Experimental Study of Nafion- and Flemion-based Ionic Polymer-metal Composites (IPMCs) with Ethylene Glycol as Solvent

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ABSTRACT

Ionic polymer-metal composites (IPMCs) consist of a perfluorinated ionomer membrane (usually Nafion® or Flemion®) plated on both faces with a noble metal such as gold or platinum and neutralized with a certain amount of counterions that balance the electrical charge of anions covalently fixed to the membrane backbone. IPMCs are electroactive materials that can be used as actuators and sensors. Their electrical-chemical-mechanical response is highly dependent on the cations used, the solvent, the amount of solvent uptake, the morphology of the electrodes, and other factors. With water as the solvent, the applied electric potential must be limited to less than 1.3V at room temperature, to avoid electrolysis. Moreover, water evaporation in open air presents additional problems. These and related factors limit the application of IPMCs with water as the solvent. Ethylene glycol has a viscosity of about 16 times that of water at room temperature, and has a greater molecular weight. It is used as an anti-freeze. Like water, it consists of polar molecules and thus can serve as a solvent for IPMCs. We present the results of a series of tests on both Nafion- and Flemion-based IPMCs with ethylene glycol as the solvent, and compare these with the results obtained using water. IPMCs with ethylene glycol as their solvent have greater solvent uptake, and can be subjected to relatively high voltages without electrolysis. They can be actuated in open air for rather long time periods, and at low temperatures. They may be good actuators when high-speed actuation is not necessary.

Keywords: ionic polymer-metal composite, actuation, ethylene glycol, Nafion, Flemion

1. INTRODUCTION

Ionic polymer-metal composites (IPMCs) are electroactive materials with potential application as actuators and sensors [1]. An IPMC consists of a perfluorinated ionomer backbone (usually Nafion® or Flemion®; see Figure 1) plated on both faces with noble metals such as platinum or platinum and gold, or gold, and neutralized with a certain amount of counterions that balance the electric charge of the anions covalently bonded to the membrane backbone.

$$- (CF_2 CF) (CF_2 CF_2)_n -$$
$$O - CF_2 CF - O - CF_2 CF_2 SO_3^-$$
$$CF_3$$

$$- (CF_2 CF) (CF_2 CF_2)_n -$$
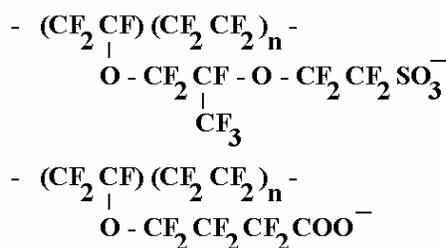$$O - CF_2 CF_2 CF_2 COO^-$$

FIG. 1. Chemical composition of Nafion (Top) and Flemion (Bottom)

The microstructure of the ionomers and the potential micro-mechanisms of the actuation of the corresponding IPMCs have been extensively studied. The electrical-chemical-mechanical response of the IPMCs depends on the neutralizing cation, the nature of the solvent and the degree of saturation, the electrode morphology, and the chemical structure and

characteristics of the polymer backbone. Modeling of the response of IPMCs with water as the solvent has been presented in previous papers [2-4]. Also many studies and experiments have been performed to determine the nature of IPMC behavior in response to an applied electric potential. The main focus in the present work is the behavior of IPMCs with ethylene glycol (EG) as the solvent. Ethylene glycol or 1,2-Ethanediol ($C_2H_6O_2$) is an organic solvent consisting of polar molecules. Ethylene glycol can be used over a wide range of temperatures. It is commonly used as an antifreeze. Some of the properties of EG are listed in Table 1.

Table 1. Some of the properties of ethylene glycol [5]

Density at 20°C (g/cm^3)	Formula Weight (g/mol)	Dielectric constant at 20°C	Viscosity at 25°C (Centipoises, cP)	Melting point (°C)	Water Solubility at 17.5°C
1.1088	62.07	41.4	16.1	-13	10 g/100 ml

2. EXPERIMENTAL STUDY

2.1 Preparation of cation incorporated polymer-metal composite

IPMC sheets are provided by Shahinpoor and Kim [6]. Perfluorosulfonic acid type (Nafion, ion exchange capacity of 0.91 meq. g^{-1}) and carboxylic type (Flemion, ion exchange capacity of 1.44 meq. g^{-1}) cation exchange membranes are studied with ethylene glycol as the solvent.

To prepare the samples for tests, first, the as received IPMC sheet is cut by a blade into rectangular pieces of about 3 cm × 0.3 cm, using a special jig. To neutralize the sample with different cations, the following procedure is used. In all the cases, the beakers containing the samples are heated in a 60°C water bath to maintain a uniform heating process. At the end of the stated time, a fresh solution is used and the step is repeated. Therefore each of the following steps is performed three times.

