Tailoring actuation of ionic polymer-metal composites through cation combination

Sia Nemat-Nasser[*] and Yongxian Wu

University of California, San Diego. Center of Excellence for Advanced Materials
9500 Gilman Drive, La Jolla, CA 92093-0416

ABSTRACT

An ionic polymer-metal composite (IPMC) consisting of a thin perfluorinated ionomer (usually, Nafion® or Flemion®) strip, platinum and/or gold plated on both faces, undergoes large bending motion when a small electric field is applied across its thickness. When the same membrane is suddenly bent, a small electric potential of the order of millivolts is produced across its surfaces. This actuation and sensing response depends on the structure of the ionomer, the morphology of the metal electrodes, the nature of cations, and the level of hydration. IPMCs in alkali-metal cation form under direct current (DC) show a fast motion towards the anode, followed by a slow relaxation. For Nafion-based IPMCs, this slow relaxation is towards the cathode, whereas for Flemion-based IPMCs, the slow relaxation continues the initial fast motion towards the anode. In contrast, the actuation of both Nafion- and Flemion-based IPMCs in tetrabutylammonium (TBA^+) cation form consists of a continuous slow motion towards the anode. We have discovered that when an IPMC is neutralized by combined Na^+ and TBA^+ cations to produce a suitable Na-TBA-form membrane, different actuation behavior results. The proportion of the cations can be tailored to obtain a desired actuation response, *e.g.*, to control the duration, speed, and the maximum amplitude of the initial motion towards the anode, or the magnitude and the speed of the subsequent relaxation. A series of cation combination tests on both Nafion- and Flemion-based IPMCs are carried out. Various essential physical properties of the IPMCs in various cation compositions are measured and compared. A summary of these results is presented.

Keywords: ionic polymer-metal composite, actuation, cation combination, Nafion, Flemion.

1. INTRODUCTION

The coupled electrical-chemical-mechanical response of hydrated IPMCs depends on the structure of their backbone ionic membrane (generally Nafion® or Flemion®), the morphology and conductivity of the metal electrodes (gold and/or platinum), the properties of cations (alkali metal or alkyl ammonium), and the level of hydration.[1] In an earlier report,[2] we have presented experimental data to characterize and compare various properties of Nafion- and Flemion-based IPMCs in different *single* cation forms. In a typical actuation test, a saturated strip of an IPMC is immersed in room temperature deionized (DI) water, with one end clamped between platinum electrodes. A small potential, *e.g.*, 1.5 V, direct current (DC), is suddenly applied and maintained until the sample comes to rest. A CCD camera records the deformation history, using a fast frame rate during the initial fast motion and a slower rate subsequently during the relaxation phase. Simultaneously, the current and potential across the thickness of the sample are recorded using a Nicolet MultiPro Data Acquisition System. The accumulated charge in the cathode boundary is obtained by the time-integration of the net current (*i.e.,* the measured current less long-time residual). The time-history of the normalized tip displacement (tip displacement divided by gauge length) is then obtained through video analysis.

A strip of Nafion-based IPMC in an alkali-metal cation form (*e.g.*, in Na^+-form) has an initial *fast* bending deformation towards the *anode* (less than 0.5 second, see Figures 1-A and 1-B), followed by a *slow* relaxation in the *opposite* direction towards the cathode (up to 1 minute, see Figure 1-A). When a strip of a Flemion-based IPMC in an alkali-metal cation form is actuated, it has an initial *fast* bending motion towards the anode. However, instead of relaxing back like the Nafion-based IPMC, it continues to bend in the *same* direction, *i.e.*, towards the *anode*, but with a decreasing speed.

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[*] sia@ucsd.edu

Moreover, a Flemion-based IPMC in the TBA[+] cation form deforms *continuously* and *gradually* towards the *anode* with a decreasing speed. No distinct initial fast motion or slow relaxation is observed for this type of IPMCs, see Figure 1-B.

