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Effect of solvents on the chemical and physical properties of ionic polymer-metal composites

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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 backbone ionomer. IPMCs are electroactive materials with potential applications as actuators and sensors. Their electrical-chemical-mechanical response is dependent on the cations used, the nature and the amount of solvent uptake, the morphology of the electrodes, the composition of the backbone ionomer, the geometry and boundary conditions of the composite element, and the magnitude and spatial and time variation of the applied potential. With water as the solvent, the applied electric potential must be limited to less than 1.3 V 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. We present the results of a series of tests on both Nafion- and Flemion-based IPMCs with ethylene glycol, glycerol, and crown ethers as solvents. IPMCs with these solvents 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. In addition, their slow response in open air allows direct observation of the physical characteristics of the cathode and anode surfaces of a cantilever during actuations. This can provide additional clues for unraveling the underpinning micromechanisms of their actuation. Remarkably, solvents are found to have profound effects on the nature of the IPMCs' actuation. For example, Nafion-based IPMCs in Li^+ form show very small back relaxation when hydrated, but extensive back relaxation with all other solvents that we have considered. On the other hand, the same membrane in the K^+ form has extensive back relaxations when solvated with water, or ethylene glycol, or glycerol, but none with 18-Crown-6. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Ionic polymer-metal composites (IPMCs) are electroactive materials with potential applications as actuators and sensors.[1] An IPMC consists of a perfluorinated backbone ionomer [usually Nafion® or Flemion®; $(CF_2CF)_m(CF_2CF_2)_n$; see Fig. 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 ionomer.[2] When a thin strip of an IPMC membrane in the solvated state is subjected to a suddenly imposed and sustained constant electric potential (dc) of several volts (1–3 V), it bends towards the anode. For Nafion-based IPMCs that are neutralized with alkali metal ions, the strip then slowly relaxes back towards the cathode, while still under electric potential.[2–4] Experimental observations[5] for Flemion-based IPMCs show that the initial actuation towards the anode is followed by slower relaxation in the same (i.e., towards the anode) direction. Hence, unlike Nafion-based IPMCs, no back relaxation has been detected for Flemion-based IPMCs, in experiments conducted so far.

With water as the solvent, initial actuation response occurs in a fraction of a second. This fast response limits the physical inspection of the sample during its actuation. Besides, the applied electric potential must be limited to less than 1.3 V at room temperature, to avoid electrolysis. Moreover, water evaporates in open air, presenting additional

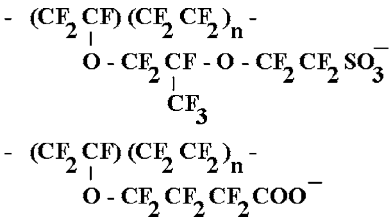

FIG. 1. Chemical structure of Nafion (top) and Flemion (bottom).

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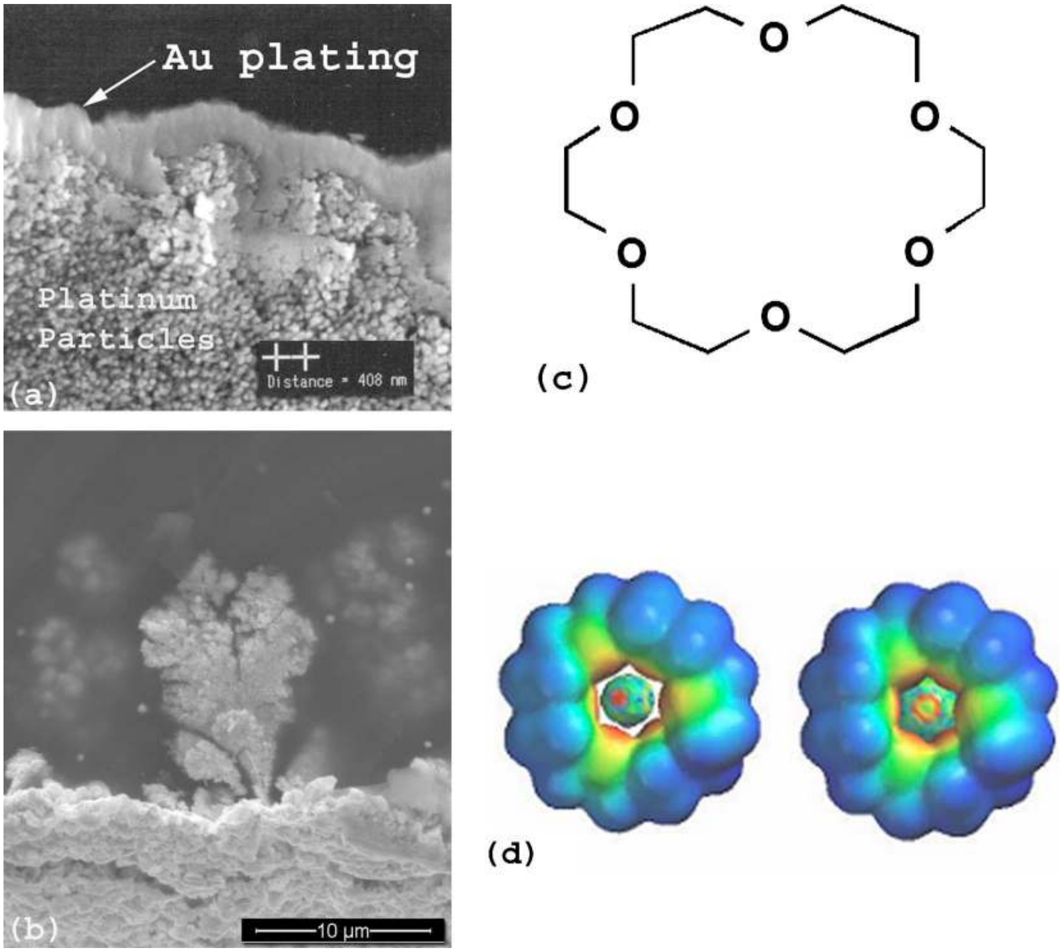

FIG. 2. (a) Cross section of a Pt/Au-plated Nafion-117 membrane at electrode region; distance between crosses is 408 nm. (b) Cross section of an Au-plated Flemion at electrode region; distance between crosses is 1 μm. (c) Chemical structure of 18-Crown-6 (each node is CH_2). (d) Na^+ ion (left) and K^+ ion (right) within macrocyclic 18-Crown-6 ligand.

problems. These and related factors limit a direct examination and the application of IPMCs with water as the solvent. Using other types of solvents that reduce the ion mobility to retard the actuation response is one way of circumventing some of these problems. The focus of the present work has been to characterize the properties and actuation response of Nafion- and Flemion-based IPMCs in different cation forms with ethylene glycol (EG), glycerol (G), and crown ethers as solvents. Those polar solvents have greater viscosity than water. The corresponding solvated IPMC can be subjected to a 2–3 V potential in open air without any adverse effects. In this manner, the actuation of the IPMCs can be carefully tuned and monitored.

II. MICROSTRUCTURE AND PROPERTIES

A. Composition and properties

IPMCs considered in the present work are made from Nafion and Flemion ionomers (Fig. 1) (see Heitner-Wirguin[6] for further information on bare Nafion). The Nafion-based composite, in the dry state, is about 180 μm thick and the Flemion-based one is about 160 μm thick (see Bennett and Leo[7] for further information on IPMC manufacturing). Samples are constituted of the following:

(1) backbone perfluorinated copolymer of polytetrafluoroetheylene with perfluorinated vinyl ether sulfonate pendants for Nafion-based IPMCs and perfluorinated propyl ether carboxylate pendants for Flemion-based IPMCs, forming interconnected nanoscale clusters;
(2) electrodes, which in Nafion-based IPMCs consist of 3–10 nm diameter platinum particles, distributed mainly within a 10–20 μm depth of both faces of the membrane, and usually covered with about 1 μm thick gold plating to improve surface conductivity; see Fig. 2(a). For Flemion-based IPMCs, the electrodes are gold, with a dendritic structure,[8] as shown in Fig. 2(b);
(3) neutralizing cations; and
(4) a solvent.

The ion exchange capacity (IEC) of an ionomer represents the amount of sulfonate (in Nafion) and carboxylate (in Flemion) groups in the material, measured in mole per unit dry polymer mass. Dry bare ionomer equivalent weight (EW) is defined as the gram dry ionomer per its mole anion. The ion exchange capacity and the equivalent weight of Nafion and Flemion are given in Table I.

For neutralizing counterions, we have used Li^+, Na^+, K^+, and Rb^+ (Rb^+ is used only for metal percentage determina-

TABLE I. Ion exchange capacity (IEC) of Nafion and Flemion, measured in millimole per gram (meq g^{-1}) and the corresponding equivalent weight (EW), measured in gram per mole (g/mol).

Membrane	IEC (meq g^{-1})	EW (g/mol)
Nafion	0.91	1100
Flemion	1.44	694.4

tion in this work). The properties of the bare ionomer, as well as those of the corresponding IPMC, change with the cation type for the same membrane and solvent.[9]

In addition to water, we have considered ethylene glycol, glycerol, and crown ethers as solvents. Ethylene glycol or 1,2-ethanediol ($C_2H_6O_2$) is an organic polar solvent that can be used over a wide range of temperatures. Glycerol or 1,2,3-propanetriol ($C_3H_8O_3$) is another polar solvent with high viscosity (1000 times the viscosity of water). Crown ethers are cyclic oligomers of ethylene glycol that serve as macrocyclic ligands to surround and transport cations [Fig. 2(c)].[10] Some of the properties of the solvents under consideration are listed in Table II.

The required crown ether depends on the size of the ion. For Nafion-based IPMCs we have used 12-Crown-4 (12CR4) when in Li^+ form, 15-Crown-5 (15CR5) when in K^+ form, and 18-Crown-6 when in Na^+ and K^+ forms. An 18-Crown-6 (18CR6) molecule has a cavity of 2.7 Å. This crown is suitable for potassium ions of 2.66 Å diameter. A schematic configuration of this crown with sodium and potassium ions is shown in Fig. 2(d).

