The effect of various solvents on the mechano- electrochemical response of ionic electro-active composites:

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The Effect of Various Solvents on the Mechano-electrochemical Response of Ionic Electro-Active Composites

A dissertation submitted in partial satisfaction of the Requirements for the degree of Doctor of Philosophy in Mechanical Engineering by

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2005
The dissertation of Shahram Zamani is approved, and it is acceptable in quality and form for publication on microfilm:

Chair

University of California, San Diego

2005
To my dad, mom, and brother

Latif, Mina, and Shayan

To my uncle family

Behzad, Farzaneh, Behnaz, and Behnam

To my sweetheart

Tina

without whom this would have been unthinkable.
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ABSTRACT OF THE DISSERTATION

The Effect of Various Solvents on the Mechano-electrochemical Response of Ionic Electro-Active Composites

by

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Doctor of Philosophy in Mechanical Engineering

University of California, San Diego, 2005

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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 1.3V 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. 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. We seek to model the IPMCs' actuation and compare results with the experimental data. The modeling rests on the observation that a sudden application of a step potential (DC) of several volts (1-3 V) alters the distribution of cations within the ionomer, forcing cations out of the clusters near the anode and additional cations into the clusters near the cathode. The clusters within a thin boundary layer near the anode are thus depleted of their cations while cations accumulate in the clusters near the cathode boundary layer. We first seek to determine the spatial and temporal variation of the cation distribution across the thickness of the IPMC for various cations and solvents, using implicit finite difference numerical solution of the basic field equations, and compare the results with those of approximate analytical estimates. Based on this information, we then calculate the changes in the osmotic, electrostatic, and elastic forces that tend to expand or contract the clusters in the anode and cathode boundary layers. Finally, we calculate the amount of solvent out of or into the clusters that produces the bending motion of the cantilever.
Chapter I

INTRODUCTION

1.1. BRIEF INTRODUCTION

Ionic polymer-metal composites have been focus of research for almost a decade now. Ionic polymer-metal composites (IPMCs) are electroactive materials with potential applications as actuators and sensors. IPMCs consist of a perfluorinated ionomer membrane (usually Nafion® or Flemion®) plated on both faces with a noble metal such as gold or platinum. They are neutralized with a certain amount of counterions. The counterions balance the electrical charge of anions covalently fixed to the backbone ionomer. The anions in Nafion are sulfonates, whereas those in Flemion are carboxylates.

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. A schematic of IPMC material and electrodes and the electric potential setup is shown in Figure 1.1. For Nafion-based IPMCs that are neutralized with alkali metals, the strip then slowly relaxes back towards the cathode, while still under electric potential [Nemat-Nasser and Zamani (2003) and Nemat-Nasser and Wu (2003)]. If the two faces are suddenly shorted, the sample further bends towards the cathode. Then it slowly relaxes back towards the anode. The sample seldom attains its original state. Experimental observations for Flemion-based IPMCs [Nemat-Nasser and Wu, 2003]
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. If the two faces of the sample are suddenly shorted, the sample bends back towards the cathode gradually.

Figure 1.1. Schematic of IPMC material and electrodes to apply the stimulated electric potential

So far, IPMCs has been tried for a movable catheter tip [Guo et al., 1995], a micropump [Guo, 1999], and a light-weight lens wiper for use abroad space probe [Bar-Cohen, 2000].
1.2. MOTIVATION OF RESEARCH

Ionic polymer-metal composites (IPMCs) are electroactive materials with potential applications as actuators and sensors [Heitner-Wirguin, 1996]. When an IPMC membrane is suddenly bent, a small potential of order of millivolts would be produced. Hence, IPMCs are soft actuators and sensors. IPMC’s electrical-chemical-mechanical response is highly dependent on the cations used, the nature and the amount of solvent uptake, the morphology of the electrodes, and other factors.

So far, tested IPMCs have water as their solvent. Their electrical-chemical-mechanical response is studied in a water bath. The initial actuation of Nafion- and Flemion-based IPMCs with alkali metals in water bath under step DC electric potential is fast. Initial actuation towards the anode under a DC step-potential for fully hydrated Nafion-based IPMCs with most alkali metals happens in fraction of a second. This makes it difficult to study potential mechanisms responsible for IPMCs electrical-chemical-mechanical behavior. Here at CEAM lab, I have used other solvents that produce very slow response in the IPMC actuation. This made it possible to observe various phenomena during the IPMC’s actuation. For Nafion-based IPMCs with alkali metals as counterions, the initial actuation towards the anode with water is less than a second. Need to observe various phenomena during electromechanical response of IPMCs necessitates using other type of solvents that reduce the speed of actuation. For Nafion-based IPMCs with alkali metals as counterions, the actuation towards the anode is followed by a slow back relaxation towards the cathode as stated earlier. 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 seconds (e.g., with most alkali metals and with water), to about 300
seconds (e.g., in K\(^+\)-form with ethylene glycol), to about 2000 seconds (e.g., in Na\(^+\)-form with glycerol), and to about 8000 seconds (e.g., in Li\(^+\)-form with 12 crown 4 solution). Experimental observations for Flemion-based IPMCs [Nemat-Nasser and Wu, 2003] 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.

Particular study was given to actuation of Nafion-based IPMCs with solvents such as ethylene glycol and glycerol, solvents possessing viscosities higher than water. Also crown ethers, that embrace cations such that they slow the actuation, were studied. Actuation of Nafion-based IPMCs with these solvents occurs in several hundreds of seconds (almost 1000 seconds for Nafion-based IPMCs with ethylene glycol as solvent) and even hours (for Nafion-based IPMCs with glycerol and crown ethers as solvents). Formation of solvent droplets on the cathode face of a Nafion-based IPMC with various solvents during back relaxation was observed. This has not been observed in case of a Nafion-based IPMC with water as solvent. This is because the IPMC actuation with water happens fast. Besides, the actuation occurs in a water bath, which makes it difficult to see any droplets. This observation further proved the contraction of the cathode boundary layer clusters during back relaxation of Nafion-based IPMCs presented by Nemat-Nasser [2002].

Also with water as the solvent, the applied electric potential must be limited to less than 1.3V at room temperature, to avoid electrolysis. To magnify the actuation amplitude of Nafion-based IPMCs, it may be necessary to apply higher electric potentials across the IPMC faces. Using solvents such as ethylene glycol and glycerol enabled us to apply
higher electric potentials (potentials up to 3V have been tested). Bigger actuation is observed for the case of IPMCs with these solvents.

Moreover, dry Nafion- and Flemion-based IPMCs do not show actuation upon application of electric potential. Thus the IPMC samples are fully solvated before stimulation by an electric potential. As stated earlier, most of the hydrated IPMCs electromechanical response studies, so far, are performed in a water bath. This is to insure that the IPMC sample stays fully hydrated during actuation. Water evaporation in open air presents additional problems. All the actuation tests of IPMCs with other solvents such as ethylene glycol, glycerol, and crown ether solution were done in open air. Small weight decrease over long period of time (actuations last hours in case of crown ether solutions) was observed. This showed that these solvents enable us to actuate IPMC in open air.

These and related factors limit the observation of experimental actuation. They further limit the application of IPMCs with water as the solvent. A systematic experimental evaluation of electromechanical response of both Nafion- and Flemion-based IPMCs with ethylene glycol, glycerol, and crown ethers as solvents is performed. IPMCs with these solvents have greater solvent uptake. They 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. The experimental results for IPMC composition, amount of solvation, stiffness, effective capacitance, and electromechanical response of IPMCs under DC potentials will be presented. Experimental stiffness and actuation results for a Nafion-based IPMC with various solvents under DC potential are compared with values
obtained from the improved Nemat-Nasser micromechanical model for Nafion-based IPMCs.