Substitution of various alkali-metal cations (Li^{+}, Na^{+}, K^{+}, Rb^{+}, and Cs^{+}) or alkyl-ammonium cations (TMA[+], TEA[+], TPA[+], and TBA[+]) yields varied deflection speeds, displacement, and degrees of relaxation for a same strip of IPMC. Thus, the actuation performance may be tailored by suitable choice of the cation.[3] Some of the advantages and disadvantages of each cation form in the actuation of IPMCs are listed in Table 1.[4]

Certain applications may require an IPMC that is optimized to have a *fast* and *large* bending deformation, and the ability to maintain this over a given time period. These properties may be attained by suitably combining the alkali-metal and alkyl-ammonium cations in an IPMC.
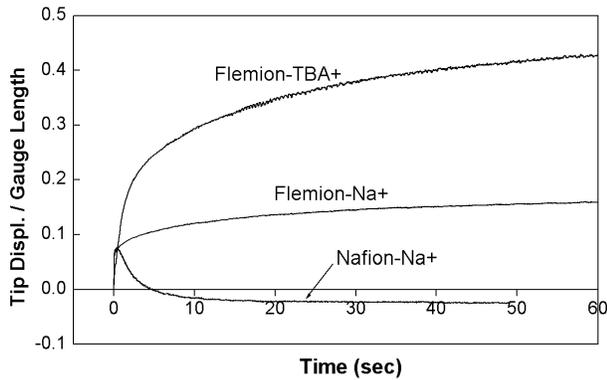

Figure 1-A. Normalized tip displacement of a Nafion- and a Flemion-based IPMC both in the Na^{+}-form, and that of the same Flemion-based IPMC in the TBA[+]-form, under 1.5V DC. *Positive* displacement represents bending towards the *anode*. Only the Nafion-based IPMC in Na^{+}-form (and other alkali-metal cations) shows a relaxation in the *cathode* direction;
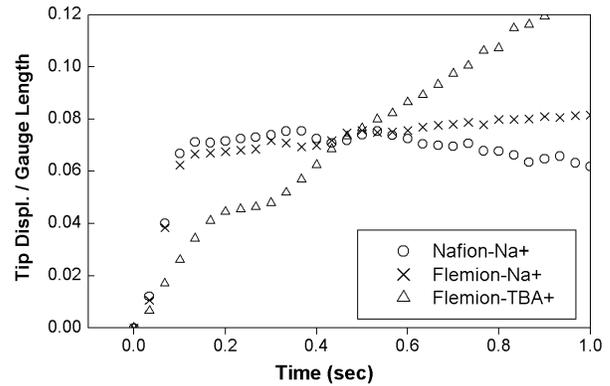
Figure 1-B. Tip displacement during the first 1 second of the actuation tests in Figure 1-A, showing the initial fast motion of Nafion- and Flemion-based IPMCs in the Na^{+}-form, and that of the same Flemion-based IPMC in the TBA[+]-form (for which no distinct fast motion is observed), recorded at 30 frame/sec (1/30 second between adjacent points).

Table 1. Some of the advantages and disadvantages of various cation forms in the actuation of IPMCs.

Cation Form	Advantages	Disadvantages
Li^{+}, Na^{+}, K^{+}, Rb^{+}, Cs^{+}, …	• Fast response • Large amplitude under high-frequency alternate current (AC)	• Nafion-based IPMCs do not hold strain under DC • Small overall displacement • Low voltage limit due to water electrolysis[5] (< 1.5 V)
TBA[+]	• Do not relax under DC • Large overall displacement • Can suppress water electrolysis at higher voltage[2] (up to 3V)	• Slow response • Small amplitude under high-frequency AC[6]

2. DESCRIPTION OF THE EXPERIMENTS

The objective is to study the physical properties, especially the actuation behavior, of IPMCs in various cation compositions. Three strips of a Nafion-based IPMC (denoted as Nafion-A, B, and C) and three strips of a Flemion-based IPMC (denoted as Flemion-A, B, and C) in the initial Na^{+}-form are prepared. The strips are about 3cm in length, 0.3cm in width, and 0.02cm in thickness, with Flemion samples being thinner, about 0.018cm thick. After recording the