B. Actuation

The electrical-chemical-mechanical response of the IPMCs depends on the neutralizing cation, the nature of the solvent and its degree of saturation, the electrode morphology, and the chemical structure and characteristics of the backbone ionomer. Experiments have been performed to study the IPMC's response to a suddenly applied step electric potential (dc). When a strip of solvated Nafion-based IPMC sample is subjected to an electric potential of several volts (1–3 V), it bends towards the anode. The speed and magnitude of this actuation towards the anode depend on the type of solvent and the neutralizing counterion. The actuation towards the anode is relatively slow with ethylene glycol as compared to that for water, and it is comparatively much slower with glycerol than with water or ethylene glycol[12] as solvents. For Nafion-based IPMCs with alkali metals as counterions and water, ethylene glycol, or glycerol as solvents, the actuation towards the anode is generally followed by a slow back relaxation towards the cathode. The back relaxation speed also depends on the type of solvent. The duration of the back relaxation phase can vary, from less than about 60 s (e.g., with most alkali metals and with water) to about 300 s (e.g., in K^+ form with ethylene glycol) and to about 2000 s (e.g., in Na^+ form with glycerol). The sample eventually reaches an equilibrium state (while the electric potential is still on), which is generally far from its initial equilibrium position. If the electric potential is removed as the two electrodes are shorted, the Nafion-based IPMC sample (under the above-mentioned conditions) displays a relatively fast bending deformation towards the cathode and then slowly relaxes back towards the anode, seldom attaining its initial state. Figure 3(a) illustrates these different phases of actuation for a Nafion-based IPMC in Na^+ form with glycerol as the solvent. For Flemion-based IPMCs with cations such as K^+ and fully solvated with ethylene glycol, *no* back relaxation has been observed. A fully solvated Flemion-based IPMC in K^+ form with ethylene glycol stimulated in air shows a relatively fast actuation towards the anode, followed by a relatively slow bending also towards the anode, until an equilibrium position is attained, while the electric potential is being maintained.

Experimental results show that an IPMC sample deforms into a circle under a constant voltage, as shown in Fig. 3(b) for a Nafion-based IPMC sample (before relaxation, while under a constant potential), suggesting that the induced bending moment is constant along the length of the sample.

With water, ethylene glycol, or glycerol as solvents, the actuation of the Nafion-based IPMCs has essentially the same qualitative character, namely, an initial bending towards the anode, followed by relaxation towards the cathode, the basic difference being the speed of actuation which directly correlates with solvent viscosity. With crown ethers, on the other hand, we have discovered that there may be a remarkable qualitative change in the actuation, depending on the cation and the crown ether. For example, Nafion-based IPMCs in Li^+ form show only a small relaxation towards the cathode with water, but with ethylene glycol, or glycerol, or 12-Crown-4 they show extensive back relaxation towards the cathode after an initial small actuation towards the anode. In the K^+ form, on the other hand, the Nafion-based IPMC shows extensive back relaxation for water, ethylene glycol, or glycerol, but no backward relaxation for the 18-Crown-6, for which the relaxation is then in the direction of the initial actuation, namely, towards the anode. Similarly, back relaxations are observed for Na^+ form IPMCs with water, ethylene glycol, glycerol, and 18-Crown-6, but not with 15-Crown-5 as solvent. In the case of 18-Crown-6, the initial bending

TABLE II. Some of the properties of ethylene glycol, glycerol, and crown ethers (see Ref. 11).

	EG	Glycerol	12-Grown-4	15-Crown-5	18-Crown-6
Density at 20 °C (g/cm^3)	1.088	1.26	1.09	1.1	1.12
Formula weight (g/mol)	62.07	92.1	176.21	220.26	264.32
Dielectric constant at 20 °C	41.4	46.53	…	…	…
Melting point (°C)	−13	18–20	16	…	42–45

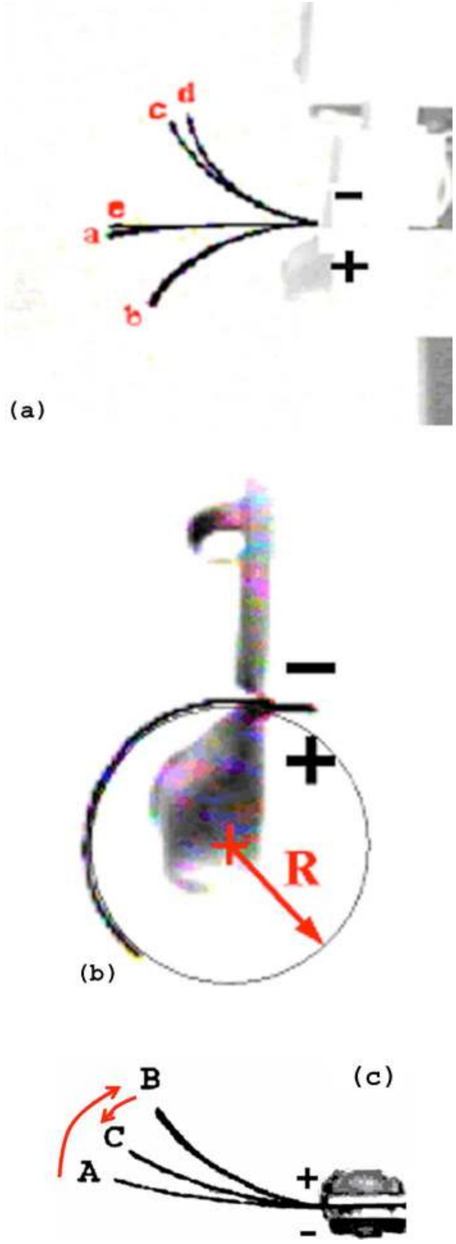

FIG. 3. (a) Different phases of a Nafion-based IPMC in Na^+ form with glycerol as solvent, under a 2 V electric potential (dc): from *a* to *b*, initial motion towards the anode; from *b* to *c*, relaxation towards the cathode; from *c* to *d*, motion upon shorting; and from *d* to *e*, back towards the anode to equilibrium state. (b) At the end of the initial actuation towards the anode (lasting about 12 min) the deformed sample of Nafion-based IPMC in Na^+ form with glycerol as solvent subjected to 2 V (dc), fits a perfect circle. (c) Different phases of a Flemion-based IPMC in K^+ form with ethylene glycol as solvent, under a 1.5 V electric potential (dc): from *A* to *B*, initial motion towards the anode; and from *B* to *C*, back towards the cathode to an equilibrium state.

towards the anode is followed by back relaxation towards the cathode, as occurs (at different speeds) when water, ethylene glycol, or glycerol is used for the solvent.

C. Some basic characteristic parameters

An important characteristic of an IPMC sample is its equivalent weight, defined as

$$\mathrm{EW}_{\mathrm{IPMC}} = \frac{\mathrm{EW}_{\mathrm{H}^+} - 1.008 + \mathrm{FW}_{\mathrm{ion}}}{\mathrm{SF}}, \tag{1}$$

where $\mathrm{EW}_{\mathrm{H}^+}$ is the equivalent weight of dry Nafion or Flemion in H^+ form which for Nafion 117 is 1100 g/mol (ion exchange capacity of $1/1100 = 0.91$ meq g^{-1}) and for Flemion is 694.4 g/mol. $\mathrm{FW}_{\mathrm{ion}}$ is the formula weight of the cation used, and SF denotes the scaling factor which accounts for the metal plating; SF is the ratio of the dry backbone polymer mass to the total mass of the IPMC sample. For the bare polymer (no metal plating), $\mathrm{SF}=1$.

Another characteristic of a solvated bare ionomer or IPMC sample is the solvent uptake,[13,14] w, defined as the ratio of the volume of the solvent absorbed by the bare or IPMC sample, and the sample volume in the dry state,

$$w = \frac{V_{\mathrm{solvent}}}{V_{\mathrm{dry}}} = \frac{1}{\rho_{\mathrm{solvent}} V_{\mathrm{dry}}} (m_{\mathrm{total}} - m_{\mathrm{dry}}), \tag{2}$$

where V_{solvent} is the volume of the absorbed solvent, V_{dry} is the volume of the dry sample, ρ_{solvent} is the mass density of the solvent, m_{total} is the total mass of the sample in the solvated form, and m_{dry} is the mass of the dry sample.

III. EXPERIMENTAL DETERMINATION OF PHYSICAL PROPERTIES

A. Nomenclature

Nafion-based IPMC samples are studied with different solvents. Flemion-based IPMCs are studied with ethylene glycol as the solvent. Samples are designated as follows: Nafion-based IPMC samples have a prefix "SH" and Flemion-based ones have a prefix "FL," with added "00," "01," and other notations to identify different samples in each set.

B. Preparation of cation-incorporated IPMCs

To prepare the samples for tests, first, the as-received IPMC sheet (either Nafion or Flemion) is cut into rectangular pieces of about 2.7×0.26 cm^2 using a special jig. The thickness of the Nafion-based composites, in the dry state, is about 180 μm, and that of Flemion-based IPMCs is about 160 μm. To neutralize the sample with different cations, the following procedure is used. In all cases, an isolated beaker containing the samples is immersed in a 60 °C water bath to maintain a uniform processing temperature. After a certain period, a fresh solution is used and the step is repeated for another cycle. In this manner, each of the following steps is performed three times before proceeding to the next step.

(1) Samples are soaked in a 6*M* nitric acid solution, and heated in the 60 °C water bath for 30 min.
(2) Samples are immersed in DI (de-ionized) water and the beaker containing them is heated in the 60 °C water bath for 5 min to remove any excess ions that may exist.
(3) Samples are immersed in a 1*M* solution of the desired alkali metal cation. To neutralize the ionomer with sodium, a 1*M* solution of NaCl is used, and to neutralize with potassium, a 1*M* solution of KCl is used. The setup

TABLE III. Dry and solvated length (*l*), width (*w*), thickness (*t*), and solvent uptake of Nafion- and Flemion-based IPMC samples in indicated cation forms.

				Dry form			Solvated form			
				l (cm)	*w* (cm)	*t* (cm)	*l* (cm)	*w* (cm)	*t* (cm)	Solvent uptake (%)
Nafion	EG	Li	12	2.661	0.2692	0.0174	4.0443	0.3470	0.309	270.9
			13	2.6753	0.2675	0.0175	4.0801	0.3511	0.306	276.3
		Na	00	2.6092	0.2655	0.0178	3.3170	0.3120	0.0238	109.42
			01	2.5746	0.2632	0.0180	3.3230	0.3129	0.0239	111.3
		K	00	2.6488	0.2435	0.0179	0.8620	0.2698	0.0206	40.9
			01	2.6715	0.2376	0.0181	2.8748	0.2661	0.0206	40.6
	G	Li	01	2.7417	0.2692	0.0174	3.4381	0.3115	0.0260	125.0
			02	2.6976	0.2650	0.0177	3.4431	0.3090	0.0260	124.8
		Na	03	2.7333	0.2783	0.0188	3.0818	0.3082	0.0232	66.7
			13	2.7301	0.2801	0.0188	3.0813	0.3104	0.0229	64.8
		K	00	2.6675	0.2677	0.0172	2.8052	0.2907	0.0196	35.9
	12CR4	Li	01	2.7660	0.2616	0.0173	3.1725	0.4313	0.0246	128.3
			12	2.7659	0.2540	0.0178	3.1720	0.3305	0.0249	131.4
			22	2.7569	0.2535	0.0180	3.1710	0.3283	0.0251	126.4
	15CRS	Na	03	2.7971	0.2864	0.0177	3.6338	0.3394	0.0299	181.6
		K	03	2.7382	0.2501	0.0178	3.0083	0.3227	0.0259	122.1
			13	2.7415	0.2441	0.0183	3.0206	0.3221	0.0274	123.7
			23	2.7487	0.2560	0.0182	3.0188	0.3222	0.275	122.8
	18CR6	Na	00	2.7978	0.2612	0.177	3.3501	0.3670	0.0267	182.3
			11	2.7847	0.2631	0.0177	3.3240	0.3655	0.0256	166.5
			02	2.7817	0.2616	0.0177	3.3240	0.3616	0.0264	170.8
		K	02	2.6612	0.2539	0.0180	3.1513	0.3528	0.0274	143.0
			03	2.6982	0.2509	0.0178	3.1435	0.3503	0.0277	147.0
Flemion	EG	K	00	2.5100	0.2495	0.0156	3.2120	0.3222	0.0219	131.2
			01	2.5190	0.2481	0.0161	3.2120	0.3240	0.0214	127.0

is kept at 60 °C for 5 min. Flemion-based samples are left in the cation solution for longer periods, extending overnight.