The long term objective of the present research is to understand the mechanisms of actuation of Nafion-based IPMCs under applied electric potentials. A brief study of Flemion-based IPMCs is considered as well.

Several models for the mechanism of IPMC actuation have been proposed. De Gennes et al. have suggested a model that incorporates water pressure gradients and the overall electric field as thermodynamic forces in Onsager formulation format [Groot and Mazur (1963) and Grot (1963)], which induce ion/water fluxes as the primary mechanisms of actuation [de Gennes et al., 2000]. Shahinpoor et al. offer an electromechanical model for IPMC motion [Shahinpoor, 1995; Shahinpoor and Thompson, 1995; Shahinpoor, 1999], and Asaka and Oguro [2000] have preferred a model by which water flow induced by pressure gradients and electro-osmotic flow may generate swelling stresses to drive actuation. Nemat-Nasser and Li [2000] presented a model that includes ion and water transport, electric field, and elastic deformation, emphasizing that ion transport may dominate the initial fast motion of IPMC materials. Study of IPMC actuation with solvents such as ethylene glycol, glycerol, and crown ethers further shows that the micro-mechanical model for actuation of IPMC presented by Nemat-Nasser [2002] describes different phases of the actuation response of IPMC under the DC potential. The present research aims to further study the mechanisms of electromechanical response of IPMCs under applied potential using other solvents that reduce the speed of different phases of actuation.
Several devices have been developed at CEAM to characterize Nafion- and Flemion-based IPMCs such as a novel mini-load frame is made and used for measuring stiffness. Electromechanical response of IPMC samples are recorded by a progressive scan digital camera that can achieve frame rates of up to 120 per second to record the actuation. A Nicolet MultiPro transient analyzer is used for data acquisition.

In this work, experimental characterizations of IPMC structures, physical and mechanical properties and the related analysis are given in Chapter 2. In Chapter 2, also, experimental results for electro-mechanical response of Nafion- and Flemion-based IPMCs are covered. In Chapter 3, based on experimental observations and the related analysis, the coupled chemo-electro-mechanical mechanism of IPMC actuation is studied. The micromechanical model of Nemat-Nasser [2002] is used as the basis of study. The charge distribution model is modified through numerical method. Also using the results of numerical method, the actuation response of Nafion-based IPMCs in various cation forms and solvents are modeled and compared with the experimental measurements.

1.3. REFERENCES


Chapter II

Experimental Study of Ionic Polymer-metal Composites with Various Solvents

2.1. 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 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 1.3V 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. 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.

2.2. INTRODUCTION

Ionic polymer-metal composites (IPMCs) are electroactive materials with potential applications as actuators and sensors [Bar-Cohen et al., 1999]. An IPMC consists of a perfluorinated backbone ionomer (usually Nafion® or Flemion®; (CF₂CF)ₘ(CF₂CF₂)ₙ; see Figure 2.1) 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 [Nemat-Nasser and Thomas, 2001]. 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 [Nemat-Nasser and Thomas (2001), Nemat-Nasser and Li (2000), and Nemat-Nasser (2002)]. Experimental observations [Nemat-Nasser and Wu, 2003] 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.

\[
\begin{align*}
\text{Nafion} &: \quad \text{(CF}_2\text{CF})_n \text{CF}_2 \text{CF}_2 \text{SO}_3^- \\
\text{Flemion} &: \quad \text{(CF}_2\text{CF})_n \text{CF}_2 \text{CF}_2 \text{COO}^- 
\end{align*}
\]

Figure 2.1. Chemical structure of Nafion (top) and Flemion (bottom)

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 1.3V at room temperature, to avoid electrolysis. Moreover, water evaporates in open air, presenting additional 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 to 3V potential in open air without any adverse effects. In this manner, the actuation of the IPMCs can be carefully tuned and monitored.

2.3. MICROSTRUCTURE AND PROPERTIES

2.3.1. Composition and Properties

IPMCs considered in the present work are made from Nafion and Flemion ionomers (Figure 2.1) [see Heitner-Wirguin (1996) for further information on bare Nafion]. The Nafion-based composite, in dry state, is about 180µm thick and the Flemion-based one is about 160µm thick [see Bennett and Leo (2003) for further information on IPMC manufacturing]. Samples are constituted of the following:

1) backbone perfluorinated copolymer of polytetrafluoroethylene with perfluorinated vinyl ether sulfonate pendants for Nafion-based and perfluorinated propyl ether carboxylate pendants for Flemion-based IPMCs, forming interconnected nanoscale clusters;

2) electrodes, which in Nafion-based IPMCs consist of 3-10nm diameter platinum particles, distributed mainly within a 10-20µm depth of both faces of the membrane, and usually covered with about 1µm thick gold plating to improve surface conductivity; see Figure 2.2. For Flemion-based IPMCs, the electrodes are gold, with a dendritic structure [Onishi et al., 2000], as shown in Figure 2.3;
(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) group 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 2.1.

Table 2.1. 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)

<table>
<thead>
<tr>
<th>Membrane</th>
<th>IEC (meq. g⁻¹)</th>
<th>EW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>0.91</td>
<td>1,100</td>
</tr>
<tr>
<td>Flemion</td>
<td>1.44</td>
<td>694.4</td>
</tr>
</tbody>
</table>

Figure 2.2. Cross section of a Pt/Au-plated Nafion-117 membrane at electrode region; distance between crosses is 408nm
For neutralizing counterions, we have used Li\(^+\), Na\(^+\), K\(^+\), and Rb\(^+\) (Rb\(^+\) is used only for metal percentage determination 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 [Onishi et al., 2001].

In addition to water, we have considered ethylene glycol, glycerol, and crown ethers as solvents. Ethylene glycol or 1,2-ethanediol (C\(_2\)H\(_6\)O\(_2\)) is an organic polar solvent that can be used over a wide range of temperatures. Glycerol, or 1,2,3-propanetriol (C\(_3\)H\(_8\)O\(_3\)) is another polar solvent with high viscosity (1,000 times the viscosity of water). Crown ethers are cyclic oligomers of ethylene glycol that serve as macrocyclic ligands to surround and transport cations (Figure 2.4) [Vögtle and Weber, 1985]. Some of the properties of the solvents under consideration are listed in Table 2.2.
Table 2.2. Some of the properties of ethylene glycol, glycerol, and crown ethers [Lide, 2003]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20°C (g/cm³)</td>
<td>1.088</td>
<td>1.26</td>
<td>1.09</td>
<td>1.1</td>
<td>1.12</td>
</tr>
<tr>
<td>Formula Weight (g/mol)</td>
<td>62.07</td>
<td>92.1</td>
<td>176.21</td>
<td>220.26</td>
<td>264.32</td>
</tr>
<tr>
<td>Dielectric Constant at 20°C</td>
<td>41.4</td>
<td>46.53</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>-13</td>
<td>18-20</td>
<td>16</td>
<td>…</td>
<td>42-45</td>
</tr>
</tbody>
</table>

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 2.7Å. This crown is suitable for potassium ions of 2.66Å diameter. A schematic configuration of this crown with sodium and potassium ions is shown in Figure 2.5.