actuation in their pure Na^+-form, the strips are immersed in the 70°C, 0.5mol/L TBAOH solution and kept there for different time periods, from 2 to 6 minutes. Because of the membrane's cation affinity, TBA^+ gradually replaces the Na^+. Before this cation exchange is fully completed, samples are removed from the solution and rinsed in the DI water, while both the Na^+ and the TBA^+ cations are present in the strips. In what follows, this combined cation form is referred to as Na-TBA-1. Various properties of the samples are then measured, including their masses and dimensions in both wet and dry forms; their actuation parameters, *i.e.*, tip displacement, current, and potential; their surface conductivity; and their longitudinal stiffness at various degrees of hydration. Then the samples are placed in the same solution for an additional time period to allow further substitution of Na^+ by the TBA^+, followed by the same set of measurements; the resulting cation combination in the samples is referred to as Na-TBA-2. Finally, the samples are again placed in the same TBAOH solution for 24 hours until equilibrium is achieved. The samples are now all in the TBA^+-form. By comparing various properties of the IPMCs containing different fractions of Na^+ and TBA^+, we are able to tailor their response for a given application.

3. DETERMINATION OF CATION COMPOSITION

The samples in each cation form are dried for 24 hours, under vacuum at 100°C. The dry masses are measured, as listed in Tables 2-A and 2-B. Samples' masses increase with increasing amounts of TBA^+ cation. The fraction of TBA^+ cation in each sample is then established and related to the corresponding measured properties.

Each sample has a constant ion capacity (fixed number of moles of cation), and fixed amounts of ionomers and metal electrodes. Therefore, the change in its dry mass in various cation forms reflects the change in the mass of its cations. From the sample's dry mass in pure Na^+-form and in pure TBA^+-form, its ion capacity is established.[2] Then, the amount of each cation for each cation combination is obtained from the corresponding dry mass. The results are reported in Tables 2-A and 2-B, together with the corresponding cation's *formula weight* (*FW*) or *equivalent formula weight* (*eqFW*, has a value between FW_{Na+} and FW_{TBA+}); the calculated values are indicated in *italic* to differentiate them from the measured values.

Table 2-A. Determination of the cation composition of Nafion-based IPMCs

Sample	Cation Form	Time in TBAOH (min)	Dry Mass (10^{-2} g)	Ion Capacity (10^{-5} mol)	FW or *eqFW* (g/mol)	Portion of TBA^+ (% by mol)
Nafion-A	Pure Na^+	0	3.674		22.99	0
	Na-TBA-1	2.5	3.703	*1.936*	*37.97*	*6.8*
	Na-TBA-2	2.5+4	3.777		*76.18*	*24.2*
	Pure TBA^+	24 hours	4.099		242.46	100
Nafion-B	Pure Na^+	0	3.794		22.99	0
	Na-TBA-1	5	3.850	*1.818*	*53.79*	*14.0*
	Na-TBA-2	5+5	3.914		*89.00*	*30.1*
	Pure TBA^+	24 hours	4.193		242.46	100
Nafion-C	Pure Na^+	0	3.945		22.99	0
	Na-TBA-1	6	4.003	*1.900*	*53.52*	*13.9*
	Na-TBA-2	6+5	4.079		*93.52*	*32.1*
	Pure TBA^+	24 hours	4.362		242.46	100

Table 2-B. Determination of the cation composition of Flemion-based IPMCs

Sample	Cation Form	Time in TBAOH (min)	Dry Mass (10^{-2} g)	Ion Capacity (10^{-5} mol)	FW or eqFW (g/mol)	Portion of TBA$^+$ (% by mol)
Flemion-A	Pure Na$^+$	0	2.675		22.99	0
	Na-TBA-1	2.5	2.813	2.016	90.44	30.7
	Na-TBA-2	2.5+4	3.001		182.34	72.6
	Pure TBA$^+$	24 hours	3.124		242.46	100
Flemion-B	Pure Na$^+$	0	2.648		22.99	0
	Na-TBA-1	5	2.875	1.996	135.04	51.1
	Na-TBA-2	5+5	3.029		211.06	85.7
	Pure TBA$^+$	24 hours	--		242.46	100
Flemion-C	Pure Na$^+$	0	2.674		22.99	0
	Na-TBA-1	6	2.926	2.016	146.18	56.1
	Na-TBA-2	6+5	3.086		224.39	91.8
	Pure TBA$^+$	24 hours	--		242.46	100

The ion capacity of each sample is equal to the number of moles of SO_3^- (Nafion) or COO^- (Flemion) in its ionomer. The charge density of Nafion-117 with the equivalent weight of 1,100 gram/mole is 0.91 mequiv g^{-1}, and that of Flemion-1.44 with equivalent weight of 694 gram/mole is 1.44 mequiv g^{-1}.[6] From this and the corresponding measured ion capacity of the sample, we can calculate the mass of its ionomers, and whence the mass of its metal electrodes. The *metal content* is a key factor for IPMC's characterization and modeling.[7] For the samples used in the present work, the average metal content is 44.9% for the Nafion- and 46.0% for the Flemion-based IPMCs. These values are very close to those reported earlier,[2] which were obtained through more extensive tests.