Dry forms of the samples are produced by placing the samples in a 100 °C drying chamber for 1 or 2 days. Samples are wrapped between two filter papers and placed in an air-tight container connected to a vacuum pump, to pump out any remaining water vapor.

To have fully solvated samples with ethylene glycol (or glycerol), dried samples are soaked for about 8 h, in a beaker containing pure ethylene glycol (or glycerol) and immersed in the 60 °C (70 °C for glycerol) water bath. In preparing various crown ether solutions, the following procedure is used. First, different amounts of crown ethers (2.5 g of 12-Crown-4 for 12CR4 solution, 4.2 g of 15-Crown-5 for 15CR5 solution, and 4.2 g of 18-Crown-6 for 18CR6 solution) are mixed separately with 150 ml of methanol. Then the solution of each crown and methanol is mixed with 10 ml of glycerol. After that, via a rotavapor, the methanol is removed from the solution. The dry Nafion-based IPMC samples in different ion forms are then immersed in the corresponding solution (12CR4 solution for Li^+ form, 15CR5 solution for Na^+ form, and 18CR6 solution for Na^+ and K^+ forms) and the isolated beaker is immersed in a 60 °C water bath for nearly 8 h to obtain fully solvated samples. In all cases, the samples are then left in the solution at ambient temperature, overnight.

C. Solvent uptake

The length and width of the samples are measured using a Mitutoyo TM microscope. The thickness is measured by a digital Mitutoyo micrometer with 0.001 mm resolution. The length, width, and thickness of the samples are measured at multiple positions along the sample, and the average values are used. Table III lists the solvent uptake, and the length, width, and thickness of IPMC samples in the dry and fully solvated states.

The solvent uptakes of fully solvated Nafion-based IPMCs in different cation forms are plotted versus the solvent formula weight in Fig. 4.

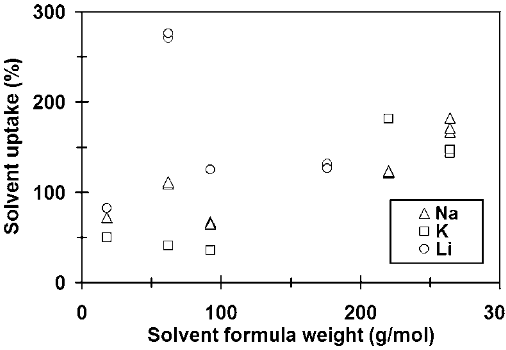

FIG. 4. Solvent uptake vs solvent formula weight (Table II) for Nafion-based IPMCs in different cation forms.

TABLE IV. Sweeling strain in the length, width, and thickness directions for Nafion- and Flemion-based IPMC samples in different cation forms, with ethylene glycol as solvent.

			Sweeling strain (%)		
Base polymer	Cation		*l*	*w*	*t*
Nafion	Na	00	27.13	17.51	33.71
		01	29.07	18.88	32.78
	K	00	8.05	10.80	15.08
		01	7.61	11.99	13.81
Flemion	K	00	27.97	29.12	40.38
		01	27.51	30.59	32.92

D. Strain induced as a result of solvation

A dry sample of a bare polymer or an IPMC in a solution absorbs solvent until the resulting pressure within its nanoscale clusters is balanced by the elastic stresses that are consequently developed within its backbone polymer membrane.[2] Table IV lists typical values of swelling strain along the length, width, and thickness of Nafion- and Flemion-based IPMCs with ethylene glycol as solvent. As can be seen, the thickness strain is greater than the strain along the length and width of the samples, possibly because the metal plating hinders expansion in the length and width directions.

E. Stiffness measurement

A miniload frame is used for stiffness measurements. A schematic of the device is shown in Fig. 5(a). The sample (either bare ionomer or IPMC) is loaded between two grips and the initial gauge length is measured by a caliper with 0.0254 mm (0.001 in.) resolution. To measure the stiffness of a fully solvated sample, the sample in the setup is immersed in a container filled with the solvent to insure continued solvation. Then the sample is subjected to several loading and unloading cycles. A National Instrument data acquisition (NI-DAQ) board and LABVIEW 4 code are used to record the loading and unloading data read from the strain gauges attached to the miniload frame. A VISUAL BASIC code, specific for this application, is also used to obtain the stress-strain curves from the strain-gauge data.

To obtain the stiffness of a strip of bare polymer or an IPMC sample at various solvent uptakes, a series of tests is performed, starting with a fully solvated sample, and proceeding as follows.

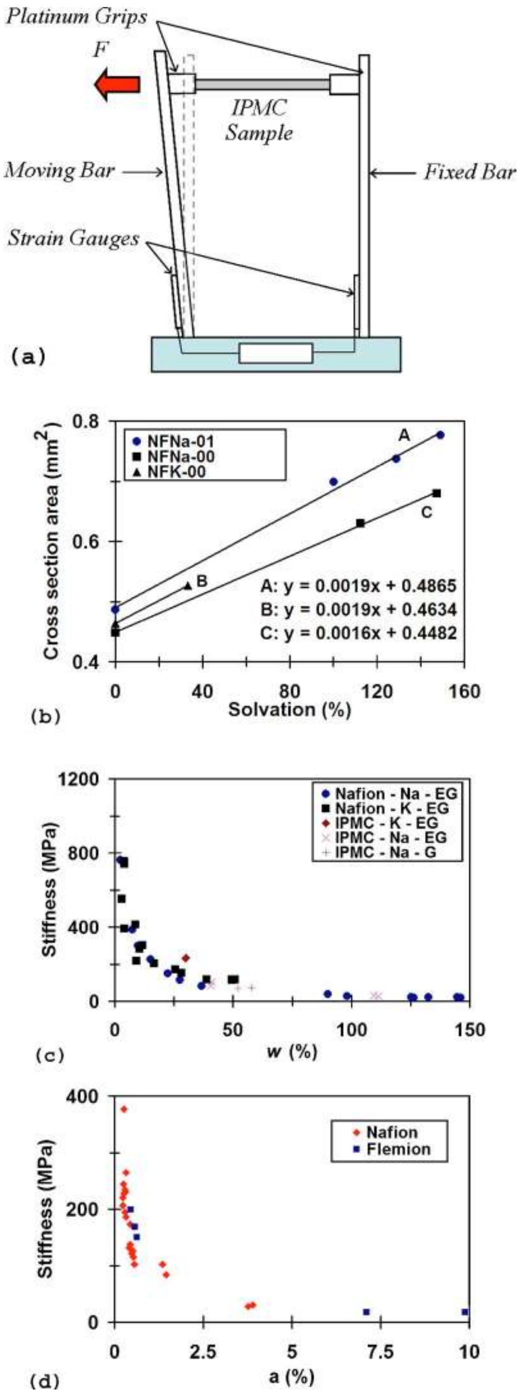

FIG. 5. (a) Schematic of the miniload frame. (b) Typical variation of the bare Nafion cross section with solvent uptake. (c) Stiffness (MPa) of bare Nafion and Nafion-based IPMCs with ethylene glycol and glycerol as solvents. (d) Stiffness (MPa) of Nafion- and Flemion-based IPMCs with water and ethylene glycol as solvents.

1. Sample is loaded between the grips and the initial length is measured.
2. Except for the fully solvated case, the sample is subjected to several loading and unloading cycles in open air.
3. Sample is removed from the miniload frame and its weight is measured. The degree of solvation can be reduced by heating the sample in a drying chamber. The sample is heated for a certain time period (e.g., 20 min, for bare Nafion samples with ethylene glycol) in a drying chamber at 100 °C. The width and thickness (to obtain the cross-sectional area) of the sample are measured.

Steps (1)–(3) are repeated several times. The cross-sectional area changes linearly with solvation, as can be seen from Fig. 5(b), which represents typical experimental results for bare Nafion. The cross-sectional area is used to calculate the corresponding stress and to obtain the stress-strain curve

TABLE V. Stiffness (MPa) and solvent uptake w (%) of Nafion- and Flemion-based IPMCs with ethylene glycol (EG) and glycerol (G) as solvents.

Base polymer				Stiffness (MPa) Load	Stiffness (MPa) Unload	w (%)
Nafion	EG	Na	00	30.3	32.9	109.4
			01	28.0	35.8	111.3
		K	00	102.7	126.7	40.9
			01	83.8	127.1	40.6
	G	Na	03	67.6	75.0	66.7
			13	73.5	82.7	64.8
Flemion	EG	K	00	17.2	24.0	131.2
			01	17.9	24.0	127.0

as a function of solvent uptake. From the weight of the sample the solvent uptake is calculated using Eq. (2).

Experimental stiffness data for fully solvated Nafion- and Flemion-based IPMC samples in different cation forms with ethylene glycol and glycerol as solvents are given in the Table V.

Figure 5(c) shows the stiffness of bare Nafion and Nafion-based IPMC samples in Na^+ and K^+ forms at various solvent uptakes with ethylene glycol and glycerol as solvents. These and similar data for bare Flemion and its IPMC can be unified into a single chart if the solvent uptake is normalized as follows:

$$a = \frac{M_{\text{solvent}}}{\text{EW}_{\text{IPMC}}} w, \tag{3}$$

where M_{solvent} is the solvent formula weight (see Table II), and EW_{IPMC} is the IPMC equivalent weight. The parameter a takes into account the effect of backbone polymer, cation form, and the solvent. Figure 5(d) shows the stiffness of Nafion- and Flemion-based IPMCs in Na^+ and K^+ forms with water and ethylene glycol as solvents, for different values of a.

