	0.71	3.45	5	
PVDF-co-HFP	PAA	3	50	137	0.75	4.21	7	
PVDF-co-HFP	PAA	4	50	205	0.90	7.57	30	
PVDF-co-HFP	PAA	4.5	50	224	0.92	8.21	39	AA
PVDF-co-HFP	PAA	5	50	319	1.06	9.53	43	
Nafion 117					0.37	0.89	32	NA
PE-co-TFE	PQ4VP	16	30	15	0.03	0.66	2	
PE-co-TFE	PQ4VP	16	50	26	0.08	1.38	6	VP1
PE-co-TFE	PQ4VP	16	90	89	0.23	3.31	26	VP2

the lower diffusion rate of the bigger monomer into the base polymers. The highest DOG of 89% was obtained for PE-co-TFE films grafted with 90 vol % of a 4-vinylpyridine solution, which is utilized in the preparation of anion IPMCs.

Because neither of the high nor low DOG values were helpful to reinforce the actuation performance of IPMCs, we chose PAA-grafted PVDF-co-HFP and PQ4VP-grafted PE-co-TFE membranes for cation and anion IPMCs, respectively. The properties of the radiation-grafted ion-exchange membranes were characterized and listed in Table 1. Water uptake is the amount of water that is absorbed in ion-exchange membranes. IEC indicates the number of moles of exchangeable mobile ions in ion-exchange membranes. The ionic conductivity is related to the transport of hydrated ions in ion-exchange membranes. All of these quantities increased with increasing DOG, meaning that larger amounts of ionic groups in ion-exchange membranes resulted in larger numbers of mobile ions, larger water uptakes, and faster transports of hydrated ions.[20] Consequently, IPMCs employing radiation-grafted ion-exchange membranes are expected to exhibit improved performance. In addition, the anion-exchange membranes via radiation grafting, that is PQ4VP-grafted ones, have much larger IEC values compared to those of anion membranes in the literature (0.19 mequiv g^{-1} for Aciplex A-172[33] and 1.23 mequiv g^{-1} for PFAM 3020[34]), providing advanced actuation performance to the resulting anion IPMCs in this study.

The PAA-grafted PVDF-co-HFP membranes with a DOG of 224% and the PQ4VP-grafted PE-co-TFE ones with DOGs of

26% and 89% were utilized for the fabrication of IPMC actuators. Through a typical reduction method,[5] platinum and gold layers were formed on the surfaces of the PAA- and PQ4VP-grafted membranes, respectively. Figure 3 displays the cross-sectional images and metal profiles for the IPMCs, observed by using scanning electron microscopy and energy-dispersive X-ray spectroscopy (EDS). Both IPMCs have continuous metal layers with a thickness of about 10 μm on their surfaces, which are typical of conventional IPMCs.[3]

The prepared IPMCs were actuated by the application of 3 V of direct current (dc) for 20 s, as illustrated in Figure 4. The cation IPMCs of PAA-grafted membranes bent toward the cathode because the mobile ions were hydrated sodium ions with positive charges. On the contrary, the anion IPMCs of PQ4VP-grafted membranes bent in the opposite direction because of their mobile ions of hydrated chloride ions with negative charges. The anion IPMCs had an important advantage over the previous anion IPMCs reported. Namely, the previous anion IPMCs were only able to be actuated in water because of its small water content,[33] whereas our anion IPMC can be actuated in the air. In addition, the anion IPMC in this study exhibited over 200% larger bending strains (~7 mm when 3 V of dc was applied for 6 s) than even the latest reported result.[34]

The actuation performance of IPMCs obtained from radiation-grafted ion-exchange membranes was quantified by using a laser displacement meter.[12,20] For each IPMC, the applied potential (2 or 3 V), laser-detection point (10 or 20