Since each pair of samples that are designated by the same letter, *e.g.*, Nafion-A and Flemion-A, is processed together simultaneously in the same environment, the results in Tables 2-A and 2-B suggest that Flemion has greater ion exchange capability than does Nafion, so that, under the same conditions (temperature, solution concentration, and exposure duration), a Flemion-based IPMC in Na$^+$-form absorbs greater amounts of TBA$^+$ (replacing Na$^+$) than does the corresponding Nafion-based IPMC.

4. RESULTS

4.1 ELECTRO-MECHANICAL RESPONSE

4.1.1   Actuation of Nafion-based IPMC in combined cation form

Figures 2-A and 2-B display the actuation of the Nafion-B IPMC in the indicated cation forms, *i.e.*, pure Na$^+$, 14.0% TBA$^+$ (Na-TBA-1), and 30.1% TBA$^+$ (Na-TBA-2). The actuation of the Nafion-based IPMC in pure TBA$^+$-form shows *very* slow response and small amplitude,[2] which is not considered here.

Comparing the actuation of the Nafion-based IPMCs in the indicated cation forms, the following observations result:

a)   For the combined cation forms, the *maximum initial tip displacement* towards the anode is increased (Figure 2-A), from 7.5% of the gauge length in the pure Na$^+$-form to 15.2% in the Na-TBA-2-form.

b)   The *duration of the motion* towards the anode is extended from 0.3 second for the pure Na$^+$-form to 1.1 seconds for the Na-TBA-1-form and then to 4.3 seconds for the Na-TBA-2-form (Figure 2-B).

c) The *tip displacement in the back relaxation* towards the cathode is decreased with increasing amounts of TBA$^+$, being the greatest for the pure Na$^+$-form (*overshoots* the initial position) and the least for the Na-TBA-2-form (*partially* recovers the initial position, see Figure 2-A).

The large size of the TBA$^+$ cation and its slow mobility within the ionomer membrane provide an explanation for the reduced deformation speed of the corresponding IPMC.[5]

Figure 3 shows the time-history of the actuation of all three Nafion-based IPMC samples in indicated combined cation forms. The label in this figure gives the percent of TBA$^+$ in each case, with the corresponding balance being Na$^+$.
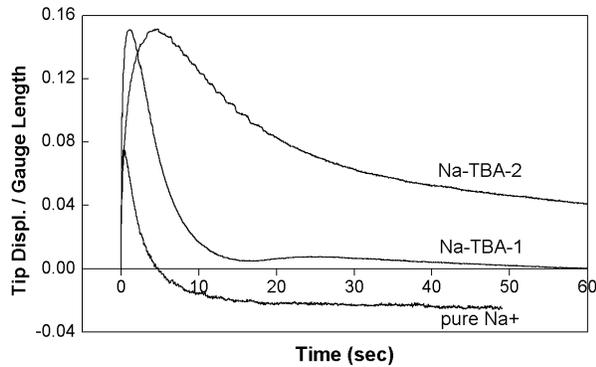
Figure 2-A. Actuation of Nafion-B IPMC in pure Na$^+$-form and in combined Na-TBA-forms. 1.5V DC is applied and sustained. Increasing amounts of TBA$^+$, increases the maximum tip displacement of the initial motion towards the anode, and decreases the back relaxation;
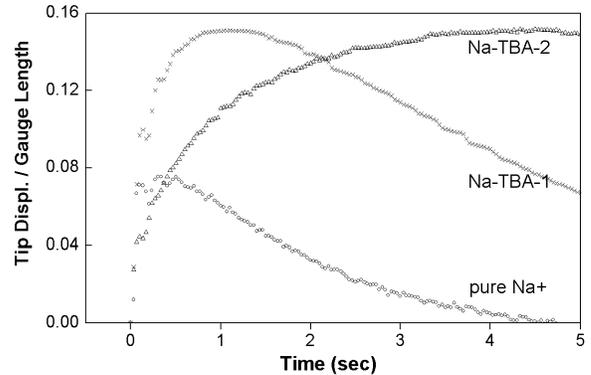
Figure 2-B. The first 5 seconds of the actuation tests in Figure 2-A. Increasing amounts of TBA$^+$, extends the duration of the initial motion towards the anode.
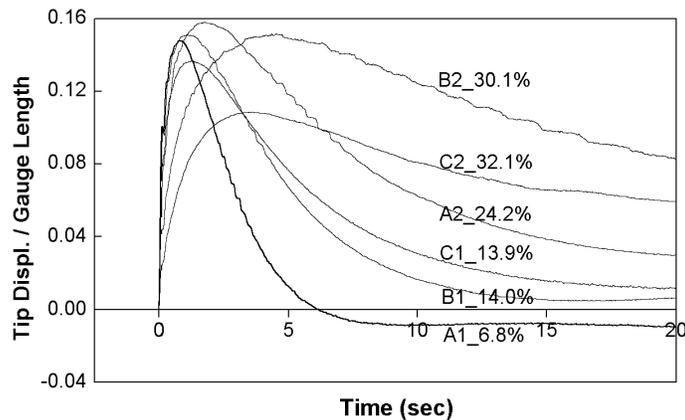