1. Samples are soaked in 6 M nitric acid solution. The setup is then heated in the 60°C water bath for 30 minutes.
2. Samples are immersed in DI water (deionized) and the beaker containing them is heated in the 60°C water bath for 5 minutes to get rid of excess ions.
3. Samples are immersed in a 1 M solution of the desired cation. The setup is heated in the 60°C water bath for 5 minutes. Flemion-based samples are left in the cation solution for longer times, extending overnight. To neutralize the ionomer with sodium, a 1 M solution of NaCl, and to neutralize the ionomer with potassium, a 1 M solution of KCl is used.

To solvate the samples with ethylene glycol, they are first dried to remove any water within the sample and then they are soaked overnight in a beaker containing pure EG in the 60°C water bath. To dry the samples, they are put in a drying chamber at 100°C for one or two days. Samples are wrapped between two filter papers and put in a container and a vacuum pump is connected to the container to take out any air in the container that might carry water vapor.

2.2 Solvent volume uptake

Several studies have been done on the swelling properties and simple modeling of clustering in ionomer membranes [7-11]. Length and width of the samples are measured by a Mitutoyo TM microscope. The thickness is measured by the digital Mitutoyo meter with 0.001 mm resolution. The length, width and thickness of the samples are measured at 2, 3 and 4 positions along the sample, and the average value is used. Dividing the mass by the volume of the sample gives the density of the sample. The solvent volume uptake is given by

$$w = \frac{V_{solvent}}{V_{dry}} = \frac{1}{\rho_{solvent} V_{dry}} (m_{total} - m_{dry}), \qquad (1)$$

where $V_{solvent}$ is the volume of solvent absorbed, V_{dry} is the volume of the dry sample, $\rho_{solvent}$ is the density of solvent, m_{total} is the total weight of the sample in the solvated form, and m_{dry} is the dry sample weight.

2.3 Stiffness measurement

The mini-load frame device for stiffness measurement is shown in Figure 2. The sample is loaded between two grips and the initial length is measured by a caliper with 0.0254mm (0.001 inch) resolution. The stiffness of the material is estimated from loading and unloading cycles.

FIG. 2. Stiffness measurement device

The stiffness measurement of the fully solvated sample is normally done in the solvent to insure full solvation during the test.

2.4 Actuation setup

Actuation behavior is studied by gripping the sample end between two platinum electrodes and applying the desired electric potential. A Pulnix 6710 progressive scan digital camera that can achieve frame rates of up to 120 per second is used to record the actuation. A Nicolet MultiPro Transient Analyzer is used for data acquisition. A schematic of the actuation system setup is shown in Figure 3.
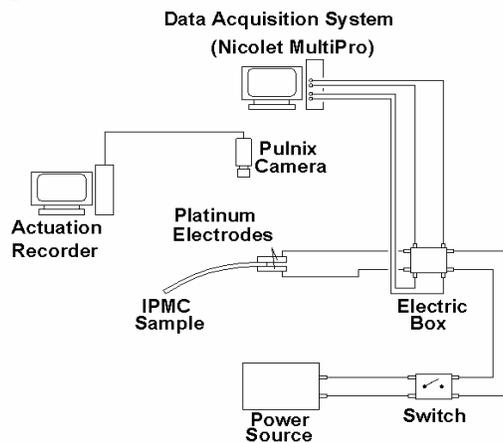

FIG. 3. Schematic of actuation system setup

The desired electric potential is applied by a Kepco PCX-MAT series power source connected to a switch. Current and voltage are recorded by a digitizer, reading the voltage outputs of an electric box. The electric box contains two outputs for the voltage corresponding to a potential across the sample and two outputs from the 10Ω-resistor potential that may be converted to current by dividing the voltage by the resistance, in post-processing. Outputs of the electric box are recorded by Nicolet board channels and displayed and recorded by Nicolet software. For our application, different data acquisition frequencies are used for different phases of the actuation. For the first 10 seconds of actuation, which is related to the application of the electric potential (sharp change in current and electrical potential), a frequency of 200 data points per second and for the rest of the actuation, a frequency of 50 data points per second is used through settings of the Nicolet board channels and software. A specific Visual C code for our application is also used to record the actuation video file with 120 frames per second, for the first 3 seconds and for the time that the current is shorted. For the rest of the actuation, a frame rate of 1 frame per second is used. After actuation, the sample's weight is measured and then the sample is put back in the solvent again. It takes some time for the sample to be solvated completely. Some tests are performed while the sample is gripped from the end and some when it is gripped from the middle. The excess solvent on the surface of sample is removed using tissue paper before actuation in air.