Figure 2.4. Chemical structure of 18-Crown-6 (Each node is CH₂)
2.3.2. 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 depends 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 [Nemat-Nasser and Zamani, 2003] 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 seconds (e.g., with most alkali metals and with water), to about 300 seconds (e.g., in K⁺-
form with ethylene glycol), and to about 2,000 seconds (e.g., in Na\textsuperscript{+}-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 2.6 illustrates these different phases of actuation for a Nafion-based IPMC in Na\textsuperscript{+}-form with glycerol as the solvent. For Flemion-based IPMCs with cations such as K\textsuperscript{+} and fully solvated with ethylene glycol, no back relaxation has been observed. A fully solvated Flemion-based IPMC in K\textsuperscript{+}-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.

Figure 2.6. Different phases of a Nafion-based IPMC in Na\textsuperscript{+}-form with glycerol as solvent, under a 2V 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
Figure 2.7. At the end of the initial actuation towards the anode (lasting about 12 minutes) the deformed sample of Nafion-based IPMC in Na\(^+\)-form with glycerol as solvent subjected to 2V (DC), fits a perfect circle.

Figure 2.8. Different phases of a Flemion-based IPMC in K\(^+\)-form with ethylene glycol as solvent, under a 1.5V 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.
Experimental results show that an IPMC sample deforms into a circle under a constant voltage, as shown in Figure 2.7 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 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.
2.3.3. Some Basic Characteristic Parameters

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

\[ EW_{\text{IPMC}} = \frac{EW_{H^+} - 1.008 + FW_{\text{ion}}}{SF}, \]  

(2.1)

where \( EW_{H^+} \) is the equivalent weight of dry Nafion or Flemion in \( H^+ \)-form which, for Nafion 117 is 1,100 g/mol (Ion exchange capacity of \( 1/1,100 = 0.91 \) meq. g\(^{-1} \)) and for Flemion is 694.4 g/mol. \( FW_{\text{ion}} \) 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), \( SF = 1 \).

Another characteristic of a solvated bare ionomer or IPMC sample is the solvent uptake [Gebel (1993), Gebel (2000)], \( w \), 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,

\[ w = \frac{V_{\text{solvent}}}{V_{\text{dry}}} = \frac{1}{\rho_{\text{solvent}} V_{\text{dry}}} (m_{\text{total}} - m_{\text{dry}}), \]  

(2.2)

where \( V_{\text{solvent}} \) is the volume of the absorbed solvent, \( V_{\text{dry}} \) is the volume of the dry sample, \( \rho_{\text{solvent}} \) is the mass density of the solvent, \( m_{\text{total}} \) is the total mass of the sample in the solvated form, and \( m_{\text{dry}} \) is the mass of the dry sample.
2.4. EXPERIMENTAL DETERMINATION OF PHYSICAL PROPERTIES

2.4.1. 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.

2.4.2. 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 cm × 0.26 cm using a special jig. The thickness of the Nafion-based composites, in the dry state, is about 180µm, and that of Flemion-based IPMCs is about 160µm. 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 minutes.
(2) Samples are immersed in DI (deionized) water and the beaker containing them is heated in the 60°C water bath for 5 minutes 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 is kept at 60°C for 5 minutes. 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 one or two 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 hours, 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 (2.5g of 12-Crown-4 for 12CR4 solution, 4.2g of 15-Crown-5 for 15CR5 solution, and 4.2g of 18-Crown-6 for 18CR6 solution) are mixed separately with 150ml of methanol. Then the solution of each crown and methanol is mixed with 10ml 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 hours to
obtain fully solvated samples. In all cases, the samples are then left in the solution at ambient temperature, overnight.

2.4.3. 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 0.001mm resolution. The length, width, and thickness of the samples are measured at multiple positions along the sample, and the average values are used. Table 2.3 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 Figure 2.9.

Figure 2.9. Solvent uptake versus solvent formula weight (Table 2.2) for Nafion-based IPMCs in different cation forms
Table 2.3. Dry and solvated length (l), width (w), thickness (t), and solvent uptake of Nafion- and Flemion-based IPMC samples in indicated cation forms

<table>
<thead>
<tr>
<th></th>
<th>Dry form</th>
<th></th>
<th></th>
<th></th>
<th>Solvated form</th>
<th></th>
<th></th>
<th></th>
<th>Solvent Uptake (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>l (cm)</td>
<td>w (cm)</td>
<td>t (cm)</td>
<td>l (cm)</td>
<td>w (cm)</td>
<td>t (cm)</td>
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<td></td>
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<tr>
<td>Nafion</td>
<td></td>
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<td></td>
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<td></td>
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<tr>
<td></td>
<td>12</td>
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<td>0.0174</td>
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<td>0.0306</td>
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<td>0.3129</td>
<td>0.0239</td>
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2.4.4. 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 nano-scale clusters is balanced by the elastic stresses that are consequently developed within its backbone polymer membrane [Nemat-Nasser and Thomas, 2001]. Table 2.4 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.

Table 2.4. Swelling strain in the length, width, and thickness directions for Nafion- and Flemion-based IPMC samples in different cation forms, with ethylene glycol as solvent

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<th>Base polymer</th>
<th>Cation</th>
<th>Swelling strain (%)</th>
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<tr>
<td></td>
<td></td>
<td>l</td>
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<tr>
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<td>Na</td>
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<td></td>
<td>01</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>00</td>
</tr>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
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</table>
2.4.5. Stiffness Measurement

A mini-load frame is used for stiffness measurements. A schematic of the device is shown in Figure 2.10. The sample (either bare ionomer or IPMC) is loaded between two grips and the initial gauge length is measured by a caliper with 0.0254mm (0.001 inch) 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 NI-DAQ board (National instrument data acquisition board), and LabVIEW 4 code are used to record the loading and unloading data read from the strain gauges attached to the mini-load 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:

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 mini-load 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 minutes, 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) to (3) are repeated several times. The cross-sectional area changes linearly with solvation, as can be seen from Figure 2.11, 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 as a function of solvent uptake. From the weight of the sample the solvent uptake is calculated, using equation (3.2).

Figure 2.10. Schematic of the mini-load frame

Figure 2.11. Typical variation of the bare Nafion cross section with solvent uptake
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 2.5.

Table 2.5. Stiffness (MPa) and solvent uptake (w %) of Nafion- and Flemion-based IPMCs with ethylene glycol (EG) and glycerol (G) as solvents

<table>
<thead>
<tr>
<th>Base polymer</th>
<th>Stiffness (MPa)</th>
<th>w (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Load</td>
<td>Unload</td>
</tr>
<tr>
<td>Nafion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EG Na 00</td>
<td>30.3</td>
<td>32.9</td>
</tr>
<tr>
<td></td>
<td>01 28.0</td>
<td>35.8</td>
</tr>
<tr>
<td>K 00</td>
<td>102.7</td>
<td>126.7</td>
</tr>
<tr>
<td></td>
<td>01 83.8</td>
<td>127.1</td>
</tr>
<tr>
<td>G Na 03</td>
<td>67.6</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td>13 73.5</td>
<td>82.7</td>
</tr>
<tr>
<td>Flemion</td>
<td>EG K 00</td>
<td>17.2</td>
</tr>
<tr>
<td></td>
<td>01 17.9</td>
<td>24.0</td>
</tr>
</tbody>
</table>

Figure 2.12 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 follow:
Figure 2.12. Stiffness (MPa) of bare Nafion and Nafion-based IPMCs with ethylene glycol and glycerol as solvents

\[ a = \frac{M_{\text{solvent}} \cdot w}{EW_{\text{IPMC}}} \]  \hspace{1cm} (2.3)

where \( M_{\text{solvent}} \) is the solvent formula weight (see Table 2.2), and \( EW_{\text{IPMC}} \) is the IPMC equivalent weight. The parameter \( a \) takes into account the effect of backbone polymer, cation form, and the solvent. Figure 2.13 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 [Nemat-Nasser (2002), Nemat-Nasser and Wu (2003)]. 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 5g 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.