The stiffness of IPMCs decreases as the solvent uptake increases. This has been shown and modeled in a previous work for the case of water as the solvent.[4,5] As stated earlier, stiffness measurement of a fully solvated sample is normally performed while the sample is immersed in the solvent to ensure sufficient solvation of each sample. Thus, it may be assumed that the weight of the sample remains constant during the stiffness measurement of the fully solvated samples. The stiffness measurement for samples treated with crown ethers as solvent has been problematic, because preparation of the crown ether solutions is a delicate task and the amount of solution that can be prepared is insufficient to have the sample immersed in the solution during the stiffness measurement. (Crown ethers are normally packaged in 5 g lots. This yields approximately 10 ml of crown ether solution.) For this reason, so far, only the actuation response of IPMCs with crown ethers has been studied.

TABLE VI. Dry weight of bare polymer, metal electrode, and metal percentage (MP) (%) of Nafion- and Flemion-based IPMC samples.

Base polymer			Polymer (g)	Metal (g)	MP (%)
Nafion	Na	00	0.022 28	0.0127	35.5
		01	0.020 86	0.0137	38.9
	K	00	0.019 79	0.0130	39.1
		01	0.020 71	0.0112	34.5
Flemion	K	00	0.018 18	0.0085	31.1
		01	0.017 32	0.0093	33.9

F. Determination of metal ion percentage

The metal weight fraction is the ratio of the electrode-metal weight to the total dry IPMC sample weight. To determine the metal weight fraction, the sample's dry weight is measured in Na^+, K^+, and Rb^+ cation forms. The procedure to prepare cation-incorporated IPMCs was discussed earlier. The following procedure is used to obtain the metal weight fraction data presented in Table VI.

(1) Samples are changed to Na^+ form, then dried in a vacuum chamber at 100 °C, for 2 days, and the dry weights of the samples are measured.
(2) Step (1) is repeated to obtain the dry weights of the same samples in K^+ and Rb^+ forms.
(3) The dry weight of the samples in different cation forms is plotted versus formula weight of the cation.

Figure 6(a) shows the dry weight versus the ion formula weight for Nafion-based samples, and Fig. 6(b) shows the results for Flemion-based samples, both with ethylene glycol as solvent. The metal weight fraction of the samples can be obtained by calculating the intercept and slope of the straight lines that are fitted to the data.

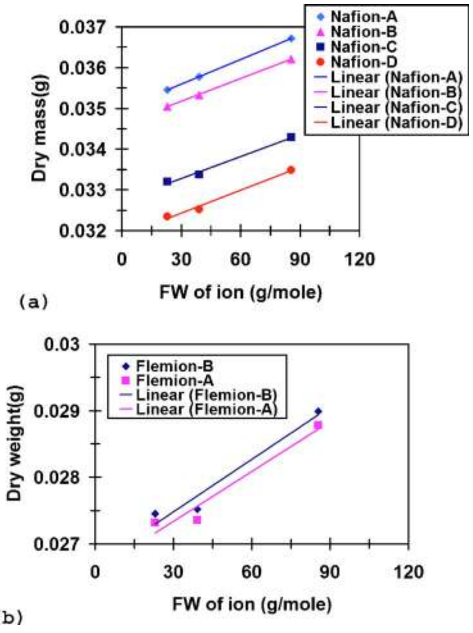

FIG. 6. (a) Variation of dry weight for different cations—Nafion-based IPMC. Samples SH5K and SH5Na. (b) Variation of dry weight with different cations—Flemion-based IPMC. Sample FL4K.

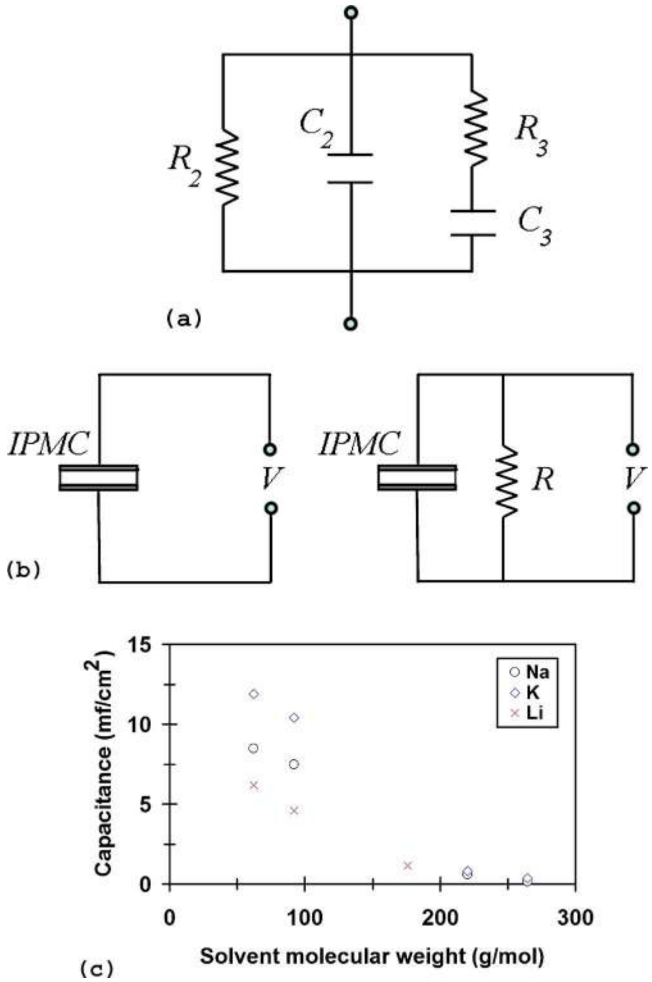

FIG. 7. (a) IPMC equivalent electric-circuit model (see Ref. 16). (b) Determination of capacitance by (left) self-discharge test and (right) external resistance discharge. (c) Effective capacitance of IPMCs in different cation forms with different solvents vs the formula weight of the solvent.

Since unsolvated IPMCs consist of polymer, metal electrodes, and the associated cations, we have, for samples in cation A and B forms,

$$m_{\mathrm{IPMC}}^{A} = m_{\mathrm{bare}} + m_{\mathrm{metal}} + m_{\mathrm{ion}}^{A}, \tag{4}$$

$$m_{\mathrm{IPMC}}^{B} = m_{\mathrm{bare}} + m_{\mathrm{metal}} + m_{\mathrm{ion}}^{B}, \tag{5}$$

where m_{bare}, m_{metal}, m_{ion}, and m_{IPMC} are the weights of bare polymer, electrodes, the cation used, and the overall IPMC, respectively. A and B refer to different cation forms. The slope n of a line connecting the corresponding points [see Figs. 6(a) and 6(b)] is given by

$$n = \frac{m_{\mathrm{IPMC}}^{A} - m_{\mathrm{IPMC}}^{B}}{\mathrm{FW}_{\mathrm{ion}}^{A} - \mathrm{FW}_{\mathrm{ion}}^{B}}. \tag{6}$$

This slope also defines the moles of ion within the sample. The weight of the polymer (consisting of bare polymer and cations) is given by

$$m_{\mathrm{polymer}} = n(\mathrm{EW}_{\mathrm{H}^{+}} - 1.008). \tag{7}$$

The weight of the dry (unsolvated) backbone polymer per unit weight of dry IPMC, SF, is defined as

$$\mathrm{SF} = \frac{m_{\mathrm{polymer}}}{m_{\mathrm{IPMC}}}, \tag{8}$$

and, therefore, we have

$$m_{\mathrm{metal}} = (1 - \mathrm{SF}) m_{\mathrm{IPMC}}. \tag{9}$$

From Figs. 6(a) and 6(b) and Eqs. (5)–(9), the metal percentage of each sample may be calculated. Typical results for Nafion- and Flemion-based IPMCs with ethylene glycol as solvent are given in Table VI. The metal percentage calculations are based on 1100 and 694.4 g/mol equivalent weights of bare Nafion and Flemion backbone polymers, respectively.

G. Effective capacitance measurement

In electrochemical systems, of interest are the processes and factors that affect the transport of charge within the electrolyte. IPMCs are made of an electric conductor (electrode) and an ionic conductor (an electrolyte). Charge is transported through the ionically conductive polymer (i.e., Nafion or Flemion). The behavior of the electrode-electrolyte interface in electrochemical systems is analogous to that of a capacitor.[15] A model of two resistors and two capacitors [Fig. 7(a)] is used for the determination of the overall capacitance of the IPMC samples.[16] The overall capacitance is calculated from the self-discharge [Fig. 7(b)] and the external discharge response of the samples.[16]

To measure the effective capacitance of a fully solvated IPMC in an alkali metal form, a square-shaped sample of about 0.5 cm^2 surface area is completely covered by two platinum electrodes, and the setup is placed in a container filled with the solvent. In the case of crown ether as the solvent, samples are sandwiched between two electrode plates and the measurements are performed in open air. A potential of 1 V is applied across the sample faces through platinum electrodes connected to a power source and the sample is left in this condition for 1 or 2 min. After being completely charged, the electric potential is removed and the variation of voltage versus time, during the discharge phase, is recorded. To observe the external resistance discharge, a 1000 Ω resistor is added in parallel with the sample [see Fig. 7(b)]. The calculated capacitance in different cation forms is listed in Table VII.

Figure 7(c) shows the effective capacitance of IPMCs in different cation forms with various solvents versus the formula weight of the corresponding solvent. A decrease in effective capacitance is observed with higher molecular weight solvents. This may be in part due to the size of the cations and the corresponding solvation shell. These values of effective capacitance are used to determine the effective permittivity. Effective permittivity controls the length of the anode and the cathode boundary layers created under the external electric field.

TABLE VII. Effective capacitance of Nafion- and Flemion-based IPMCs with different solvents.

Base polymer			Capacitane (mF/cm^2)
Nafion	Ethylene glycol	Na	8.5
		K	11.9
	Glycerol	Na	7.50
	12-Crown-4	Li	1.15
	15-Crown-5	Na	0.58
	18-Crown-6	Na	0.15
		K	0.36
Flemion	Ethylene glycol	K	3.2

IV. ELECTROMECHANICAL RESPONSE

In a typical IPMC open-air actuation test, first, the excess surface solvent is removed using tissue paper, and one end of the sample is gripped between two platinum electrodes. Then, the sample is actuated by a suddenly imposed and sustained constant electric potential (dc). When the sample comes to rest, the electric potential is removed and the two electrodes are shorted. After actuation, the sample's weight is measured and then the sample is put back in the solvent until completely solvated.

A Pulnix 6710 progressive scan digital camera that can achieve frame rates of up to 120/s 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 Fig. 8(a).