The accumulated charge is calculated from the area under the "Current-Time" curve, reduced by the contribution of the internal resistance of the sample.

The number of ion exchange sites may be calculated, by taking into account the dry mass of the sample.

$$N_{SO_3^-} = \frac{m_{dry}}{EW_{ion}}, \tag{2}$$

where EW_{ion} is the equivalent weight, evaluated for bare sample (no metal electrodes). It is given by equation (3).

$$EW_{ion} = \frac{EW_{H^+} - 1.008 + FW_{ion}}{SF}, \tag{3}$$

where EW_{H^+} is the equivalent weight of the polymer (either Nafion or Flemion) in protonated form (e.g. Nafion 117 in the H^+-form has the equivalent weight of 1,100g dry sample per mole SO_3^-) and FW_{ion} is the formula weight of the ion used. $FW_{ion} = 23$ g/mol for the Na^+ cation and 39 g/mol for the K^+. SF is the mass of dry ionomer backbone per unit mass of dry IPMC. For bare samples, SF=1. It is a scaling factor that measures the mass fraction of the added metal electrodes. The metal percentage calculations are based on 1,100 g/mol and 694.4 g/mol for the equivalent weight of bare Nafion and Flemion, respectively. The number of ion exchange sites gives the corresponding number of cations that can reside in the polymer clusters (in the cases we are dealing with, each sulfonate group attracts one alkali metal ion). This value can be used to define the total charge. Generally, the total transferred charge is a small percentage of the total number of cations within the IPMC sample in all the studied cases. The accumulated charge is calculated as a percentage of the charge moved to the cathode. The time-history of normalized curvature (active sample length divided by radius of curvature) is obtained through video analysis.

3. RESULTS AND DISCUSSION

3.1 Volume uptake and stiffness results

Table 2 lists the volume uptake of IPMC samples in hydrated form and when solvated with ethylene glycol. Values presented are the average values for several samples. As it appears, samples solvated with ethylene glycol have higher volume uptake, no matter what cation or polymer backbone is used.

Based on the method described earlier, the stiffness of the samples with ethylene glycol as solvent is obtained and listed in Table 3 for several indicated samples.

Table 2. Volume uptake of IPMC samples in X^+-form solvated with ethylene glycol and water

IPMC	Volume Uptake (%)	
	Ethylene Glycol	Water
Nafion-based IPMC in Na^+-form	110	48
Nafion-based IPMC in K^+-form	41	30
Flemion-based IPMC in K^+-form	148	35

Table 3. Stiffness and volume uptake in Nafion- & Flemion-based IPMCs; ethylene glycol

Base Polymer	Cation	Sample	Stiffness (MPa)		Volume Uptake (%)
			Load	Unload	
Nafion	K	SH5K-00	102.7	126.7	40.9
		SH5K-01	83.8	127.1	40.6
	Na	SH5Na-00	30.3	32.9	109.42
		SH5Na-01	28	35.8	111.3
Flemion	K	FL4K-00	17.2	24	169.3
		FL4K-01	17.9	24	127

A dimensionless parameter, a, is defined as the ratio of the solvent formula weight to the IPMC equivalent weight multiplied by the volume uptake;

$$a = \frac{M_{solvent}}{EW_{ion}} w , \tag{4}$$

where $M_{solvent}$ = 18 g/mol for water and 62 g/mol for ethylene glycol. This parameter is to account for the different polymer backbone, different cation forms, and the different solvents. Figure 4 shows the stiffness of different IPMC samples in Na^+ and K^+ forms. Nafion and Flemion polymer backbone IPMCs are used with two different solvents, water and ethylene glycol.
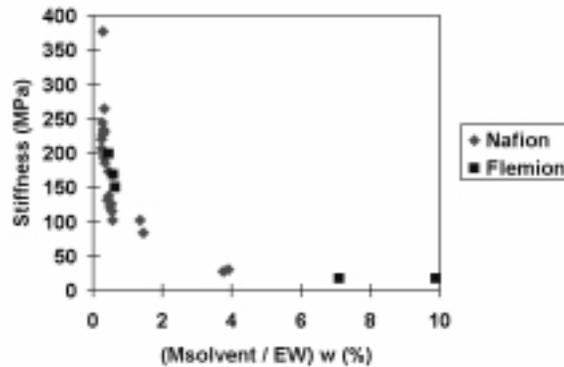
FIG. 4. Stiffness (MPa) – Nafion- and Flemion-based IPMC samples with water and ethylene glycol as solvents

The stiffness of IPMCs decreases as the volume uptake increases. This has been shown and a model has been presented in previous works for the case of water as the solvent [3].