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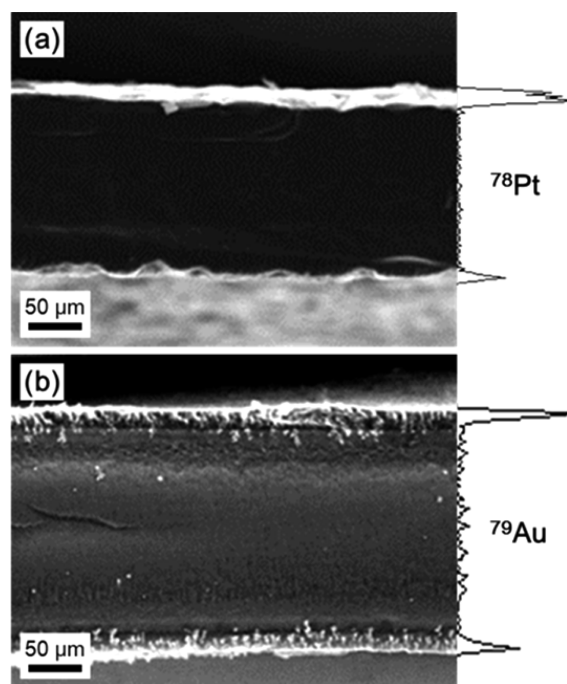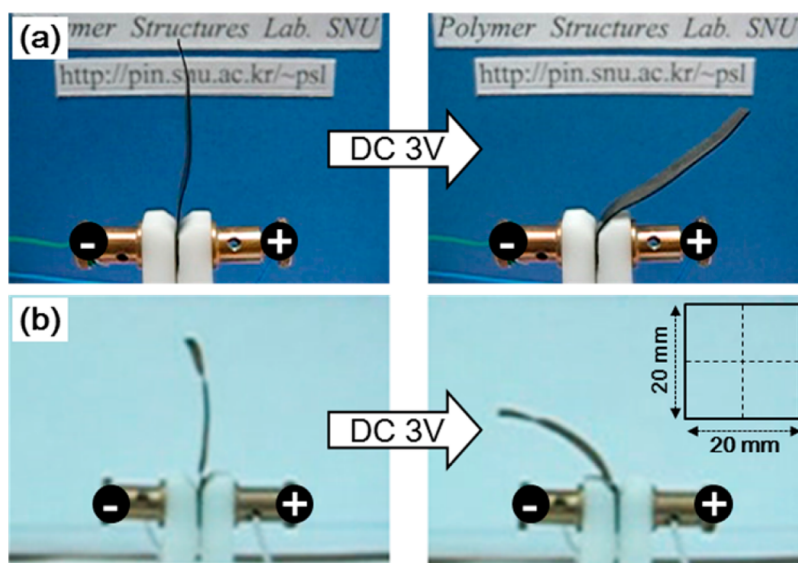
Figure 3. Cross-sectional images of (a) the cation IPMC (AA IPMC) of PAA-grafted PVDF-*co*-HFP membranes and (b) the anion IPMC (VP2 IPMC) of PQ4VP-grafted PE-*co*-TFE membranes. Each image contains the metal (platinum for the former and gold for the latter) profiles through the thickness observed by EDS.

mm away from the grip), and frequency (0.5 or 1 Hz) under alternating-current (ac) voltages were adjusted; in this manner, the displacement values of IPMCs could be more distinct. Figure 5 shows the actuation properties of the cation IPMC employing PAA-grafted membranes (AA IPMC). When a dc voltage of 2 V was applied for 50 s, the maximum displacement was about 2.2 mm. In addition, applying an ac voltage of 3 V at a frequency of 1 Hz to the IPMC resulted in a displacement of about 0.5 mm. These displacement values were comparable to

those of Nafion-based IPMC (NA IPMC). On the basis of the amount of ionic groups in ion-exchange membranes, the AA IPMC is expected to show a larger displacement than NA IPMC. However, because AA and NA IPMCs have equivalent ionic conductivity (Table 1), the amount of moving water when a potential was applied to these two IPMCs would be about the same. Accordingly, the large water content in AA IPMC would rather cause the relatively small volume change of the anode and cathode sides of AA IPMC, resulting in a small bending strain. On the other hand, the large water uptake and relatively low ionic conductivity of PAA-grafted membranes compared to Nafion seem to be effective in preventing the back-diffusion of water in IPMCs. As presented in Figure 5a, the problem of back-relaxation, which often arises for NA IPMCs,[37] was not observed for AA IPMC.

The response speed of AA IPMC, which was determined from the slope of the curves of the displacement versus time, was slower than that of NA IPMC. The difference in speed was particularly noticeable under ac potentials. AA IPMC was actuated slowly in the initial period of changing potentials, whereas NA IPMC immediately bent in the opposite direction when a reverse potential was applied, as shown in Figure 5b. This might be attributed to the difference in ionic groups between the two ion-exchange membranes. PAA-grafted membranes had carboxyl groups, while Nafion contained sulfonate groups. The sulfonate groups in Nafion ($pK_a = -6$)[38,39] can dissociate cations more readily than the carboxyl groups in PAA-grafted membranes (pK_a of PAA = 5.5−6.5),[40] so that the ion transport in PAA-grafted membranes would be slower than that in Nafion membranes.