The desired electric potential is applied by a Kepco PCX-MAT series power source, connected through a switch. The current and voltage are recorded by a digitizer, reading the voltage outputs of the readout box. The readout box contains two outputs for the voltage corresponding to the potential across the sample thickness [see Fig. 8(b)] and two outputs from the 10 Ω resistor potential that may be converted to current by dividing the voltage by the resistance. Outputs of the electric box are recorded and displayed through Nicolet board channels, using the associated software. For our application, different data acquisition frequencies are used for different phases of the actuation. For the first 10 s of actuation, 200 data points/s are recorded, and for the rest of the actuation, only 50 data points/s are captured. A VISUAL C code, specific for our application, is also used to video record the actuation at 120 frames/s during fast actuation phases and at 1 frame/s for the rest of the test.

The accumulated charge is calculated from the area under the current-time curve, reduced by the contribution of the internal resistance of the sample [see Fig. 8(c)]. The number of ion exchange sites (sulfonate groups for Nafion- and carboxylate groups for Flemion-based IPMCs) gives the corresponding total number of cations that is incorporated in the polymer (for monovalant cations, each sulfonate group attracts one metal ion). This value is used as the total (positive or negative) charge (TC) in the sample. The normalized transferred charge is defined as the ratio of the transferred charge to this total charge. Generally, the total transferred charge is a small percentage of the TC within an IPMC sample. The time history of the normalized curvature (active sample length divided by radius of curvature) is obtained through video analysis. It should be mentioned that, in most cases, the accumulated charge does not return to zero immediately after the IPMC sample is shorted. Redistribution of cations back to the original state may take a rather long time, which means that the IPMC remains partially charged (like a battery) for a while after shorting. Eventually, however, the charges are lost and all the clusters return to their original individually neutral state; the IPMC sample always is electrically neutral.

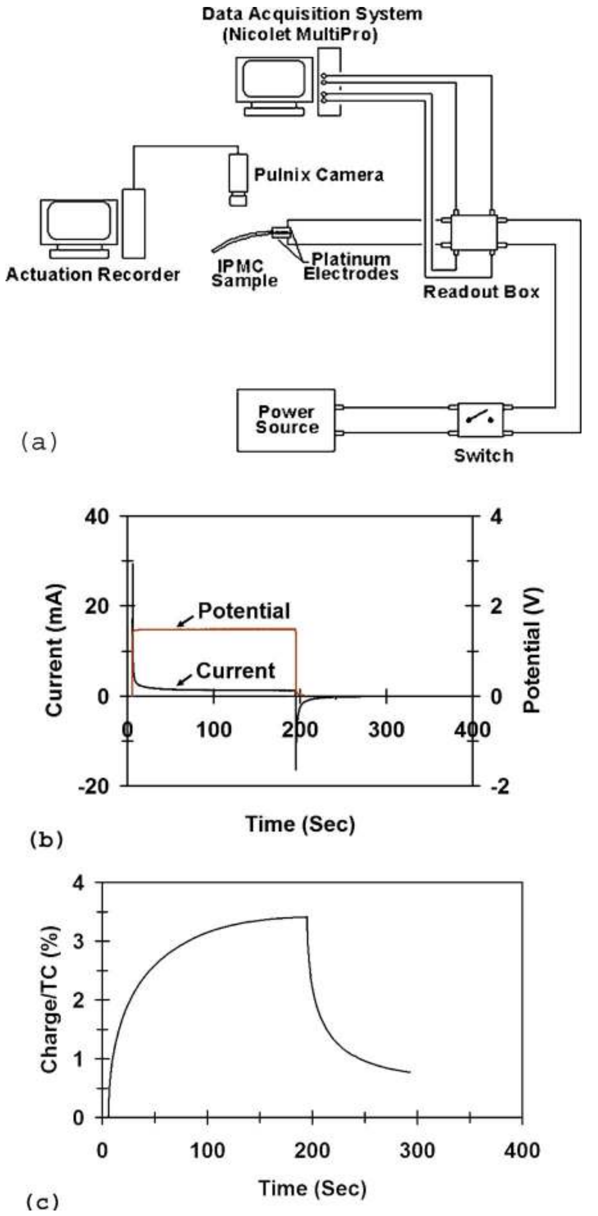

FIG. 8. (a) Schematic of actuation system setup. (b) Typical variation of the voltage and current across the sample faces, when a constant electric potential (dc) (1.5 V) is suddenly imposed and sustained for 300.0 s and then shorted; Nafion-based IPMC in K$^+$ form with ethylene glycol as solvent. (c) Typical calculated time history of normalized transferred charge (cations) corresponding to data in (b); Nafion-based IPMC in K$^+$ form with ethylene glycol as solvent.

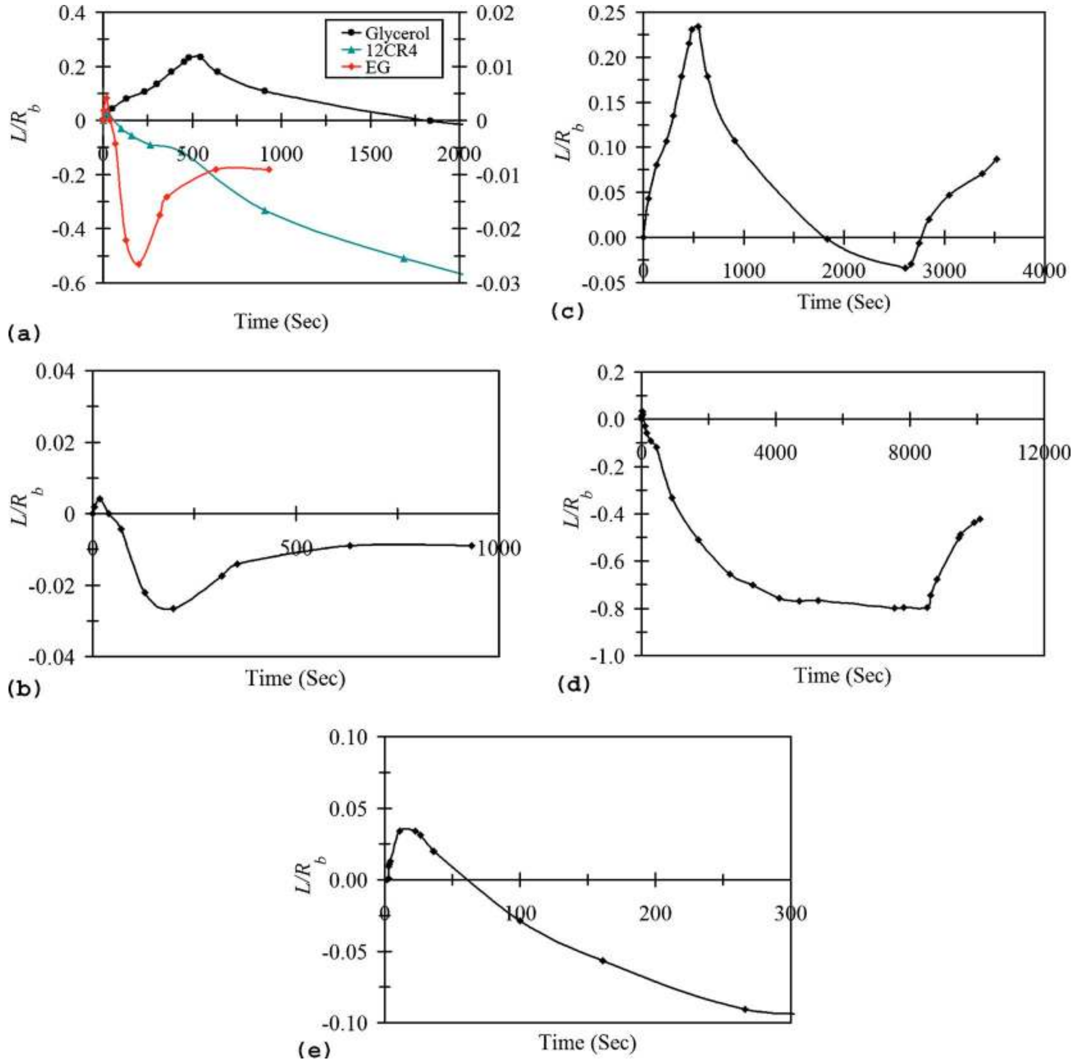

FIG. 9. (a) Comparison of different actuation phases of Nafion-based IPMC in Li$^+$ form with ethylene glycol (diamonds; shorted at 199.2 s), glycerol (circles; shorted at 2611.1 s), and 12-Crown-4 (triangles; shorted at 8514.0 s) as solvents under 2 V dc electric potential. The ethylene glycol data are presented on the secondary (right hand) axis. Only the initial 2000 s of actuation are presented. (b) Normalized curvature vs time for Nafion-based IPMC in Li$^+$ form under 2 V electric potential with ethylene glycol as solvent; shorted at 199.2 s. (c) Normalized curvature vs time for Nafion-based IPMC in Li$^+$ form under 2 V electric potential with glycerol as solvent; shorted at 2611.1 s. (d) Variation of normalized curvature vs time for a Nafion-based IPMC in Li$^+$ form with 12-Crown-4 as solvent under a 2 V dc electric potential; shorted at 8514.0 s. (e) The first 300 s of actuation of Nafion-based IPMC in Li$^+$ form with 12-Crown-4 as solvent under a 2 V electric potential.

A. Actuation of IPMCs in Li$^+$ form with various solvents

Nafion-based IPMC samples in Li$^+$ form and with various solvents show an initial actuation towards the anode when they are stimulated by a dc electric potential in open air. The magnitude, speed, and duration of this actuation depend on the type of solvent used. Following the initial actuation, the sample relaxes in the reverse direction (towards the cathode), eventually reaching an equilibrium state. When the potential is removed, the sample actuates back towards the anode, but seldom attains its initial configuration. Figure 9(a) shows the first 2000 s of this actuation for indicated solvents. In what follows, each of the cases displayed in this figure is further detailed.

With ethylene glycol, the initial actuation towards the anode occurs in about 18 s, when the sample is stimulated by a 2 V dc electric potential in open air. The subsequent back relaxation towards the cathode is much slower. After 199.2 s, the potential is removed. The sample then actuates back towards the anode, but does not attain its initial state. Figure 9(b) displays these actuation phases.