3.2 Nafion-based IPMC in K^+-form

Actuation is performed in air, using a DC potential. In all cases the weight of the sample before and after actuation is measured. Samples actuated in open air show an increase in weight after actuation. Figures 5-A, 5-B and 5-C show the

actuation of a Nafion-based IPMC in K$^+$-form, when a DC potential of 1.5 volt is applied. The variation of curvature, current and accumulated charge over time are studied. Current is shown in milli-Ampere (mA).
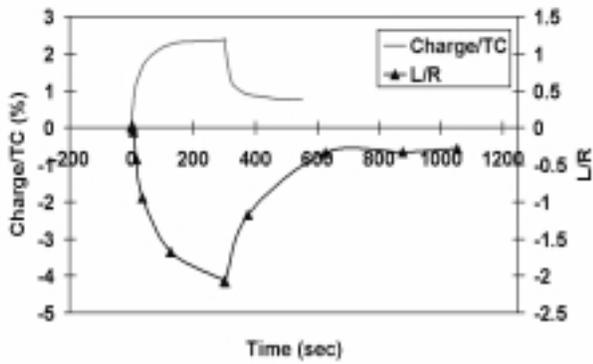

FIG. 5-A. Accumulated charge and normalized curvature versus time; Nafion-based IPMC in K$^+$-form (SH5K-00); ethylene glycol as solvent; 1.5 volt
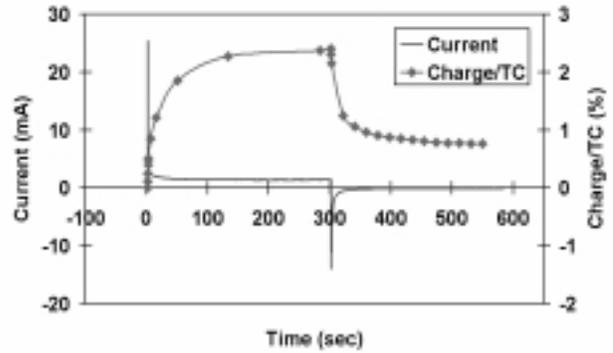
FIG. 5-B. Current and accumulated charge versus time; Nafion-based IPMC in K$^+$-form (SH5K-00); ethylene glycol as solvent; 1.5 volt
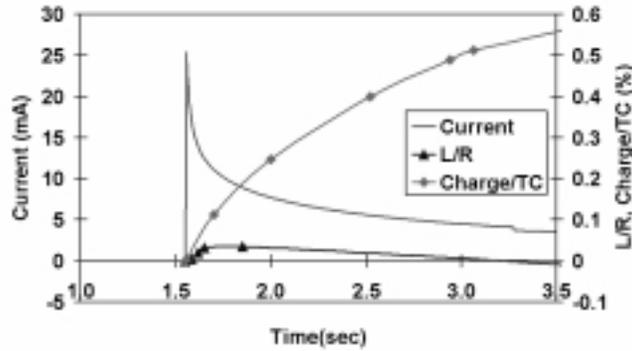
FIG. 5-C. Current, accumulated charge and normalized curvature versus time; (first 2 seconds of actuation); Nafion-based IPMC in K$^+$-form (SH5K-00); ethylene glycol as solvent; 1.5 volt

Actuation toward the anode in less than 0.3 seconds, with a peak magnitude of almost 3.6% for the normalized curvature, is observed. The accumulated charge at this time is about 0.162% of the total charge. Then the sample starts to relax back gradually and take the equilibrium position, after 302 seconds at which the total charge transferred reaches 2% of the total charge. Back relaxation toward the cathode is observed while the charge is still building up within the cathode boundary layer. When equilibrium is almost reached, the current is shorted. The sample then shows a small motion toward the cathode and then starts to bend back toward the anode, reaching a new equilibrium position after 1,054 seconds. At this time, the accumulated charge is almost 0.66% and the normalized curvature is offset about 28% from the original position.