Figure 2.13. Stiffness (MPa) – of Nafion- and Flemion-based IPMCs with water and ethylene glycol as solvents
2.4.6. 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 IPMC’s was discussed earlier. The following procedure is used to obtain the metal weight fraction data, presented in Table 2.6:

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 2.14. Variation of dry weight for different cations - Nafion-based IPMC - Samples SH5K and SH5Na](image)
Figure 2.15. Variation of dry weight with different cations - Flemion-based IPMC -
Samples FL4K

Figure 2.14 shows the dry weight versus the ion formula weight for Nafion-based
samples, and Figure 2.15 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.

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

\begin{align*}
m^\Lambda_{IPMC} &= m^{bare} + m^{metal} + m^{\Lambda}_{ion}, \\

m^B_{IPMC} &= m^{bare} + m^{metal} + m^{B}_{ion},
\end{align*}

(2.4) \hspace{1cm} (2.5)
where $m_{\text{bare}}$, $m_{\text{metal}}$, $m_{\text{ion}}$, and $m_{\text{IPMC}}$ 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 Figures 2.14 and 2.15) is given by

$$n = \frac{m_{\text{IPMC}}^A - m_{\text{IPMC}}^B}{FW_{\text{ion}}^A - FW_{\text{ion}}^B}. \quad (2.6)$$

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

$$m_{\text{polymer}} = n(EW_{H^+} - 1.008). \quad (2.7)$$

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

$$SF = \frac{m_{\text{polymer}}}{m_{\text{IPMC}}}. \quad (2.8)$$

and, therefore, we have

$$m_{\text{metal}} = (1 - SF)m_{\text{IPMC}}. \quad (2.9)$$
From Figures 2.14 and 2.15 and equations (2.5)-(2.9), 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 2.6. The metal percentage calculations are based on 1,100 g/mol and 694.4 g/mol equivalent weight of bare Nafion and Flemion backbone polymers, respectively.

Table 2.6. Dry weight of bare polymer, metal electrode, and metal percentage (MP) (%) of Nafion- and Flemion-based IPMC samples

<table>
<thead>
<tr>
<th>Base polymer</th>
<th>Polymer (g)</th>
<th>Metal (g)</th>
<th>MP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na 00</td>
<td>0.02228</td>
<td>0.0127</td>
<td>35.5</td>
</tr>
<tr>
<td>01</td>
<td>0.02086</td>
<td>0.0137</td>
<td>38.9</td>
</tr>
<tr>
<td>K 00</td>
<td>0.01979</td>
<td>0.0130</td>
<td>39.1</td>
</tr>
<tr>
<td>01</td>
<td>0.02071</td>
<td>0.0112</td>
<td>34.5</td>
</tr>
<tr>
<td>Flemion</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K 00</td>
<td>0.01818</td>
<td>0.0085</td>
<td>31.1</td>
</tr>
<tr>
<td>01</td>
<td>0.01732</td>
<td>0.0093</td>
<td>33.9</td>
</tr>
</tbody>
</table>

2.4.7. Effective Capacitance Measurement

In electro-chemical 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 electro-chemical systems is analogous to that of a capacitor [Bard
A model of two resistors and two capacitors (Figure 2.16) is used for the determination of the overall capacitance of the IPMC samples [McGee, 2002]. The overall capacitance is calculated from the self-discharge (Figure 2.17) and the external discharge response of the samples [McGee, 2002].

To measure the effective capacitance of a fully solvated IPMC in an alkali metal form, a square-shaped sample of about 0.5cm [Nemat-Nasser and Thomas, 2001] 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 1V 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 minutes. 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 1,000Ω resistor is added in parallel with the sample (see Figure 2.17). The calculated capacitance in different cation forms is listed in Table 2.7.

![IPMC equivalent electric-circuit model](image)

Figure 2.16. IPMC equivalent electric-circuit model [McGee, 2002]
Figure 2.17. Determination of capacitance by (left) self-discharge test and (right) external resistance discharge

Figure 2.18 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.

Figure 2.18. Effective capacitance of IPMCs in different cation forms with different solvents versus the formula weight of the solvent
Table 2.7. Effective capacitance of Nafion- and Flemion-based IPMCs with solvents

<table>
<thead>
<tr>
<th>Base polymer</th>
<th>Capacitance (mF/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td></td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>Li 6.2</td>
</tr>
<tr>
<td></td>
<td>Na 8.5</td>
</tr>
<tr>
<td></td>
<td>K 11.9</td>
</tr>
<tr>
<td>Glycerol</td>
<td>Li 4.6</td>
</tr>
<tr>
<td></td>
<td>Na 7.50</td>
</tr>
<tr>
<td></td>
<td>K 10.4</td>
</tr>
<tr>
<td>12-Crown-4</td>
<td>Li 1.15</td>
</tr>
<tr>
<td>15-Crown-5</td>
<td>Na 0.58</td>
</tr>
<tr>
<td></td>
<td>K 0.8</td>
</tr>
<tr>
<td>18-Crown-6</td>
<td>Na 0.15</td>
</tr>
<tr>
<td></td>
<td>K 0.36</td>
</tr>
<tr>
<td>Flemion</td>
<td>Ethylene glycol K 3.2</td>
</tr>
</tbody>
</table>

2.5. ELECTRO-MECHANICAL 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 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 2.19.
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 Figure 2.20) 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 seconds of actuation, 200 data points per second are recorded, and for the rest of the actuation, only 50 data points per second are captured. A Visual C code, specific
for our application, is also used to video record the actuation at 120 frames per second during fast actuation phases and at 1 frame per second 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 Figure 2.21). 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 monovalent 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.

Figure 2.20. 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 300.0sec and then shorted; Nafion-based IPMC in K⁺-form with ethylene glycol as solvent
2.5.1. 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 2.22 shows the first 2000 seconds of this actuation for indicated solvents. In what follows, each of the cases displayed in this figure is further detailed.
Figure 2.22. Comparison of different actuation phases of Nafion-based IPMC in Li$^+$-form with Ethylene glycol (diamonds; shorted at 199.2 sec), Glycerol (circles; shorted at 2,611.1 sec), and 12-Crown-4 (triangles; shorted at 8,514.0 sec) as solvents under 2V DC electric potential. The ethylene glycol data are presented on the secondary (right-hand) axis. Only the initial 2,000 seconds of actuation are presented.

With ethylene glycol, the initial actuation towards the anode occurs in about 18 seconds, when the sample is stimulated by a 2V DC electric potential in open air. The subsequent back relaxation towards the cathode is much slower. When the potential is removed after 199.2 sec, the sample actuates back towards the anode, but does not attain its initial state. Figure 2.23 displays these actuation phases.

With Glycerol, the sample may be subjected to relatively large potentials without electrolysis (the electrolysis potential for glycerol is around 10V) and without any significant solvent losses in open air. Because of glycerol's high viscosity (0.934 Pa-Sec
at 25°C, almost 1,000 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.