Figure 3. Actuation of Nafion-based IPMCs in various indicated TBA$^+$ and the balance Na$^+$ cation forms (three samples are from the same IPMC sheet).

In general, replacing greater amounts of Na$^+$ by TBA$^+$ in a given Nafion-based IPMC sample produces slower motion, greater maximum displacement towards the anode, and less back relaxation towards the cathode. Thus, under an alternating potential (AC) with a given frequency (fraction of Hertz to tens of Hertz), it may be possible to adjust the cation combination so as to maximize the actuation amplitude and minimize the back relaxation. Nafion-based IPMCs in pure Na$^+$-form or with small amounts of TBA$^+$ perform better at high-frequency AC, whereas for low-frequency actuation, greater amounts of TBA$^+$ may produce greater amplitude motion.

4.1.2 Actuation of Flemion-based IPMC in combined cation form

Figures 4-A and 4-B display the actuation of the Flemion-B IPMC in the indicated cation forms, *i.e.*, pure Na^+, 51.1% TBA^+ (Na-TBA-1), and 85.7% TBA^+ (Na-TBA-2).

Comparing the profiles of the actuation displacement of the Flemion-based IPMCs in the indicated cation forms, the following observations result:

a) A Flemion-based IPMC in pure Na^+-form has an initial fast motion towards the anode, reaching up to 40% of its total displacement in about 0.1 sec (Figure 4-B). With the increasing amounts of TBA^+ cation, the magnitude of this initial fast motion diminishes (11% in Na-TBA-1-form) and eventually disappears (only 2% in Na-TBA-2-form).

b) The long-term relaxation motion (Figure 4-A) of Flemion-based IPMCs is towards the anode and produces the major part of the overall displacement. The sample with greater amount of TBA^+ cation produces larger total tip displacement in its forward relaxation motion.

Thus Flemion-based IPMCs in pure Na^+-form or with small amounts of TBA^+ have good high-frequency AC actuation, whereas those with large amounts of TBA^+ have good low-frequency AC actuation.
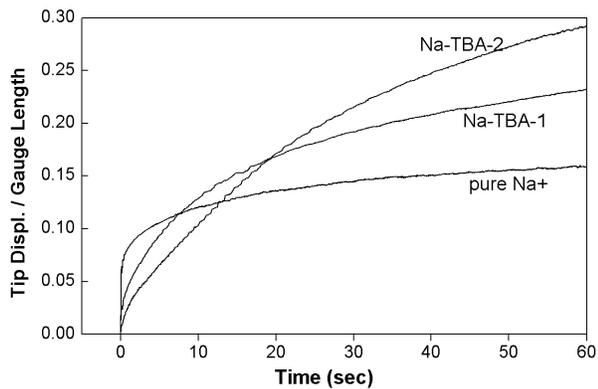