3.3 Flemion-based IPMC in K$^+$-form

Actuation of a Flemion-based IPMC in K$^+$-form is quite different from that of the Nafion-based sample. Considerable bending toward the anode without back relaxation is observed. After the current is shorted, it takes a while for the sample to bend back toward the cathode and reach its new equilibrium position. In this case, a very slow return is observed. Figures 6-A to 6-C show the variation of the current, the normalized accumulated charge, and the normalized curvature over time.
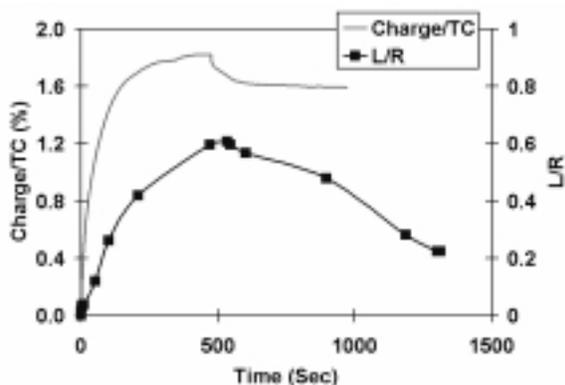
FIG. 6-A. Accumulated charge and normalized curvature versus time; Flemion-based IPMC in K$^+$-form (FL4K-00) with ethylene glycol as solvent; 1.5 volt
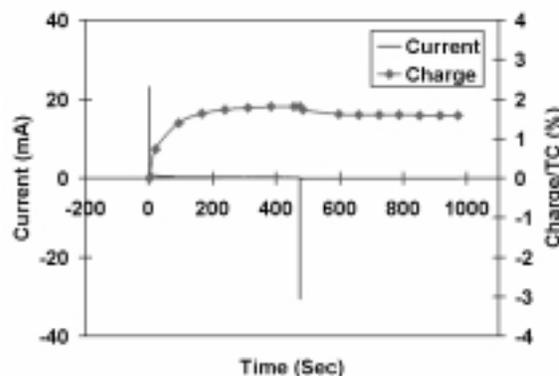

FIG. 6-B. Current and accumulated charge versus time; Flemion-based IPMC in K$^+$-form (FL4K-00) with ethylene glycol as solvent; 1.5 volt
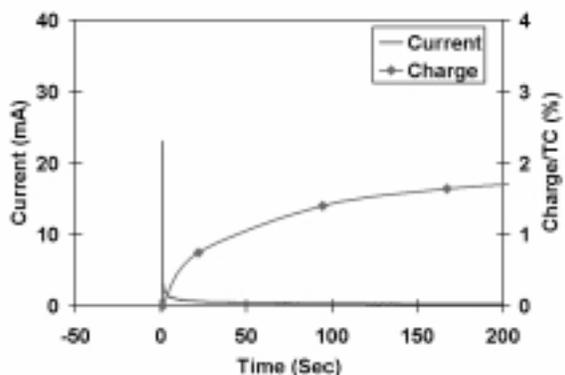

FIG. 6-C. Current and accumulated charge versus time over 200 seconds; Flemion-based IPMC in K$^+$-form (FL4K-00) with ethylene glycol as solvent; 1.5 volt

FIG. 6-D. Circle fitted to deformed sample; Flemion-based IPMC in K$^+$-form (FL4K-00) with ethylene glycol as solvent; 1.5 volt; end of bending toward anode before shorting (474 Seconds)

The sample starts to bend toward the anode as a potential of 1.5 volt is applied. The maximum normalized curvature observed is almost 60.7% and the corresponding accumulated charge is 1.823%. Then after 474 seconds the current is shorted and the sample starts to bend back after a short time. A circle may be fitted to the deformed sample. This shows a constant bending moment, as has been assumed in a previous paper [3]. Figure 6-D shows this observation at 474 seconds (before shorting).

Results of application of different potentials are shown in Figures 7-A and 7-B. Electric potentials of 1.5, 2, and 2.5 volts are considered and shown in these figures. Variation of the normalized curvature versus time is shown in Figure 7-A and the variation of the charge versus time is shown in Figure 7-B.
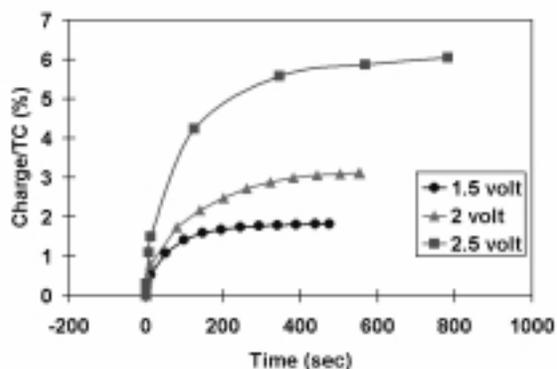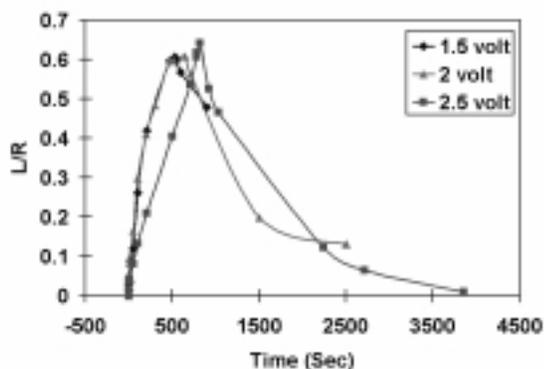
FIG. 7-A. Normalized curvature for 1.5, 2 and 2.5 volts; Flemion-based IPMC in K^+- form with ethylene glycol as solvent