![Figure 2.23](image)

**Figure 2.23.** Normalized curvature versus time for Nafion-based IPMC in Li⁺-form under 2V electric potential with ethylene glycol as solvent; shorted at 199.2 sec

As shown in Figure 2.24, under a 2V DC potential, the actuation towards the anode occurs in almost 550 seconds. Then the sample bends back towards the cathode, slowly reaching an equilibrium state at around 2,600 seconds. The sample is shorted at 2611.1 sec. 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, measured current flow reveals continued accumulation of cations in the cathode boundary layer. According to a model proposed by Nemat-Nasser [2002], the actuation of IPMCs is a result of coupled electro-chemo-mechanical 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 electro-static 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 into 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.

![Graph](image1)

Figure 2.24. Normalized curvature versus time for Nafion-based IPMC in Li\(^+\)-form under 2V electric potential with glycerol as solvent; shorted at 2,611.1 sec

The response with 12-Crown-4 as the solvent is similar but much slower, as shown in Figure 2.25; see also Figure 2.26 which shows the first 300 seconds of actuation. The back relaxation in this case lasts almost 8,500 seconds (2 hours and 20 minutes). The
sample is shorted at 8514.0 sec. Upon shorting the two electrode faces, the sample gradually actuates back towards the anode, but does not reach an equilibrium state even after 1,500 seconds.

Figure 2.25. Variation of normalized curvature versus time for a Nafion-based IPMC in Li\(^+\)-form with 12-Crown-4 as solvent under a 2V DC electric potential; shorted at 8,514.0 sec

Figure 2.26. The first 300 seconds of actuation of Nafion-based IPMC in Li\(^+\)-form with 12-Crown-4 as solvent under a 2V electric potential
2.5.2. Actuation of IPMCs in Na\textsuperscript{+}-form with Various Solvents

Nafion-based IPMC samples in Na\textsuperscript{+}-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 2.27 shows actuation for Nafion-based IPMC samples in Na\textsuperscript{+}-form with indicated solvents.

![Figure 2.27. Comparison of different actuation phases of Nafion-based IPMC in Na\textsuperscript{+}-form with Ethylene glycol (diamonds; shorted at 281.1sec), Glycerol (circles; shorted at 2,610.0sec), and 15-Crown-5 (triangles; shorted at 1,837.0sec) as solvents under DC electric potential](image)

The sample that was used to test the actuation of Nafion-based IPMC in Na\textsuperscript{+}-form with ethylene glycol as solvent, showed very poor surface conductivity, basically due to
the presence of many microcracks within the electrodes (see Figure 2.28), 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 150Ω. The resulting actuation under a 2V potential together with the accumulated charge are shown in Figures 2.29, 2.30. The sample actuates towards the anode, but once the normalized curvature reaches 3.5% it remains in that position for 4.3 seconds before slowly relaxing back towards the cathode. After 281.1 seconds, the current is shorted, but the sample continues to bend an additional 1% towards the cathode in 11 seconds 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 2.28. Surface texture of Nafion-based IPMC in Na⁺- form with ethylene glycol as solvent; left: 200 magnification; right: 3,000 magnification
Figure 2.29. Accumulated charge and normalized curvature versus time; Nafion-based IPMC in Na\(^+\)-form with ethylene glycol as solvent; 2V; the solvent volume uptake is 55\% and surface resistance is 150\(\Omega\); shorted at 281.1sec

Figure 2.30. Accumulated charge and normalized curvature versus time (100 seconds of actuation): Nafion-based IPMC in Na\(^+\)-form with ethylene glycol as solvent; 2V; the solvent volume uptake is 55\% and surface resistance is 150\(\Omega\); shorted at 281.1sec
Figure 2.31 shows the variation of the curvature as a function of time for a fully solvated (as summarized in Table 2.3) Nafion-based IPMC in Na\(^+\)-form with glycerol as solvent, under 2V DC electric potential; various phases of this actuation are displayed in Figure 2.6. The actuation is extensive but very slow due to glycerol's high viscosity, with the \(L/R_b\) exceeding 1. Then the sample begins to relax back towards the cathode (from b to c, in Figure 2.6) for about 2,000 seconds. This occurs several seconds after the sample ceases its initial bending towards the anode. Upon shorting at 2610.0 sec of actuation, the sample actuates further towards the cathode (Figure 2.6; from c to d) and then it begins to bend back towards the anode to reach an equilibrium position (Figure 2.6; position e). The duration of this phase is relatively long (hours needed for this phase).

Figure 2.31. Different actuation phases of Nafion-based IPMC in Na\(^+\)-form with glycerol as solvent under a 2V electric potential; see also Figure 2.6; shorted at 2,610.0sec

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 seconds (Figure 2.31), and the slight back relaxation towards the cathode to an equilibrium state takes an additional 1000 seconds. When the potential is removed at 1837.0sec of actuation, the sample actuates further towards the cathode and then bends back towards the anode. The sample does not attain the initial configuration.

![Graph](image)

Figure 2.32. Different actuation phases of Nafion-based IPMC in Na\(^+\)-form with 15-Crown-5 as solvent under a 2V DC electric potential; shorted at 1,837.0sec

We have also studied the IPMC actuation with Na\(^+\) and 18-Crown-6 as solvent. Unlike K\(^+\) that perfectly encapsulated by the 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 3V DC potential in open air, produces bending towards the anode that lasts about 700 seconds, 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 Figure 2.32 (compare with Figure 2.31) which shows the variation of the normalized tip displacement (tip displacement divided by gauge length of the sample) as a function of time.

![Graph showing tip displacement over time](image)

Figure 2.33. Different actuation phases of Nafion-based IPMC in Na\(^+\)-form with 18-Crown-6 as solvent under a 3V electric potential

### 2.5.3. 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 Nafion-based IPMC in K\(^+\)-form does not have any back relaxation towards the cathode, as shown in Figures 2.34, 2.35.
Figure 2.34. Comparison of different actuation phases of Nafion-based IPMC in K$^+$-form with Ethylene glycol (diamonds; shorted at 300.0sec), Glycerol (circles; shorted at 1,036.1sec), and 18-Crown-6 (triangles; shorted at 669.0sec) as solvents under 2.5V DC electric potential.

With 18-Crown-6 as the solvent and under a 2.5V DC potential in open air, the sample bends continuously towards the anode for almost 669 seconds. There is no back relaxation towards the cathode, in this case. After the voltage is removed after 669 seconds by shorting the two electrode faces, the sample actuates gradually back towards the anode. Figure 2.35 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 [Nemat-Nasser and Wu, 2003]. 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 2.5V DC potential in open air, shows no motion during the first 75 seconds. 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 1,000 seconds, and then it reverses its motion, bending towards the anode to reach an equilibrium state after almost 4000 seconds. 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 Figures 2.36, 2.37.
Figure 2.36. Different actuation phases of Nafion-based IPMC in K\(^+\)-form with 15-Crown-5 as solvent under a 2.5V electric potential

Figure 2.37. 50 seconds of actuation of Nafion-based IPMC in K\(^+\)-form with 15-Crown-5 as solvent under a 2.5V electric potential applied at t = 0 sec

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 seconds. Then the sample bends back towards the cathode.
slowly, reaching an equilibrium state at around 1,035 seconds. When the potential is removed at 1036.1 seconds of actuation, the sample actuates back towards the anode, not attaining the initial configuration. Figures 2.38 and 2.39 show the variation of normalized curvature over time for this sample actuated in open air under 2V DC potential.

Figure 2.38. Different actuation phases of Nafion-based IPMC in K\(^+\)-form with glycerol as solvent under a 2V electric potential; shorted at 1,036.1 sec

Figure 2.39. 100 seconds of actuation of Nafion-based IPMC in K\(^+\)-form with glycerol as solvent under a 2V electric potential applied at t = 2.4 sec
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 1.5V 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 seconds. After the current is shorted at 534.5 seconds, 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 Figures 2.40, 2.41, where Figure 2.41 shows the first 3 seconds response of the samples.