With glycerol, the sample may be subjected to relatively large potentials without electrolysis (the electrolysis potential for glycerol is around 10 V) and without any significant solvent losses in open air. Because of glycerol's high viscosity (0.934 Pa at 25 °C, almost 1000 times that of water), the actuation is quite slow, allowing direct examination of the sample's surface impression, as it goes through different actuation phases. As shown in Fig. 9(c), under a 2 V dc potential, the actuation towards the anode occurs in almost 550 s. Then the sample bends back towards the cathode, slowly reaching an equilibrium state at around 2600 s. The sample is shorted at 2611.1 s. During this back relaxation, solvent droplets are seen to appear on the cathode surface, as the cathode boundary layer is contracting. In this same period, the measured current flow reveals continued accumulation of cations in the cathode boundary layer. According to a model proposed by Nemat-Nasser,[4] the actuation of IPMCs is a result of coupled electrochemomechanical interaction that occurs within the clusters in relatively thin boundary layers in the anode and cathode regions. Under an applied potential, the anode boundary layer is depleted of its cations, while additional cations continue to accumulate within the clusters in the cathode region, carrying with them their solvation molecules. The resulting cation-anion interaction produces electrostatic forces that tend to expand the clusters in the anode boundary layer and contract those in the cathode boundary layer, dominating the hydraulic (due to added solvent) and osmotic (due to higher ion concentration) effects during the back relaxation towards the cathode, and squeezing solvent molecules out of the clusters in the cathode boundary layer onto the IPMC's surface. Indeed, when the potential is removed, the sample actuates back towards the anode and the droplets disappear into the IPMC sample.

The response with 12-Crown-4 as the solvent, under 2 V dc, is similar but much slower, as shown in Fig. 9(d); see also Fig. 9(e) which shows the first 300 s of actuation. The back relaxation in this case lasts almost 8500 s (2 h and 20 min). The sample is shorted at 8514.0 s. Upon shorting the two electrode faces, the sample gradually actuates back towards the anode, but does not reach an equilibrium state even after 1500 s.

B. Actuation of IPMCs in Na^+ form with various solvents

Nafion-based IPMC samples in Na^+ form and with various solvents also show an initial actuation towards the anode followed by reverse relaxation, when they are stimulated by a dc electric potential in open air. When the potential is removed, the samples actuate back towards the anode, but do not attain their initial states. Figure 10(a) shows actuation for Nafion-based IPMC samples in Na^+ form with indicated solvents, when stimulated by a 2 V dc potential.

The sample that was used to test the actuation of Nafion-based IPMC in Na^+ form with ethylene glycol as solvent showed very poor surface conductivity, basically due to the presence of many microcracks within the electrodes [see Fig. 10(b)], also leading to rather poor actuation. To remedy this, the sample was dried for about half an hour at 100 °C, reducing the volume of the uptake solvent to 55%. The surface resistance was then measured to be 150 Ω. The resulting actuation under a 2 V potential together with the accumulated charge are shown in Figs. 10(c) and 10(d). The sample actuates towards the anode, but once the normalized curvature reaches 3.5%, it remains in that position for 4.3 s before slowly relaxing back towards the cathode. After 281.1 s, the current is shorted, but the sample continues to bend an additional 1% towards the cathode in 11 s before starting to bend back towards the anode. Eventually the sample reaches an equilibrium state, about 12% from the original position. Both surfaces of the sample appeared dry at the beginning of the test, but during the actuation, the cathode face appeared wet while the anode face continued to look dry.

Figure 10(e) shows the variation of the curvature as a function of time for a fully solvated (as summarized in Table III) Nafion-based IPMC in Na^+ form with glycerol as solvent, under a 2 V dc electric potential; various phases of this actuation are displayed in Fig. 3(a). The actuation is extensive but very slow due to glycerol's high viscosity, with the L/R exceeding 1. Then the sample begins to relax back towards the cathode [from b to c, in Fig. 3(a)] for about 2000 s. This occurs several seconds after the sample ceases its initial bending towards the anode. Upon shorting at 2610.0 s of actuation, the sample actuates further towards the cathode [Fig. 3(a), from c to d] and then it begins to bend back towards the anode to reach an equilibrium position [Fig. 3(a), position e]. The duration of this phase is relatively long (hours needed for this phase).

With 15-Crown-5, a Nafion-based IPMC sample in Na^+ form bends towards the anode when it is stimulated by a dc electric potential in open air, and its reverse relaxation towards the cathode is very small, as compared with the other sodium-based cases discussed above. The motion towards the anode happens in almost 630 s [Fig. 10(f)], and the slight back relaxation towards the cathode to an equilibrium state takes an additional 1000 s. When the potential is removed at 1837.0 s of actuation, the sample actuates further towards the cathode and then bends back towards the anode. The sample does not attain the initial configuration.

We have also studied the IPMC actuation with Na^+ and 18-Crown-6 as solvent. Unlike K^+ that is perfectly encapsulated by this crown ether, the Na^+ cation is not a perfect match for 18-Crown-6. This fact appears to have a profound effect on the actuation of the corresponding IPMC. In this case, stimulation by a 3 V dc potential in open airproduces bending towards the anode that lasts about 700 s, but, unlike with the 15-Crown-5, the sample now shows extensive back relaxation towards the cathode, while the potential is still on, as shown in Fig. 10(g) [compare with Fig. 10(f)] which shows the variation of the normalized tip displacement (tip displacement divided by gauge length of the sample) as a function of time.

C. Actuation of IPMCs in K^+ form with various solvents

We have also examined the response of cantilevered Nafion-based and Flemion-based IPMCs in K^+ form with several solvents. The Nafion-based samples show initial actuation towards the anode. Remarkably, and unlike with ethylene glycol and glycerol, with 18-Crown-6, a Nafion-based IPMC in K^+ form does not have any back relaxation towards the cathode, as shown in Figs. 11(a) and 11(b).

With 18-Crown-6 as the solvent and under a 2.5 V dc potential in open air, the sample bends continuously towards the anode for almost 669 s. There is no back relaxation towards the cathode, in this case. After the voltage is removed after 669 s by shorting the two electrode faces, the sample actuates gradually back towards the anode. Figure 11(b)

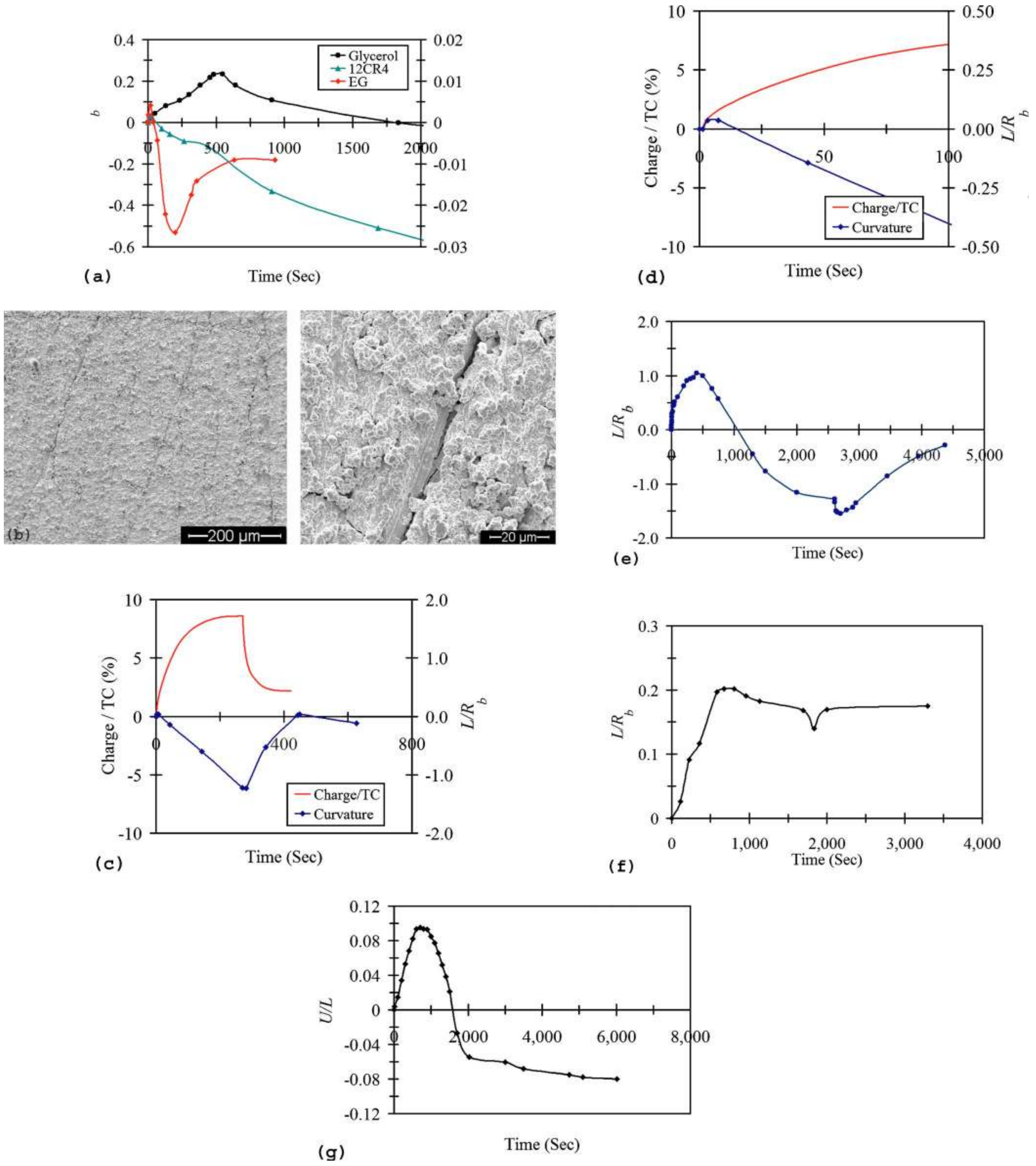

FIG. 10. (a) Comparison of different actuation phases of Nafion-based IPMC in Na$^+$ form with ethylene glycol (diamonds; shorted at 281.1 s), glycerol (circles; shorted at 2610.0 s), and 15-Crown-5 (triangles; shorted at 1837.0 s) as solvents under dc electric potential. (b) Surface texture of Nafion-based IPMC in Na$^+$ form with ethylene glycol as solvent; left: 200 magnification; right: 3000 magnification. (c) Accumulated charge and normalized curvature vs time; Nafion-based IPMC in Na$^+$ form with ethylene glycol as solvent; 2 V; the solvent volume uptake is 55% and surface resistance is 150 Ω; shorted at 281.1 s. (d) Accumulated charge and normalized curvature vs time (100 s of actuation): Nafion-based IPMC in Na$^+$ form with ethylene glycol as solvent; 2 V; the solvent volume uptake is 55% and surface resistance is 150 Ω; shorted at 281.1 s. (e) Different actuation phases of Nafion-based IPMC in Na$^+$ form with glycerol as solvent under a 2 V electric potential; see also Fig. 3 *A*; shorted at 2610.0 s. (f) Different actuation phases of Nafion-based IPMC in Na$^+$ form with 15-Crown-5 as solvent under a 2 V dc electric potential; shorted at 1837.0 s. (g) Different actuation phases of Nafion-based IPMC in Na$^+$ form with 18-Crown-6 as solvent under a 3 V electric potential.