FIG. 7-B. Accumulated charge for 1.5, 2 and 2.5 volts; Flemion-based IPMC in K^+- form with ethylene glycol as solvent

3.4 Nafion-based IPMC in Na^+-form

Nafion-based IPMC samples in Na^+-form did not show a *good* actuation with total volume uptake of almost 110%. One of the reasons might have been the increase in surface resistance due to the high volume uptake. Many small microscopic cracks appear on the gold surface resulting in poor surface electric conductance. The surface texture is shown in Figure 8 under this condition.
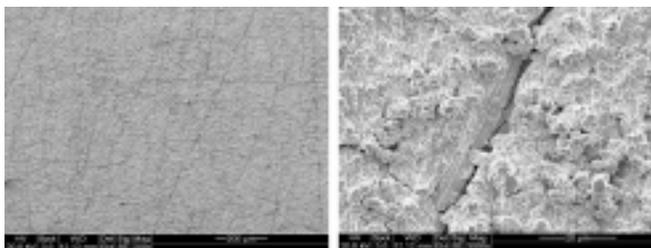
FIG. 8. Surface texture; left: 200 magnification; right: 3000 magnification; Nafion-based IPMC in Na^+- form with ethylene glycol as solvent

To overcome this kind of deficiency, samples are dried for almost half an hour in an oven at 100°C. The volume uptake reaches almost 55% and the surface resistance is measured to be 150 Ω. A potential of 2 volts is applied and the actuation behavior is shown in Figure 9-A and Figure 9-B.
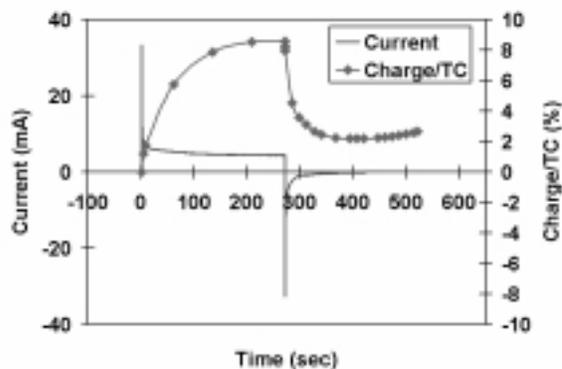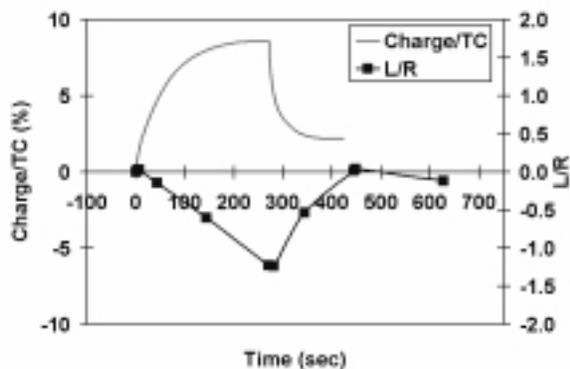

FIG. 9-A. Accumulated charge and normalized curvature versus time; Nafion-based IPMC in Na^+-form (SH5Na-00) with ethylene glycol as solvent; 2 volts; volume uptake 55% and surface resistance of 150 Ω

FIG. 9-B. Current and accumulated charge versus time; Nafion-based IPMC in Na^+-form (SH5Na-00) with ethylene glycol as solvent; 2 volts; volume uptake 55% and surface resistance of 150 Ω

For clarity the variation of the normalized curvature and accumulated charge for 100 seconds of actuation is shown in Figure 9-C.
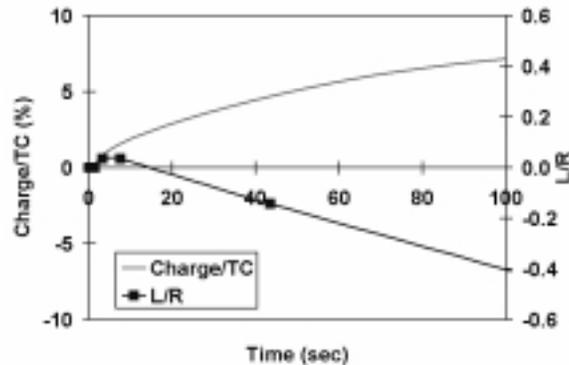

FIG. 9-C. Accumulated charge and normalized curvature versus time (100 seconds of actuation): Nafion-based IPMC in Na^+-form (SH5Na-00) with ethylene glycol as solvent; 2 volts; volume uptake 55% and surface resistance of 150 Ω

The sample starts to actuate toward the anode after the potential is applied and a maximum normalized curvature of 3.5% is reached. Then it remains in that position for 4.3 seconds and then slowly starts to relax back toward the cathode. After 270 seconds the current is shorted. The sample bends for another 1% toward the cathode in 11 seconds, and starts to bend back toward the anode. The sample again passes the original position and the normalized curvature reaches 4% and then, the sample bends back toward the cathode and it reaches an offset of about 12% from the original position.