Figure 2.40. Normalized curvature versus time; Nafion- and Flemion-based IPMC samples in K⁺-form with ethylene glycol as solvent under 1.5V electric potential; the Nafion-based IPMC is shorted at 300.0sec and the Flemion-based one is shorted at 534.5sec
Figure 2.41. Normalized curvature versus time (3 seconds of actuation); Nafion- and Flemion-based IPMC samples in K\(^+\)-form under 1.5V electric potential

Figure 2.42. Normalized transferred charge versus time; Nafion- and Flemion-based samples in K\(^+\)-form under 1.5V electric potential; the Nafion-based IPMC is shorted at 300.0sec and the Flemion-based one is shorted at 534.5sec

Variations of the normalized transferred charge versus time for Nafion- and Flemion-based IPMCs in K\(^+\)-form, under 1.5V potential, are presented in Figure 2.42. 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 build-up, followed by a continuous slower accumulation, although the resulting actuations are quite dissimilar.

2.6. SUMMARY 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. IPMCs with heavy and viscous solvents have slower actuations, higher solvent uptakes, smaller stiffness at fully solvated states, and lower overall capacitance, compared to IPMCs with water as their solvent. 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. Nafion-based IPMCs with alkali metals have relatively late and long back relaxation with ethylene glycol and glycerol, but not necessarily with crown ethers. With glycerol, they have slower actuation than with ethylene glycol as solvent. It is believed that cations carry solvent molecules as they move from the anode towards the cathode under an electric field. With high molecular weight solvents that possess higher viscosity, ion mobility is decreased. This is supported by the measured corresponding slow charge accumulation and actuation. The slow actuation associated with these solvents also has enabled us to observe various phases of the IPMC response under an electric potential. Experimental results for various solvents clearly show 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 electro-chemo-mechanical 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 are measured to continue to accumulate there.

Both the initial relatively fast motion and the subsequent back relaxation of Nafion-based IPMCs have been modeled based on micromechanisms proposed by Nemat-Nasser [2002]. This starts 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 details are given in a separate paper [Nemat-Nasser and Zamani, 2005] 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 peculiar observed behaviour 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.

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, 1980) 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, 2005). 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 pseudo-dipole. 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 assumed to vary with the associated volume fraction of the solvent. The former is calculated using a micro-mechanical model proposed by Nemat-Nasser and Hori [1999] and used for this specific application by Nemat-Nasser and Li [2000]. 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 [2002] and Nemat-Nasser and Zamani [2005] with illustrations, and the model predictions are verified experimentally by Nemat-Nasser and Wu [2003] 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, we have considered as illustration a Nafion-based IPMC in $K^+$-form with ethylene glycol as the solvent. Figure 2.43 compares the model and the experimental results. The physical parameters are given in Table 2.8 and Table 2.9. These and the values of the model
parameters, given in Table 2.4, are used to model the actuation of the same IPMC when subjected to 1.5V DC electric potential for about 300 seconds and then shorted. The results are shown in Figure 2.44 together with the measured data.

Figure 2.43. 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

Figure 2.44. Variation of normalized curvature over time for a 26mm strip of cantilevered Nafion-based IPMC in K\(^+\)-form with ethylene glycol, subjected to 1.5V DC electric potential; shorted at 300.0sec. The heavy solid curve is the model and the geometric figures connected by solid line is experimental results
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, 1969), 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, $\ell$, and a natural time scale, $\tau$, 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 2.10. 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, $\tau_i$. 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 [2002] and Nemat-Nasser and Zamani [2005].
Table 2.8. Physical parameters for Nafion-based IPMC in K⁺-form with ethylene glycol (EG)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Dimensions (mm)</td>
<td>28.620×2.698×0.206</td>
</tr>
<tr>
<td>Density of bare ionomer in K⁺-form (g/cm³)</td>
<td>( \rho_b = 2.07 )</td>
</tr>
<tr>
<td>Fixed anion concentration (mol/m³)</td>
<td>1,185</td>
</tr>
<tr>
<td>Initial volume fraction of solvent uptake</td>
<td>( w_0 = 0.38 )</td>
</tr>
<tr>
<td>Bare ionomer stiffness at indicated solvent uptake (%)</td>
<td>( Y_b = 748 \text{MPa, } w=0.04 ) ( Y_b = 148 \text{MPa, } w=0.32 )</td>
</tr>
<tr>
<td>Percentage of metal</td>
<td>0.63</td>
</tr>
<tr>
<td>Electrode-metal density (g/cm³)</td>
<td>( \rho_m = 20 )</td>
</tr>
<tr>
<td>Electrode-metal stiffness (MPa)</td>
<td>75,000</td>
</tr>
<tr>
<td>Applied electric potential (V)</td>
<td>( \phi_0 = 1.5 )</td>
</tr>
</tbody>
</table>
Table 2.9. Physical parameters for Nafion-based IPMC in K⁺-form with ethylene glycol (EG)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective dielectric constant</td>
<td>$\kappa = 2.20 \times 10^{-2}$</td>
</tr>
<tr>
<td>Effective capacitance (mF/cm²)</td>
<td>11.9</td>
</tr>
<tr>
<td>Bulk dielectric constant of EG</td>
<td>41</td>
</tr>
<tr>
<td>FW of EG (g/mol)</td>
<td>62.1</td>
</tr>
<tr>
<td>Density of EG (g/cm³)</td>
<td>1.11</td>
</tr>
<tr>
<td>FW of cation (K⁺) (g/mol)</td>
<td>39</td>
</tr>
<tr>
<td>Cation-anion valence</td>
<td>$\nu = 2$</td>
</tr>
<tr>
<td>Coordination number (CN)</td>
<td>4</td>
</tr>
<tr>
<td>Dynamic solvation number (SN)</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2.10. Model parameters for Nafion-based IPMC in K\(^+\)-form with ethylene glycol (EG)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster size (nm)</td>
<td>(a = 2.5)</td>
</tr>
<tr>
<td>Natural and relaxation time constants (sec)</td>
<td>(\tau = 0.4) (\tau_1 = 5)</td>
</tr>
<tr>
<td>Stiffness constants (m(^2))</td>
<td>(a_1 = 3.966 \times 10^{-20}) (a_2 = -0.182 \times 10^{-20})</td>
</tr>
<tr>
<td>Stress concentration factor</td>
<td>(A_B = 0.7)</td>
</tr>
<tr>
<td>Equilib. fraction of residual cations in cathode BL</td>
<td>(r_0 = 0.1)</td>
</tr>
<tr>
<td>Osmotic factor</td>
<td>(\phi = 1)</td>
</tr>
<tr>
<td>Natural length scale (m)</td>
<td>(\ell = 2.85 \times 10^{-7})</td>
</tr>
<tr>
<td>Cathode BL length</td>
<td>(L_C = 3.58\ell)</td>
</tr>
<tr>
<td>Diffusivity (cm(^2)/sec)</td>
<td>(D_A = 1 \times 10^{-3})  (D = 1 \times 10^{-13})</td>
</tr>
<tr>
<td>Initial porosity</td>
<td>(n_0 = 0.01)</td>
</tr>
</tbody>
</table>
2.7. REFERENCES