Figure 4-A. Actuation of Flemion-B IPMC in pure Na^+-form and in combined Na-TBA-forms. 1.5V DC is applied and sustained. Increasing amounts of TBA^+, increases the long-term total tip displacement towards the anode;
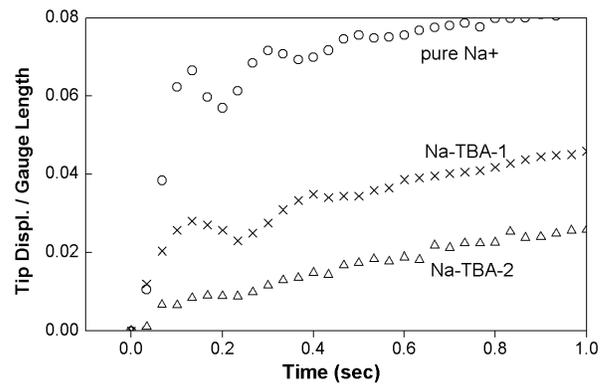
Figure 4-B. The first 1 second of the actuation tests in Figure 4-A. The sample in pure Na^+-form has an initially fastest response, which is reduced with increasing TBA^+ content.

By controlling the ion-exchange conditions (reaction temperature, solution concentration, exposure time scale, *etc.*), the amount of each cation in the IPMC can be controlled in order to optimize the required actuation behavior, *e.g.*, the duration of the initial fast motion towards the anode, or the extent of the subsequent relaxation. In this manner, one can induce diverse actuations in the same IPMC strip.

4.1.3 Accumulated charge

The current and the potential across the samples' thickness are recorded during the actuation tests. The accumulated charge, representing the total charge transported by the cations during the actuation, is calculated by time-integration of the current, upon subtraction of the long-time residual current (if any). This accumulated charge is normalized by dividing it by the total moles of ion capacity of the sample (or, the amount of total fixed charge, in Coulombs).

During the actuation (the process of charging) of both Nafion- and Flemion-based IPMCs in various cation compositions, the charge accumulates quickly soon after the application of the voltage, and then tends to remain constant once the sample reaches an equilibrium state with essentially no further actuation. Less than 10% of the sample's fixed

charge has been transported to the cathode during this process. Comparing with the corresponding tip displacement, it is seen that the charge accumulation for Flemion-based IPMCs is linearly related to the tip displacement over the entire actuation process, as the two curves have very similar time-variations. However, for Nafion-based IPMCs, a very different phenomenon is observed. The initial speed of the fast displacement (towards the anode) proportionally correlates with the speed of charge accumulation. After this fast motion, while charge is still being transported to the cathode, the sample shows extensive back relaxation in the opposite direction.[2]

For Nafion-based IPMC samples in various cation compositions, the total amounts of transported charge towards the cathode are calculated (using residual current as 0 mA) and compared with the corresponding tip displacement, see Figures 5-A and 5-B. Again, the results indicate that the relaxation part of the actuation of Nafion-based IPMCs in pure Na+-form and Na-TBA-forms is towards the cathode despite the fact that charges continue to accumulated within the cathode boundary (Figure 5-B).

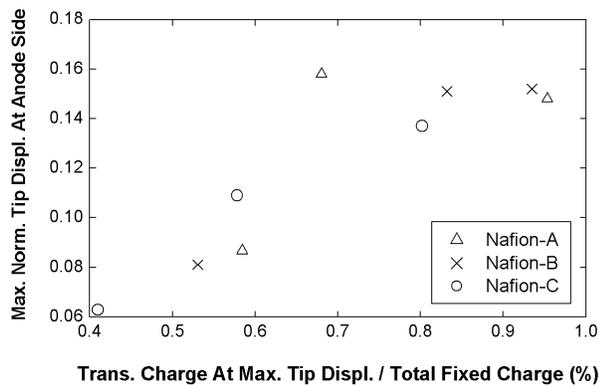**Trans. Charge At Max. Tip Displ. / Total Fixed Charge (%)**

Figure 5-A. Normalized transported charge at the maximum tip displacement towards the anode for Nafion-based IPMCs in various cation compositions. Generally, for Nafion-based IPMCs, the initial tip displacement towards the anode correlates with the amount of transported charge to cathode;