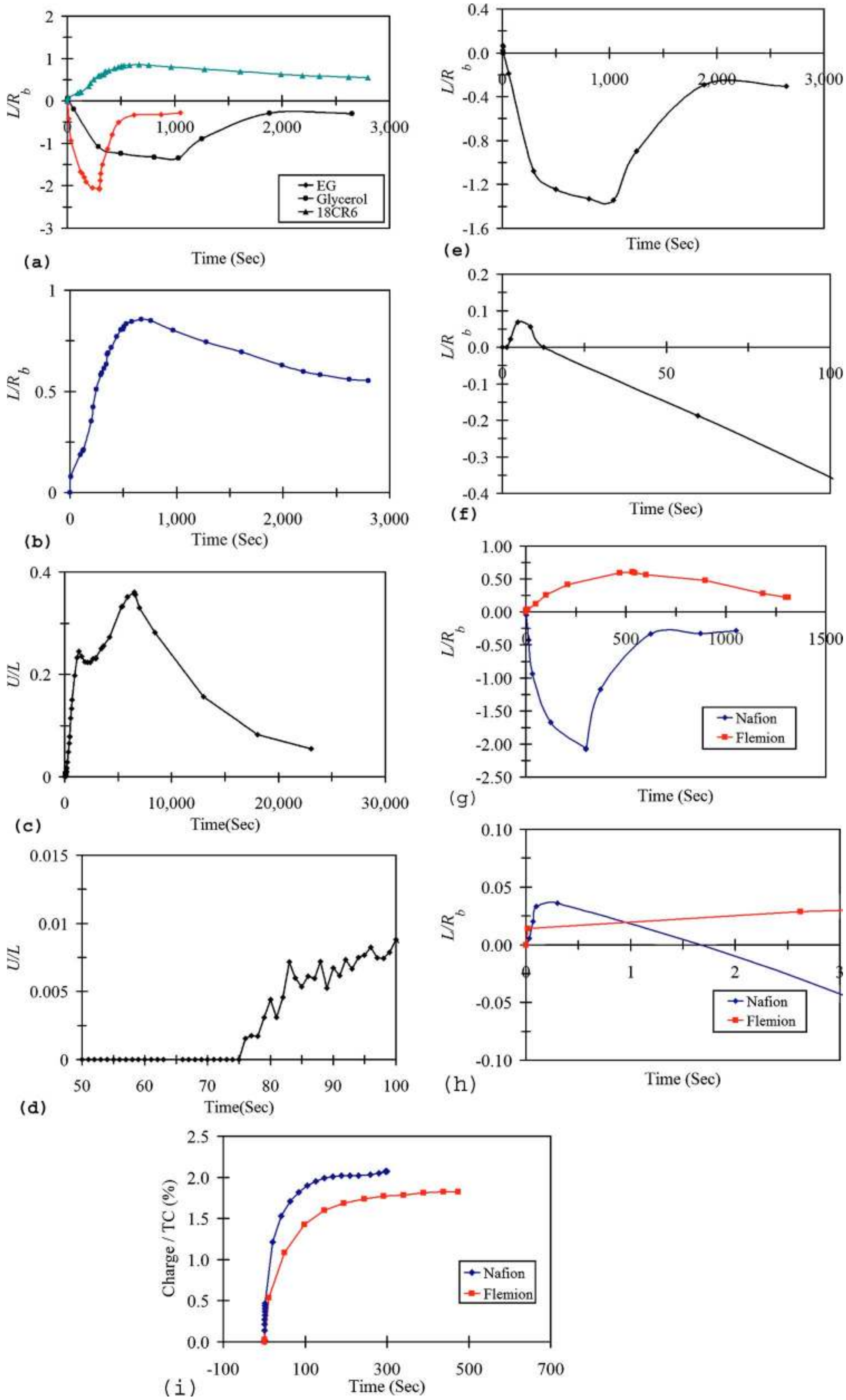

FIG. 11. (a) Comparison of different actuation phases of Nafion-based IPMC in K$^+$ form with ethylene glycol (diamonds; shorted at 300.0 s), glycerol (circles; shorted at 1036.1 s), and 18-Crown-6 (triangles; shorted at 669.0 s) as solvents under 2.5 V dc electric potential. (b) Different actuation phases of Nafion-based IPMC in K$^+$ form with 18-Crown-6 as solvent under a 2.5 V electric potential; shorted at 669.0 s. (c) Different actuation phases of Nafion-based IPMC in K$^+$ form with 15-Crown-5 as solvent under a 2.5 V electric potential. (d) 50 s of actuation of Nafion-based IPMC in K$^+$ form with 15-Crown-5 as solvent under a 2.5 V electric potential applied at $t=0$ s. (e) Different actuation phases of Nafion-based IPMC in K$^+$ form with glycerol as solvent under a 2 V electric potential; shorted at 1036.1 s. (f) 100 s of actuation of Nafion-based IPMC in K$^+$ form with glycerol as solvent under a 2 V electric potential applied at $t=2.4$ s. (g) Normalized curvature vs time; Nafion- and Flemion-based IPMC samples in K$^+$ form with ethylene glycol as solvent under 1.5 V electric potential; the Nafion-based IPMC is shorted at 300.0 s and the Flemion-based one is shorted at 534.5 s. (h) Normalized curvature vs time (3 s of actuation); Nafion- and Flemion-based IPMC samples in K$^+$ form under 1.5 V electric potential. (i) Normalized transferred charge vs time; Nafion- and Flemion-based samples in K$^+$ form under 1.5 V electric potential; the Nafion-based IPMC is shorted at 300.0 s and the Flemion-based one is shorted at 534.5 s.

shows the variation of the normalized curvature over time. This response is similar to the response of Nafion-based IPMCs in tetrabutylammonium (TBA$^+$) form with water as solvent.[5] This response may be attributed to the size of the cations in the TBA$^+$ case and the size of the solvated cations in the 18-Crown-6 case.

With 15-Crown-5 as the solvent, a cantilevered Nafion-based IPMC sample in K$^+$ form under a 2.5 V dc potential in open air shows no motion during the first 75 s. Then, the sample bends towards the anode until the normalized tip (tip displacement divided by gauge length of the sample) is almost 0.24. At this point, the sample returns back towards the cathode, in a period of almost 1000 s, and then it reverses its motion, bending towards the anode to reach an equilibrium state after almost 4000 s. Upon removing the electric potential, when the two faces of the sample are shorted, the sample gradually actuates back towards the cathode. The time variation of the normalized tip displacement is shown in Figs. 11(c) and 11(d).

A Nafion-based IPMC sample in K^+ form and with glycerol bends towards the anode when it is stimulated by a dc electric potential in open air. This actuation towards the anode happens in almost 7 s. Then the sample bends back towards the cathode slowly, reaching an equilibrium state at around 1035 s. When the potential is removed at 1036.1 s of actuation, the sample actuates back towards the anode, but does not attain its initial configuration. Figures 11(e) and 11(f) show the variation of normalized curvature over time for this sample actuated in open air under 2 V dc potential.

We have also studied the actuation of Flemion-based IPMCs in K^+ form with ethylene glycol as solvent. The material shows a different behavior, having no back relaxation. Under a 1.5 V dc electric potential, the sample bends relatively rapidly towards the anode and then begins to relax in the same direction (i.e., towards the anode), until an equilibrium state is gradually attained after about 500 s. After the current is shorted at 534.5 s, the sample starts to bend back first relatively quickly and then gradually, towards the cathode, eventually reaching an equilibrium state after a rather long time. Actuation results for fully solvated Nafion- and Flemion-based IPMCs in K^+ form with ethylene glycol as the solvent are compared in Figs. 11(g) and 11(h), where Fig. 11(h) shows the first 3 s response of the samples.

This difference in the relaxation response of the Flemion- and Nafion-based IPMCs can be attributed to the difference in the acidity (pK_a) of the sulfonates (e.g., about −5.1 for trifluoromethane-sulfonic acid, CF_3SO_3H, triflate) in the Nafion, as compared with that of carboxylates (e.g., about 0.23 for trifluoroacetic acid, CF_3COOH) in the Flemion backbone polymers used in the corresponding IPMCs. The strong acidity of the sulfonate groups within the clusters in the cathode boundary layer provides the necessary driving force to restructure the distribution of the cations there, gradually changing the net electrostatic forces within the clusters. We note that the electrostatic forces are basically dominant in the actuation of the IPMC, particularly when the effective dielectric constant of the cluster decreases due to the increase in its ion density. Thus, this reorganization of the cations eventually produces a net contracting effect on the clusters in the cathode side, leading to the expulsion of solvents to the cathode-side surface of the Nafion-based IPMC but not the Flemion-based one, as was observed in our experiments. Also, the electrode structure and composition of the two IPMCs are quite different, affecting the corresponding response.

Variations of the normalized transferred charge versus time for Nafion- and Flemion-based IPMCs in K^+ form, under 1.5 V potential, are presented in Fig. 11(i). The total transferred charge in each case is a small fraction of the total positive charge within the ionomer. The charge accumulation for the two cases is quite similar, with an initial fast buildup, followed by a continuous slower accumulation, although the resulting actuations are quite dissimilar.

V. SUMMARY, CONCLUSIONS, AND COMMENTS ON MODELING

The electrical-chemical-mechanical response of IPMCs depends on the neutralizing cation, the nature and the degree of saturation of the solvent, the electrode morphology, and the chemical structure and characteristics of the backbone polymer. Based on our experimental results, the following are noteworthy overall conclusions.

(1) IPMCs with heavy and viscous solvents have slower actuations, higher solvent uptakes, smaller stiffness at fully solvated states, and lower overall capacitance, compared to the same IPMCs but with water as their solvent.

(2) IPMCs with ethylene glycol, glycerol, and crown ether solutions as solvents can be subjected to relatively high electric potentials without electrolysis. They can be actuated in open air for rather long time periods, and at low temperatures.

(3) Nafion-based IPMCs with alkali metals have relatively late and long back relaxation with ethylene glycol and glycerol; this is true even for Nafion-based IPMCs in Li^+ form that show minimal back relaxation when hydrated.

(4) Nafion-based IPMCs with alkali metals show remarkably different responses with crown ethers as their solvents. In Li^+ form with 12-Crown-4, the response under a dc potential involves extensive but slow back relaxation, whereas in Na^+ form with 15-Crown-5 it shows very little back relaxation, and, most interestingly, in K^+ form with 18-Crown-6, there is no back relaxation at all; i.e., the initial motion towards the anode is followed by a slow relaxation in the same direction. This last response, which is similar to that of an IPMC in TB^+ form, may be attributed to the size of the cations in the 18-Crown-6 solvent. On the other hand, the sample in Na^+ form with 18-Crown-6 shows extensive back relaxation, whereas in K^+ form with 15-Crown-5, there is some back relaxation towards the cathode but this is then reversed and the sample relaxes back towards the anode while still under the dc potential.