2.8. ACKNOWLEDGEMENTS

We wish to thank Drs. Steve Wax (DARPA), Len Buckley (NRL), Carlos Sanday (NRL), and Randy Sands for their initial support of this research at UCSD which has been continued now for a while without external funding at UCSD’s CEAM. We are grateful to Professor Mohsen Shahinpoor and Dr. K. J. Kim for providing the Nafion-based IPMC samples; to Dr. K. Asaka for providing the Flemion-based IPMC samples; to Dr. Yosi
Bar-Cohen for his continued interest and stimulating interaction; to Mr. Jon Isaacs and Mr. Dave Lischer for developing the experimental equipment and techniques; and to Dr. Jeff McGee for helpful code to obtain the effective capacitance. This work has been supported by CEAM of the University of California, San Diego.
Chapter III

Modeling of Electro-chemo-mechanical Response of Ionic Polymer-metal Composites with Various Solvents

3.1. 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 the necessary amount of counterions that balance the electrical charge of anions that are covalently fixed to the backbone ionomer. IPMCs are electroactive materials with potential applications as soft 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 temporal variation of the applied potential. Our most recent experimental results show that solvents can have most profound effects on the nature of the IPMCs’ actuation. For example, we have discovered experimentally that 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. In the present paper, we seek to model the IPMCs' actuation and compare results with the experimental data. The modeling rests on the observation that a sudden application of a step potential (DC) of several volts (1-3 V) alters the distribution of cations within the ionomer, forcing cations out of the clusters near the anode and additional cations into the clusters near the cathode. The clusters within a thin boundary layer near the anode are thus depleted of their cations while cations accumulate in the clusters near the cathode boundary layer.

We first seek to determine the spatial and temporal variation of the cation distribution across the thickness of the IPMC for various cations and solvents, using implicit finite difference numerical solution of the basic field equations, and compare the results with those of approximate analytical estimates. Based on this information, we then calculate the changes in the osmotic, electrostatic, and elastic forces that tend to expand or contract the clusters in the anode and cathode boundary layers. Finally, we calculate the amount of solvent out of or into the clusters that produces the bending motion of the cantilever. Comparing the model results with those of experimental measurement, we have arrived at remarkably good agreements. Indeed, our nanoscale-based model correctly predicts the unexpected influence of solvents on the actuation of IPMCs.

3.2. INTRODUCTION

Ionic polymer-metal composites (IPMCs) are electroactive materials with potential applications as actuators and sensors [Bar-Cohen et al., 1999]. When a cantilevered IPMC sample is subjected to a suddenly applied potential (DC) of several volts (1-3V), the electric field alters the distribution of cations within the ionomer, forcing them to
move from the anode towards the cathode. The clusters within a thin boundary layer near the anode are thus depleted of their cations while cations accumulate in the clusters near the cathode boundary layer. The distribution of cations under an applied potential may be modeled using the Nernst-Planck equation to define the flux of species under electrochemical potential diffusion and the Poisson equation to relate the concentration of species to the electric field. In this manner the approximate analytical solution of Nemat-Nasser [2002] can be checked and improved, arriving at a better prediction of the experimentally observed cation transfer as a function of time.

An efficient computer algorithm has been developed [Brumleve and Buck, 1978] for numerical simulation of membrane transport based on the Nernst-Planck and Poisson equations, and using an implicit finite-difference method. In this work, we follow a similar methodology and find the spatial and temporal variation of cations within an IPMC sample that is subjected to an electric potential. Then, based on the knowledge of the cation imbalance within the clusters (but not in the IPMC), we calculate the changes in the osmotic, electrostatic, and elastic forces that tend to expand or contract the corresponding clusters. From this we calculate the amount of solvent out of or into the clusters, and predict the resulting bending motion of the cantilever.

3.3. MICROSTRUCTURE AND PROPERTIES

3.3.1. Composition and Properties

Ionic polymer-metal composites (IPMCs) are electroactive materials with potential applications as actuators and sensors [Bar-Cohen et al., 1999]. An IPMC consists of a perfluorinated backbone ionomer (usually Nafion® or Flemion®; (CF₂CF)ₘ(CF₂CF₂)ₙ; see
Figure 3.1) plated on both faces with noble metals such as platinum or platinum and gold, or gold, and neutralized with the necessary amount of counterions that balance the electric charge of the anions covalently bonded to the ionomer [Nemat-Nasser and Thomas, 2001]. 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.

\[
\begin{align*}
- & (\text{CF}_2 \text{CF}) (\text{CF}_2 \text{CF}_2)_n - \\
O & - \text{CF}_2 \text{CF} - O - \text{CF}_2 \text{CF}_2 \text{SO}_3^- \\
\text{CF}_3
\end{align*}
\]

\[
\begin{align*}
- & (\text{CF}_2 \text{CF}) (\text{CF}_2 \text{CF}_2)_n - \\
O & - \text{CF}_2 \text{CF}_2 \text{CF}_2 \text{COO}^-
\end{align*}
\]

Figure 3.1. Chemical structure of Nafion (top) and Flemion (bottom)

### 3.3.2. Actuation of IPMCs

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 (1-3V), it bends towards the anode. For Nafion-based IPMCs that are neutralized with alkali metal cations and solvated by water, ethylene glycol, or glycerol, the strip then slowly relaces back towards the cathode, while still under electric potential [Nemat-Nasser and Li, 2000, Nemat-Nasser and Thomas, 2001, Nemat-Nasser, 2002, and Nemat-Nasser et al., 2005]. 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. Experimental observations [Nemat-Nasser and Wu, 2003] 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.

Thus, with water, ethylene glycol, or glycerol as solvents, the actuation of the Nafion-based IPMCs has essentially the same qualitative character, the basic difference being the speed of actuation which directly correlates with solvent viscosity. With crown ethers, on the other hand, we discovered experimentally [Nemat-Nasser et al., 2005] 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 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. Our nano-scale model correctly predicts all these results, as is summarized and illustrated in this paper.

3.3.3 Micro-mechanisms of Actuation

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 in 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 thus 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.

3.3.4. Some Basic Characteristic Parameters

An important parameter that characterizes an ionomer, is its ion content, defined by

\[
EW_{ion} = \frac{EW_{H^+} - 1.008 + FW_{ion}}{SF},
\]  

(3.1)
where $EW_{H^+}$, is the equivalent weight of dry Nafion polymer in $H^+$-form, which for Nafion 117 is almost 1100g/mol (Ion exchange capacity of $1/1100 = 0.99$ meq. g$^{-1}$). $FW_{ion}$ is the formula weight of the cation used, and $SF$ accounts for the metal plating, being the ratio of the dry backbone polymer mass to the total mass of the IPMC sample. For the bare polymer (no metal plating), $SF = 1$.

Another characteristic of solvated sample is the solvent uptake that affects both the stiffness and actuation behavior of the material. Solvent uptake is defined as the ratio of the volume of the absorbed solvent to the volume of dry IPMC sample,

$$w = \frac{V_s}{V_d} = \frac{1}{\rho_s V_d}(m_{total} - m_d),$$  \hspace{1cm} (3.2)

where $V_s$ is the volume of the absorbed solvent, $V_d$ is the volume of the dry sample, $\rho_s$ is the density of the solvent, $m_{total}$ is the total mass of the sample in the solvated form, and $m_d$ is the dry sample mass.