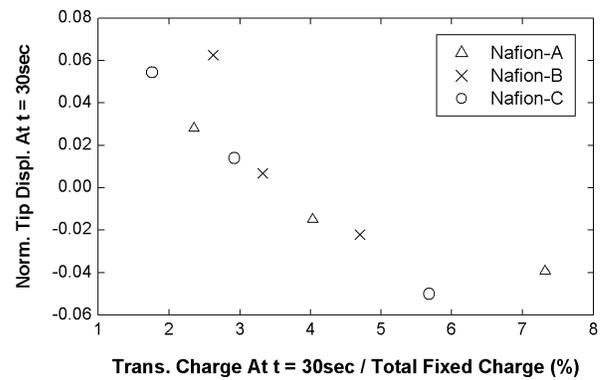**Trans. Charge At t = 30sec / Total Fixed Charge (%)**

Figure 5-B. Normalized transported charge after 30 seconds of actuation of Nafion-based IPMCs in various cation compositions, showing back relaxation towards the cathode despite the fact that charges continue to accumulate within the cathode boundary.

4.2 DIMENSIONS AND WATER UPTAKE

Sample's dimensions and weight are measured in both wet and dry forms. The wet form refers to the water-saturated state, attained by immersing the sample in DI water until equilibrium is reached. The dry form is obtained by placing the sample in a furnace, at 100°C and under vacuum, for 24 hours. Both Nafion- and Flemion-based IPMCs greatly swell as large size TBA+ molecules diffuse into the membrane. This is clearly seen in Figure 6, where the dry volume is plotted as a function of mole percent TBA+.

The level of hydration, defined by the volume of water uptake divided by the volume of dry-form IPMC, is one of the most important factors determining the properties of IPMCs, especially the wet-form stiffness and the actuation activity. The water uptake depends strongly on three conditions: environmental water state (vapor or liquid), cation type, and temperature.[1] In our tests, samples are immersed in water and the temperature during ion exchange is kept around 70°C. Thus the variation in the hydration level is basically due to the nature of the cations (Figure 7).

The hydration level decreases with increasing amounts of TBA+ in both Nafion- and Flemion-based IPMCs. For a same Na-TBA cation composition, the hydration volume of Flemion-based IPMC is always higher than that of Nafion-based IPMC, as is seen in Figure 7.
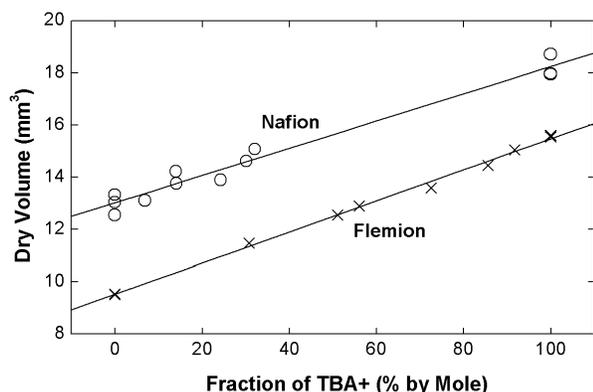
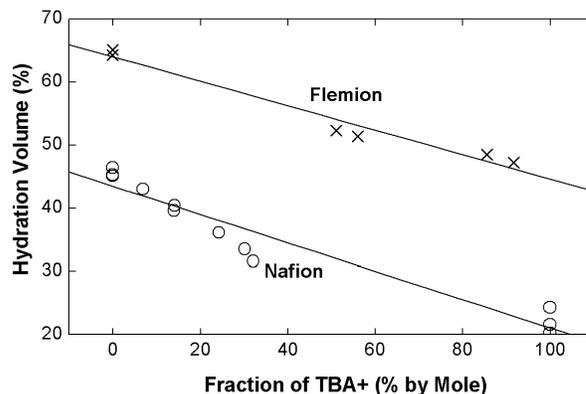Figure 6. Volume of dry-form IPMCs in various cation compositions.