The surface of the sample seems dry at the beginning of the test. However, following the test, the cathode face is wet and the anode face looks dry. Surface conductance is still poor. So, another case with lower volume uptake is also considered. The sample is put in a drying chamber under vacuum, at 100°C for 30 minutes; this time, a volume uptake of almost 33% is obtained. The surface resistance is 60 Ω, which although still high, is better than before. This time, a potential of 1.5 volt is applied and the actuation behavior is studied. Figures 10-A to 10-C show the variation of the current, the normalized charge and the normalized curvature versus time, for this case.

For this sample, a larger bending toward the anode is observed. The normalized curvature reaches almost 9%. Successive frames taken at various phases of actuation are shown in Figure 10-D.
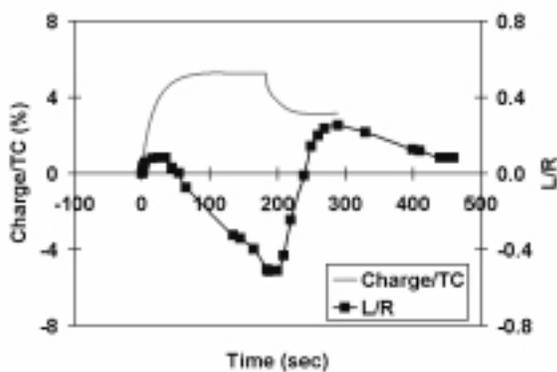

FIG. 10-A. Accumulated charge and normalized curvature versus time; Nafion-based IPMC in Na^+-form (SH5Na-00) with ethylene glycol as solvent; 1.5 volt; volume uptake 33% and surface resistance of 60 Ω
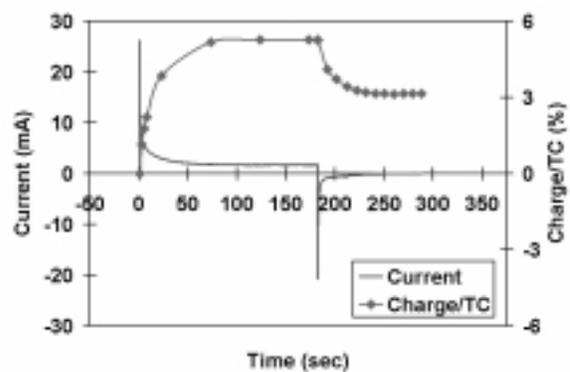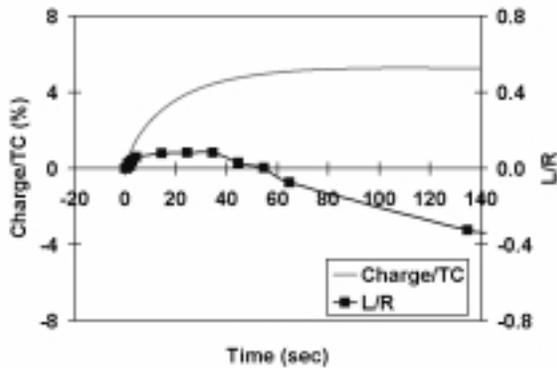

FIG. 10-B. Current and accumulated charge versus time; Nafion-based IPMC in Na^+-form (SH5Na-00) with ethylene glycol as solvent; 1.5 volt; volume uptake 33% and surface resistance of 60 Ω

FIG. 10-C. Accumulated charge and normalized curvature versus time (140 seconds); Nafion-based IPMC in Na$^+$-form (SH5Na-00) with ethylene glycol as solvent; 1.5 volt; volume uptake 33% and surface resistance of 60 Ω
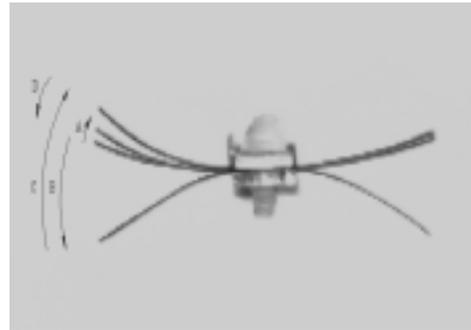

FIG. 10-D. Different phases of actuation; Nafion-based IPMC in Na$^+$-form (SH5Na-00) with ethylene glycol as solvent; 1.5 volt; volume uptake 33% and surface resistance of 60 Ω

4. SUMMARY AND COMPARISON

Actuation results for IPMC's with different ionomers and cations, are summarized. Variation of the accumulated and the normalized charge versus time for Nafion- and Flemion-based IPMCs in K$^+$-form and Nafion-based IPMCs in Na$^+$-form (under potential of 1.5 volts) are presented in Figure 11-A and 11-B. For Nafion-based IPMCs in Na$^+$-form, the case when the volume uptake is 33% is used, since, then, a *relatively good* surface conductivity is attained.