(5) IPMCs that are solvated with glycerol have slower actuation than with ethylene glycol which also shows slower response than that with water. This is directly related to the viscosity of the solvent, because the ion mobility decreases as the solvent viscosity increases; note that, at room temperature, glycerol is about 1000 times more viscous than water. The fact that ions are less mobile with, e.g., glycerol is also supported by the measured corresponding slow charge accumulation that is two orders of magnitude slower than that with water. In addition, the solvent itself flows more slowly when it is more viscous, which slows down the solvent's flow in and out of the clusters in response to the osmotic and other cluster pressures. The combined slow ion and solvent transport in high-viscosity solvents results in the overall slower actuation that has been observed experimentally. The slow actuation associated with high-viscosity solvents also has enabled us to observe various phases of the IPMC response under an electric potential.

(6) Experimental results for various solvents clearly show

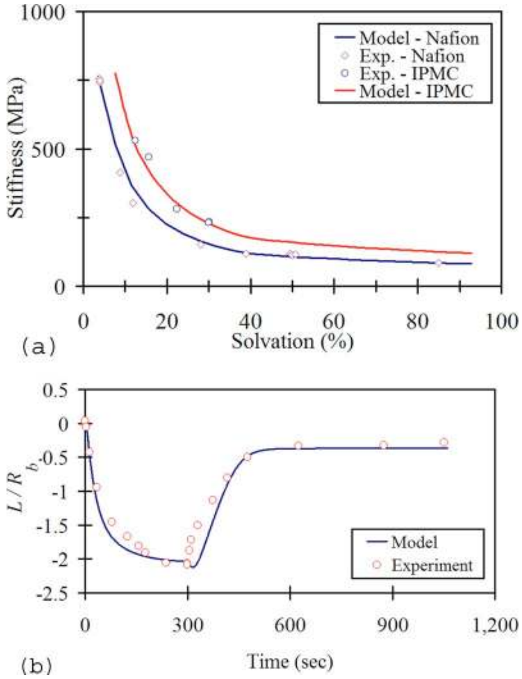

FIG. 12. (a) Uniaxial stiffness (Young's modulus) of bare Nafion 117 (data points and the solid curve, model) in K^+ form vs volume fraction of ethylene glycol. (b) Variation of normalized curvature over time for a 26 mm strip of cantilevered Nafion-based IPMC in K^+ form with ethylene glycol, subjected to 1.5 V dc electric potential; shorted at 300.0 s. The heavy solid curve is the model and the open circles are the experimental results.

TABLE VIII. Physical parameters for Nafion-based IPMC in K^+ form with ethylene glycol (EG).

Sample dimensions (mm)	$28.620 \times 2.698 \times 0.206$
Density of bare ionomer in K^+ form (g/cm^3)	$\rho_B = 2.07$
Fixed anion concentration (mol/m^3)	1185
Initial volume fraction of solvent uptake	$w_0 = 0.38$
Bare ionomer stiffness at indicated solvent uptake (%)	$Y_B = 748$ MPa, $w = 0.04$ $Y_B = 148$ MPa, $w = 0.32$
Percentage of metal	0.63
Electrode-metal density (g/cm^3)	$\rho_M = 20$
Electrode-metal stiffness (MPa)	75 000
Applied electric potential (V)	$\phi_0 = 1.5$
Effective dielectric constant	$\bar{\kappa} = 2.20 \times 10^{-2}$
Effective capacitance (mF/cm^2)	11.9
Bulk dielectric constant of EG	41
FW of EG (g/mol)	62.1
Density of EG (g/cm^3)	1.11
FW of cation (K^+) (g/mol)	39
Cation-anion valence	$\upsilon = 2$
Coordination number (CN)	4
Dynamic solvation number (SN)	0

> that, even though the ions do carry solvent molecules through their solvation shell, it is *not* the resulting hydraulic pressure in the clusters within the cathode boundary layer that causes the actuation. Instead, it is the coupled electrochemomechanical effects that produce the actuation and actually squeeze out solvents from the cathode clusters onto the IPMC's free surface on the cathode side. Indeed, while the cathode side is being compressed during the back relaxation, charges, as measured, continue to accumulate there.

Both the initial relatively fast motion and the subsequent relaxation of Nafion-based IPMCs have been modeled based on micromechanisms proposed by Nemat-Nasser.[4] The details are given in a separate paper (Nemat-Nasser and Zamani)[17] together with comparison with the experimental results that are presented in this paper. Remarkably, the model correctly produces both qualitatively and, with reasonable accuracy, quantitatively all observed, rather peculiar, behaviors of this class of soft actuators. In what follows, we briefly discuss the basic steps and give results for a strip of cantilevered Nafion-based IPMC in K^+ form with ethylene glycol as the solvent.

We start with the modeling of the stiffness of both the bare ionomer and the corresponding IPMC in each cation form at various degrees of solvation, identifying and evaluating several micro-structural parameters that are also necessary for the modeling of the corresponding actuation. The basic idea for modeling the stiffness is that, when a dry sample of a bare ionomer or an IPMC is placed in a solvent bath, it absorbs solvent until the internal cluster pressure, produced by the osmotic and electrostatic forces within the cluster, is balanced by the elastic stresses that are consequently developed within its (solvated) backbone membrane. The backbone membrane is modeled as a neo-Hookian (Atkin and Fox[18]) material whose moduli depend on the volume fraction of the solvent uptake. From this observation the stiffness of the membrane can be calculated as a function of the solvent uptake for various cations (see Nemat-Nasser and Zamani[17]). The electrostatic forces within the clusters are assumed to be produced by the interaction among conjugate pairs of sulfonate and its neutralizing cation that form a pseudodipole. The dipoles within each cluster are uniformly distributed over a spherical surface that represents the cluster, and the resulting interaction forces are calculated in terms of the charge density, dipole arm, and the effective dielectric constant of the cluster. Both the dielectric constant and the dipole arm are allowed to vary with the associated volume fraction of the solvent. The former is calculated using a micromechanical model proposed by Nemat-Nasser and Hori[19] and used for this specific application by Nemat-

TABLE IX. Model parameters for Nafion-based IPMC in K^+ form with ethylene glycol (EG).

Cluster size (nm)	$a = 2.5$
Natural and relaxation time constants (s)	$\tau = 0.4$ $\tau_1 = 5$
Stiffness constants (m^2)	$a_1 = 3.966 \times 10^{-20}$ $a_2 = -0.182 \times 10^{-20}$
Stress concentration factor	$A_B = 0.7$
Equilibrium fraction of residual cations in cathode BL	$r_0 = 0.1$
Osmotic factor	$\phi = 1$
Natural length scale (m)	$\ell = 2.85 \times 10^{-7}$
Cathode BL length	$L_C = 3.58\ell$
Diffusivity (cm^2/s)	$D_A = 1 \times 10^{-3}$ $D = 1 \times 10^{-13}$
Initial porosity	$n_0 = 0.01$

Nasser and Li.[3] The square of the dipole arm is assumed to vary linearly with the volume fraction of the solvent. This involves two adjustable parameters, a_1 and a_2, that are then fixed using the measured results. The modeling of the corresponding IPMC includes one adjustable parameter, A_B, that represents the fraction of the average stress carried by the bare membrane in the composite. The calculation details are given by Nemat-Nasser[4] and Nemat-Nasser and Zamani[17] with illustrations, and the model predictions are verified experimentally by Nemat-Nasser and Wu[5] for both Nafion- and Flemion-based bare ionomers and the corresponding IPMCs in various cation forms, over the entire range of hydration, from fully saturated to completely dry. To check the model for application to the present experimental results, consider as illustration a Nafion-based IPMC in K^+ form with ethylene glycol as the solvent. Figure 12(a) compares the model and the experimental results. The physical parameters are given in Table VIII. These and the values of the model parameters, given in Table IV, are used to model the actuation of the same IPMC when subjected to 1.5 V dc electric potential for about 300 s and then shorted. The results are shown in Fig. 12(b) together with the measured data.

The basic idea underpinning the actuation modeling is that the application of an electric potential produces two thin boundary layers, one near the anode and the other near the cathode electrodes. As a result, the clusters in the anode boundary layer are gradually depleted of their cations, while those in the cathode boundary layer are gradually supplied with additional cations. The cation imbalance within the clusters (but not the IPMC) changes the osmotic, electrostatic, and elastic forces that tend to expand or contract the corresponding clusters, forcing the solvents out of or into the clusters, and producing the bending motion of the cantilever. Therefore, in this model, the volume fraction of the solvent within each boundary layer is assumed to be controlled by the effective pressure in the corresponding clusters produced by the osmotic, electrostatic, and elastic forces. These forces cause the cathode boundary layer to contract during the back relaxation, expelling the extra solvents onto the IPMC's surface while cations continue to accumulate within the cathode boundary layer. This, in fact, is what we have observed in open air during the very slow back relaxation of IPMCs that are solvated with ethylene glycol and particularly with glycerol.

To model the distribution of the cations over the thickness of the IPMC as a function of time, the Nernst equation is used to represent the cation flux (Lakshminarayanaiah[20]), the electrostatics equations are used to account for the electric field within the membrane, and the continuity equations and the necessary boundary conditions are used to ensure charge conservation and consistency with the imposed boundary data. The coupled equations yield a natural length scale ℓ and a natural time scale τ that characterize the dimension of the boundary layer and the speed of the ion mobility, respectively. The length scale is of the order of a few hundred nanometers, and the time scale is of the order of fractions of a second; see Table IX. Initially the variation of the cation density in the cathode and anode boundary layers is centrally symmetric, but once the clusters near the electrodes in the anode boundary layer are depleted of their cations, the length of the anode boundary layer increases as cations move out of its clusters, while cations are added to the clusters in the cathode boundary layer. Under the influence of these extra cations and because of the strong acidity of the sulfonates, there is a redistribution of the cations within the clusters in the cathode boundary layer that occurs at a rate defined by another time scale τ_1. This modifies the effective dipole-cation interaction forces, thereby contributing to the back relaxation.

The coupled equations are solved incrementally, at each step calculating the resulting effective pressure in the anode and cathode clusters. Then, using the rate form of the continuity equation for the solvent and a linear diffusion equation, the changes in the volume fraction of the solvent in the anode and cathode boundary layers are calculated together with the resulting volumetric strains and hence the increment of the induced bending curvature. The calculations also include the dependence of the stiffness of the IPMC on the volume fraction of the solvent that varies along the thickness and in time. A great deal of simplification is achieved using order-of-magnitude estimates and neglecting terms that are comparatively small; for details, see Nemat-Nasser[4] and Nemat-Nasser and Zamani.[17]

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