Figure 6 presents the actuation behaviors of anion IPMCs based on the PQ4VP-grafted membranes with DOGs of 26% (VP1) and 89% (VP2). When a dc voltage of 2 V was applied for 100 s, the maximum displacements of the IPMCs of VP1 and VP2 were approximately 1.1 and 2.0 mm, without back-relaxation, respectively. Furthermore, as cation IPMCs did, highly symmetric bending motions under ac potential were observed for both VP1 and VP2 IPMCs. This result implies

Figure 4. Photographs of (a) the cation IPMC of PAA-grafted PVDF-*co*-HFP membranes and (b) the anion IPMCs of PQ4VP-grafted PE-*co*-TFE membranes, actuated by 3 V of dc for 20 s. The actuation of the IPMCs in parts a and b was recorded under identical magnification. The scale bar is included in part b.
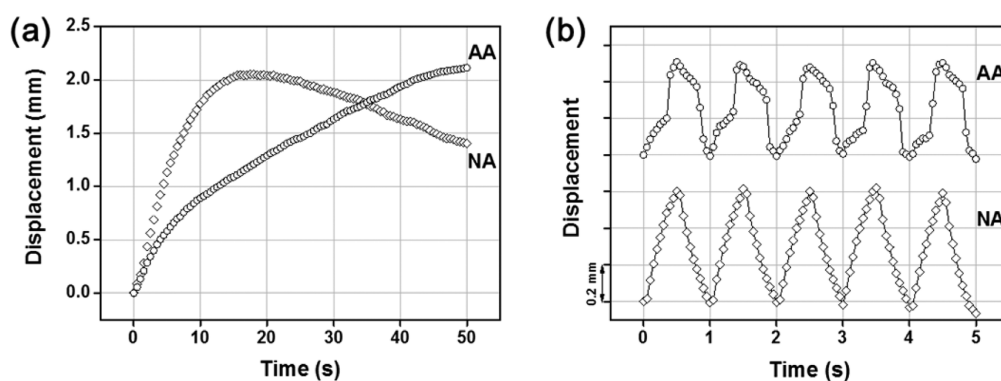
Figure 5. Displacement curves of cation IPMCs. The actuation was measured at a point of 10 mm away from the grip with (a) 2 V of dc and at a point of 20 mm away from the grip with (b) 3 V of ac in the form of a step wave at a frequency of 1 Hz. The thicknesses of AA and NA IPMCs were about 280 and 240 μm, respectively.
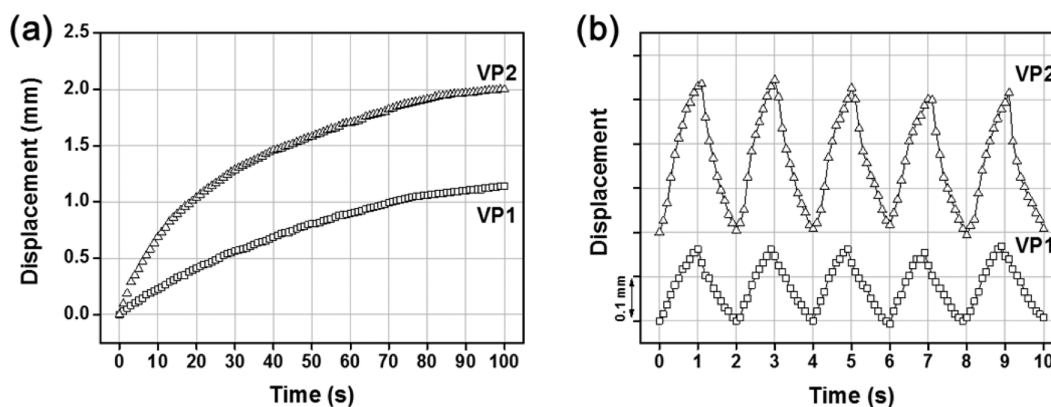
Figure 6. Displacement curves of anion IPMCs. The actuation was measured at a point of 20 mm away from the grip with (a) 2 V of dc and (b) 3 V of ac in the form of a step wave at a frequency of 0.5 Hz. The thickness of both VP1 and VP2 IPMCs was about 250 μm.

that these IPMC actuators were properly fabricated. Upon an ac voltage of 3 V at 0.5 Hz, the peak displacements of VP1 and VP2 IPMCs were approximately 0.17 and 0.34 mm, respectively. VP2 IPMC exhibited a larger bending displacement as well as a faster response than VP1 IPMC, which was thought to be a natural result of the ion-exchange membrane containing a larger number of ionic groups.