Figure 7. Water uptake of IPMCs in various cation compositions

4.3 SURFACE CONDUCTIVITY

The surface conductivity of each sample in each cation form is measured in terms of specific surface resistance (in Ωcm/cm). The results are shown in Figures 8-A and 8-B. Generally, the Flemion-based IPMC samples used in the tests have better surface conductivity than the Nafion ones. The great increase in specific surface resistance from pure Na^+- to pure TBA^+-form is thought to be due to the greater swelling of the ionomer in the TBA^+-form, which opens up the cracks within the electrodes.[2]
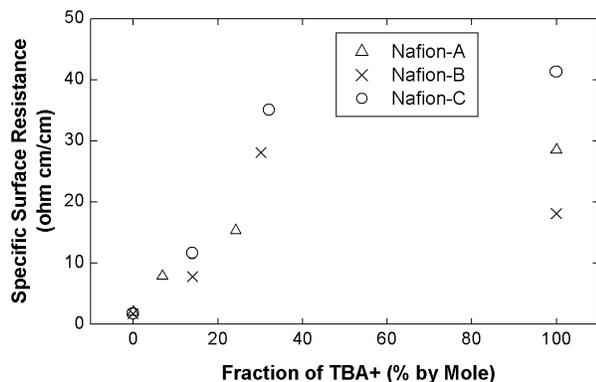

Figure 8-A. Specific surface resistance of Nafion-based IPMCs in various cation compositions;
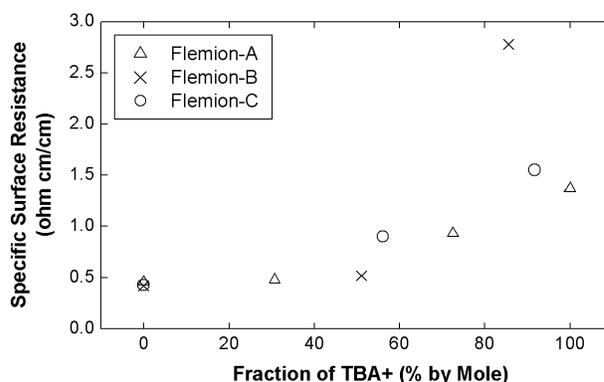

Figure 8-B. Specific surface resistance of Flemion-based IPMCs in various cation compositions.

5. OTHER METHODS TO OBTAIN CATION COMBINATION

The cations other than Na^+ and TBA^+ may be used in combination to tailor an IPMC's actuation. Li^+, K^+, and TMA^+ may be good choices for one of the components.

A possible disadvantage of the method obtaining combined cation forms mentioned above is brought by the insufficient time of ion exchange, which may cause non-equilibrium along the cross-section of the IPMC sample. Large TBA^+ cation may only stay within the outer layers of the membrane instead of distributing uniformly. An alternative method is changing the cation from proton-form (H^+-form) *directly* to the desired combined cation form, which can be realized by

immersing H^+-form IPMC samples in a combined salt or base solution with both cations, until equilibrium. The ratio of cations in the IPMC can be adjusted by properly changing the concentration of each salt or base in the combined solution. A Nafion-based IPMC in Na^+-form is used in such a test. The sample is changed to H^+-form and then immersed in a combined solution, with 0.7 mol/L NaCl and 0.3 mol/L TBAOH, at 60°C, for 24 hours. The actuation behavior observed is quite similar as the one shown in Figure 2. The initial displacement towards the anode is greatly extended (up to 4 seconds) and the sample relaxes back (towards the cathode) to its original position.

6. CONCLUSIONS

The method of ion-exchange reaction can be tailored in order to obtain IPMCs in desired combined cation forms. For IPMCs in various Na-TBA cation compositions, the actuation behavior as well as other physical properties show remarkable variation from those of pure Na^+-form to those of pure TBA^+-form. The duration of the initial bending towards the anode, and the subsequent relaxation towards the cathode for Nafion-based IPMCs, can be controlled by properly adjusting the corresponding cation content. For Nafion-based IPMCs in Na-TBA forms, the actuation activities are greatly improved by this method. Comparing with switching among various types of single cations, the method of cation combination is proved to be more promising in that, the actuation behavior thus obtained is more diverse, more continuous. For certain requirements in actual applications, we may always find a cation composition, in which IPMC samples show optimized actuation behavior. The future study will be focused on the AC actuation of IPMCs in combined cation forms, and also exploring different cation combinations.

ACKNOWLEDGEMENT

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