As can be seen from the Fig. 11-A, less cations are transferred to the cathode side in Flemion-based IPMCs. For more clarity, 3 seconds of actuation is presented in Figure 11-C. The Nafion-based IPMC sample in Na$^+$-form has a 33% volume uptake.

Relaxation while the potential is still applied may be observed in Nafion-based samples. Nafion-based IPMCs in K$^+$-form show a faster actuation than Nafion-based IPMCs in Na$^+$-form.
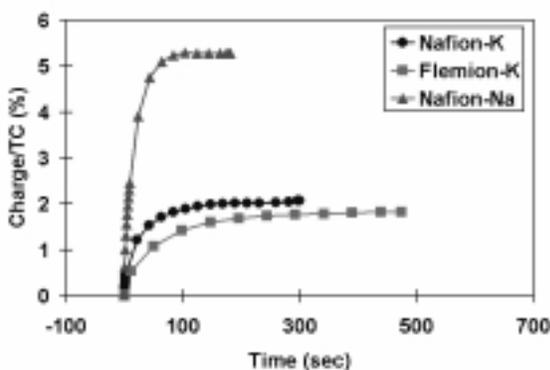

FIG. 11-A. Normalized accumulated charge versus time; Nafion- & Flemion-based samples in different cation forms; 1.5 volt
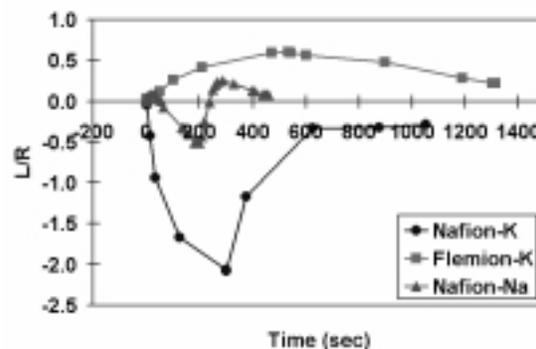

FIG. 11-B. Normalized curvature charge versus time; Nafion- & Flemion-based IPMC samples in different cation forms; 1.5 volt
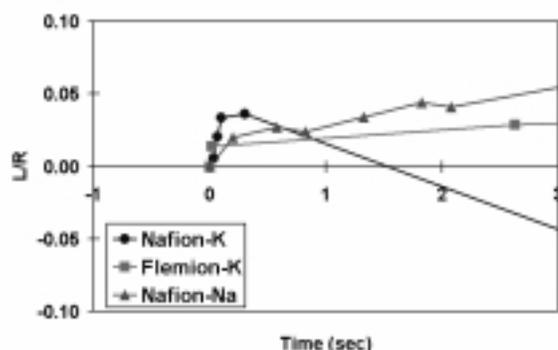
FIG. 11-C. Normalized curvature versus time (3 seconds of actuation); Nafion- & Flemion-based IPMC samples in different cation forms; 1.5 volt

As mentioned earlier, the advantages of IPMC actuation with solvents such as ethylene glycol is actuation at higher potentials and actuation in open air. As a comparison to results of using ethylene glycol as the solvent, the results of the actuation of an IPMC sample with water as the solvent are presented. Actuation with water as the solvent is *faster* and in most cases, Nafion-based IPMC relaxation starts in less than a second. A summary of the results is listed in Table 4.

Table 4. Summary and comparison of IPMC with water and ethylene glycol as solvents

Water	Ethylene glycol
Shorter actuation in air	*Longer* actuation in air
Better results when actuated in water	Better results when actuated in air
Restriction on applied potential	Higher potential may be applied
Relatively *faster* actuation	Relatively *Slower* actuation
Relatively *early* relaxation (In case of Nafion-based IPMC)	Relatively *late* relaxation (In case of Nafion-based IPMC)
Higher overall capacitance for IPMC	Lower overall capacitance for IPMC
Greater stiffness for IPMC	Smaller stiffness for IPMC
Lower Volume uptake	Higher Volume uptake

ACKNOWLEDGEMENT

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