Even though these anion IPMCs showed significant improvement over previous anion IPMCs in the literature,[33,34] their actuation properties were still inferior to those of conventional cation IPMCs, in terms of the maximum displacement and response speed. We believe it is partly due to the difference in the mobile ions in IPMCs. It has been known that the mobile ions in ion-exchange membranes affect the actuation of IPMCs.[7−10] Smaller ions with higher charge density can attract more water molecules by means of electrostatic attraction.[41] Sodium ions have a larger degree of hydration than chloride ions, which results in a larger volume change of IPMCs motivated by the movement of the hydrated ions. The cation IPMCs with mobile ions of sodium ions consequently exhibit superior actuation performance compared to the anion IPMCs with mobile ions of chloride ions. The other reason for the poor actuation properties of anion IPMCs may be related to the water content in IPMCs. Water in IPMCs plays a role as the transport medium for mobile ions. A large amount of water in the membranes provides wide pathways for mobile ions and enhanced ionic conductivity. In addition, IPMCs are actuated by the movement of water molecules with

mobile ions. Hence, the water content in IPMCs to a certain level is essential in increasing the bending strain and response speed of IPMCs. However, compared to the cation-exchange membranes, the anion-exchange membranes in this study still contain a smaller amount of water, which might be under the levels. We are investigating the approaches to reinforce the actuation performance of anion IPMCs.

3. CONCLUSIONS

In preparation of the ion-exchange membranes for IPMC by radiation grafting, the key structural parameter in determining the property of the IPMC appeared to be the content of ionic groups introduced. The DOG and ion conductivity were controllable by regulating the grafting conditions. The prepared cation IPMC exhibited comparable actuation displacement with NA IPMC under the same applied voltage. However, back-relaxation, which lowers the displacement of NA IPMC, was not observed. The actuation displacement and speed of the prepared anion IPMC were much greater than those reported previously in the literature for other anion IPMCs, although they were still smaller than those of cation IPMCs partly because of the characteristic of anions. It is demonstrated that preparing an ion-exchange membrane by radiation grafting ionic group onto the hydrophobic fluoropolymer backbone is an effective way of fabricating IPMCs with desirable performance.

4. EXPERIMENTAL SECTION

Materials. Acrylic acid (99%) and 4-vinylpyridine (95%), purchased from Aldrich, were purified by distillation under reduced pressure. All other chemicals were used as received. PVDF-*co*-HFP (M_n = 130000), methyl iodide (99%), tetraammineplatinum chloride hydrate (98%, $[Pt(NH_3)_4]Cl_2 \cdot xH_2O$), sodium borohydride (98%), hydrogen tetrachloroaurate trihydrate (99.9+%, $HAuCl_4 \cdot 3H_2O$), sodium L-ascorbate (99+%), sodium carbonate (99%), lithium chloride (99%), sodium chloride (99+%), methanol (99+%), a sodium hydroxide standard solution (0.1 M), and a hydrochloric acid standard solution (0.1 M) were purchased from Aldrich. PE-*co*-TFE (M_n = 120000) and a Nafion 117 film (thickness = ~180 μm) were obtained from DuPont.

Radiation Grafting. PVDF-*co*-HFP and PE-*co*-TFE were molded into films with a thickness of ~100 μm by using a heat press (Carver Inc., model 4386). The films were irradiated with γ-rays using a ^{60}Co source at Korea Atomic Energy Research Institute (KAERI, Daejeon, Korea).[20] The irradiation was performed at room temperature under a nitrogen atmosphere. The total absorbed dose of the samples was 50 kGy, and the irradiation rate was 7.0 kGy h^{-1}.

The irradiated films were immersed in monomer solutions for graft polymerization. Deionized water was used as a solvent for acrylic acid. The concentration of the monomer solution was 50 vol %, and the reaction temperature was 70 °C. The grafting time was varied to control the amount of grafted acrylic acid. The resulting films were Soxhlet-extracted with deionized water for 12 h to remove the residual monomer and homopolymer adhering to the film surfaces. During the grafting of 4-vinylpyridine, methanol was employed as a solvent. The irradiated films were soaked in each monomer solution, with concentrations of 30, 50, and 90 vol % at 60 °C for 16 h. Then, the films were Soxhlet-extracted with methanol for 48 h. After all grafted films were dried to a constant weight, the DOG was determined as follows.

$$DOG\ (\%) = \frac{W_g - W_i}{W_i} \times 100$$

where W_g and W_i are the weights of the grafted and initial films, respectively.

To offer ionic groups to 4-vinylpyridine, the grafted films were quaternized by dipping in a 50 vol % methyl iodide/methanol solution for 48 h.[30,31] The films then were rinsed with methanol several times, followed by boiling in distilled water for 3 h.

Characterization of the Membrane Properties. The properties of the ion-exchange membranes prepared via radiation grafting were characterized. For measurement of the water uptake, the membranes were dried to a constant weight and then sufficiently hydrated with deionized water. The water uptake is calculated as follows.

$$water\ uptake\ (g/g) = \frac{W_{wet} - W_{dry}}{W_{dry}}$$

where W_{wet} and W_{dry} are the weights of the wetted and dried ion-exchange membranes, respectively.

To quantify IEC values, PAA-grafted membranes were dried to a constant weight and soaked in a known volume of a 0.1 M sodium hydroxide solution for 48 h to exchange protons in the membranes for sodium ions. The amount of protons was measured by titration of the exchanged solution with a 0.1 M hydrochloric acid solution.[37] For PQ4VP-grafted membranes, the anions in the membranes were thoroughly exchanged for hydroxide ions by using a 0.1 M sodium hydroxide solution.[39] After removal of excess solution, the samples were immersed in a known volume of a 0.1 M sodium chloride solution, in order to exchange the hydroxide ions for chloride ions again. Then, the amount of the exchanged hydroxide ions was measured by titration with a 0.1 M hydrochloric acid solution. IEC is defined as follows.

$$IEC\ (mequiv/g) = \frac{M_{ex}}{W_{dry}}$$

where M_{ex} is the number of moles of mobile ions in the membrane that were exchanged and W_{dry} is the weight of the dried ion-exchange membranes.

For measurement of the ionic conductivity, PAA-grafted membranes were fully hydrated with a 0.1 M sodium carbonate aqueous solution, in order to convert the mobile cations to sodium ions, as would occur under real actuation conditions. PQ4VP-grafted membranes were hydrated with a 0.1 M lithium chloride aqueous solution to convert mobile anions to chloride ions. Both membranes were cut into a standard size of $10 \times 40\ mm^2$ and then inserted into the cell for measurement of the ionic conductivity with a four-point probe.[42] The impedance analyzer (Zahner IM6) was operated in galvanostatic mode with an ac amplitude of 0.01 mA over the frequency range from 1 MHz to 10 mHz using the Nyquist method.

Fabrication of IPMCs. Cation and anion IPMCs were fabricated with ion-exchange membranes prepared via radiation grafting. The membranes were cut into a size of $50 \times 50\ mm^2$, and their surfaces were sandpapered to acquire uniform metal electrodes. PAA-grafted membranes were immersed in a 0.5 wt % aqueous solution of tetraammineplatinum chloride hydrate to convert their mobile cations into $[Pt(NH_3)_4]^{2+}$.[5] After rinsing with deionized water, the membranes were soaked in a water bath (300 mL) at 40 °C with stirring. Then, 5 mL of a 5 wt % aqueous solution of sodium borohydride was added every 30 min for 12 h, resulting in the reduction of platinum layers on both surfaces of the membranes. For PQ4VP-grafted membranes, the mobile anions in the membranes were fully exchanged for $[AuCl_4]^-$ in a 0.5 wt % aqueous solution of hydrogen tetrachloroaurate trihydrate.[33] For the formation of gold electrodes, a 5 wt % aqueous solution of sodium L-ascorbate was utilized as a reducing agent.

The cross-sectional morphology of the metal electrodes was observed with a scanning electron microscope (JEOL JSM5310). The metal profile (platinum or gold) in IPMCs was analyzed by EDS.

Actuation of IPMCs. Before actuation tests, mobile ions in IPMCs were unified by soaking in saturated aqueous solutions of certain salts. Cation IPMCs employing PAA-grafted membranes or Nafion were immersed in a solution of sodium carbonate for 24 h to fix the mobile ions to sodium ions. Anion IPMCs prepared with PQ4VP-grafted membranes were dipped in a lithium chloride solution for 24 h in order for the mobile ions to exchange for chloride ions.

After IPMCs were cut into strips with a width of 5 mm and a length of 40 mm, the strips were mounted on a laser displacement meter.[12,20] When a voltage is applied, the laser displacement meter measures the displacement of IPMCs. The detailed conditions for actuation tests of IPMCs are as follows. The displacement of cation IPMCs was measured at 10 and 20 mm from the grip of the strips for dc and ac potentials, respectively. The dc potential was 2 V and the ac potential was 3 V in the form of a step wave at a frequency of 1 Hz. The detection point for anion IPMCs was located at 20 mm from the grip when a dc voltage of 2 V and an ac voltage of 3 V were applied in the form of a step wave at a frequency of 0.5 Hz.

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Author Contributions
∥The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. J.H.P. and M.J.H. contributed equally to this work.

Notes
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■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on December 15, 2014, with errors in Figure 1. The corrected version was reposted on December 24, 2014.