Concentration of anions in bare membrane, $C^-$, is the number of anions (in mole) per unit volume (in cm$^3$) of the solvated sample, defined by

$$C^- = \frac{\rho_d}{EW_{ion}} \frac{1}{1+w},$$  \hspace{1cm} (3.3)

where $\rho_d$ is the dry density of IPMC sample.
3.4. MODELING OF STIFFNESS VERSUS SOLVATION

A dry sample of a bare polymer or an IPMC in a solution absorbs the solvent until the resulting pressure within clusters is balanced by the elastic stresses that are consequently developed within its backbone polymer membrane. From this observation, we calculate the stiffness of the membrane as a function of the volume fraction of the solvent uptake for various cations. We first consider the balance of cluster pressure and elastic stresses for the bare polymer (no metal plating) to calculate the stiffness of the bare membrane for a given solvent uptake. Then we use the results to calculate the stiffness of the corresponding IPMC by including the effect of the added metal electrodes. The procedure also provides a way of estimating the microstructural parameters that are needed for modeling of the actuation of IPMCs. For Nafion-based IPMCs, the overall stiffness of both the bare membrane and the corresponding IPMC has been measured directly as a function of the degree of the solvation. Therefore, the results can be subjected to experimental verification.

The pressure developed within the cluster, $p_c$, can be shown [Nemat-Nasser, 2002] to be given by

$$p_c = \frac{vQ_B}{W} K_0 \phi + \frac{1}{3K_e} Q_B^2 \frac{\pm \alpha^2}{W^2}, \quad K_0 = \frac{RT}{F}, \quad Q_B = \frac{\rho_B F}{E \lambda_{mon}}, \quad (3.4)$$

where $\phi$ is the practical osmotic coefficient, $\alpha$ is the effective length of the dipole, $F$ is the Faraday constant, $\nu$ is the cation-anion valence ($\nu = 2$ for monovalent cations), $R =$
8.314 J/mol/K is the universal gas constant, $T = 300 K$ is the test (room) temperature, $\rho_b$ is the density of the bare ionomer, and $\kappa_e$ is the effective permittivity. Furthermore, from the balance of the elastic resistance of the membrane against the cluster expansion and the cluster pressure, it is shown that the stiffness, $K(w)$, of the bare polymer can be estimated as follows [Nemat-Nasser, 2002]:

$$K = \frac{p_e 1 + w}{w_0 I_n}, \quad I_n = \frac{1 + 2An_0}{n_0(1 + An_0)^{1/2}} - \frac{1 + 2A}{(1 + A)^{1/3}}, \quad A = \frac{w}{w_0} - 1,$$  \hspace{1cm} (3.5)

where $n_0$ and $w_0$ are the initial (dry) porosity and initial void ratio respectively. The IPMC stiffness, $\bar{Y}_{IPMC}$, is now given by

$$\bar{Y}_{IPMC} = \frac{Y_M Y_B}{BA_{w}Y_M + (1 - BA_{w})Y_B}, \quad B = \frac{(1 + \bar{w})(1 - f_M)}{1 + \bar{w}(1 - f_M)}, \quad \bar{w} = w(1 - f_M)^{-1},$$  \hspace{1cm} (3.6)

$$f_M = \frac{(1 - SF)\rho_B}{(1 - SF)\rho_B + SF\rho_M}.$$

(3.7)

where $f_M$ is the volume fraction of the metal plating in a dry sample, $Y_M$ and $Y_B$ are the Young’s moduli of the metal plating and bare ionomer, respectively, $\rho_M$ is the density of the metal plating, and $A_B$ is the concentration factor that accounts for the contribution of the bare ionomer in carrying the average overall stress within the sample.
To estimate $\kappa_e$, the effective cluster electric permittivity, as a function of the solvent uptake, $w$, note that solvent molecules are polar. As part of the solvation shell of an ion, a polar solvent has a dielectric constant of, say, $\varepsilon_1$, whereas as free molecules its dielectric constant is much larger, say, $\varepsilon_2$, both at room temperature. To estimate the solvent dielectric constants in bulk and as a part of solvation shell, we use the following equation [Hasted et al., 1948]:

$$\varepsilon E = \frac{4\pi}{M_{\text{solute}}} \frac{n^2 + 2}{3} L\left(\frac{n^2 + 2}{2} \frac{\mu m}{kT} E\right) + \frac{3}{2} (n^2 - 1) E, \quad (3.8)$$

where $M_{\text{solute}}$ is the solvent’s molecular weight, $n$ is its refractive index, $E$ is the applied electric field, $\mu_m$ is the dipole moment, $k$ is Boltzmann’s constant, and $L$ is the Langevin function defined by

$$L(y) = \coth(y) - \frac{1}{y}. \quad (3.9)$$

The refractive index, $n$, and the dipole moment, $\mu_m$, of the solvents under study are given in Table 3.1; data from [Lide, 2003]. The calculated dielectric constants are shown in Table 3.2.
Table 3.1. Refractive index, $n$, and dipole moment, $\mu_m$, of water, glycerol, and ethylene glycol at room temperature [Lide, 2003]

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Glycerol</th>
<th>Ethylene glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>1.3336</td>
<td>1.4735</td>
<td>1.3834</td>
</tr>
<tr>
<td>$\mu_m$ (Debye)</td>
<td>1.90</td>
<td>2.56</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Table 3.2. Calculated dielectric constant in bulk and as a part of solvation shell of an ion for various solvents using equation (3.8)

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>Glycerol</th>
<th>Ethylene glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$</td>
<td>6.2</td>
<td>9.4</td>
<td>7.7</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>78.4</td>
<td>46.5</td>
<td>41.0</td>
</tr>
</tbody>
</table>

To find the number of moles of cations within a given sample of bare ionomer, we use the measured solvent uptake, $w$, sample length, $L$, width, $w_d$, and thickness, $2H$, and its dry density, $\rho_d$. For example, for a sample in $K^+$-form with $FW_{ion} = 39\text{g/mol}$, $w = 1.47$, $L = 2.6982\text{cm}$, $w_d = 0.2509\text{cm}$, $2H = 0.0178\text{cm}$ (resulting in $1.18 \times 10^{-8}\text{cm}^3$ for volume), and $\rho_d = 2.07\text{g/cm}^3$, the cation content in moles then is,

$$x_c = \left( \frac{\rho_d}{EW_{ion}} \frac{1}{1 + w} \right) (1 + w)V_d = 2.15 \times 10^{-5}. \quad (3.10)$$
In the solution of 4.2g of 18CR6 \((m_{18CR6} = 4.2g)\) and 10ml of glycerol \((V_G = 10ml)\) (see Nemat-Nasser et al. (2005) for details on preparation of the crown ether solutions), the moles of glycerol, \(x_G\), is given by

\[
x_G = \frac{\rho_x V_G}{M_G} = 0.137,
\]

where \(M_G\) represents the molecular weight of the glycerol. We calculate moles of crown, say, \(x_{18CR6}\), to be

\[
x_{18CR6} = \frac{m_{18CR6}}{M_{18CR6}} = 0.016.
\]

Using (3.11) and (3.12), we obtain,

\[
\frac{x_G}{x_{18CR6}} = 9.
\]

We assume that the same ratio holds in the backbone ionomer. The total weight change due to the solvation is given by

\[
M_G x_G + M_{18CR6} x_{18CR6} = m_{\text{total}} - m_d.
\]
Using equation (3.13), moles of glycerol, $y_G$, and 18CR6, $y_{18CR6}$, within the sample are

$$y_G = 1.7 \times 10^{-4}, \quad y_{18CR6} = 1.9 \times 10^{-5}.$$ (3.15)

Then, the mole of solvent per mole of ion is

$$\frac{y_G}{x_c} = 8 \frac{\text{moles of glycerol}}{\text{mole of cation}}, \quad \frac{y_{18CR6}}{x_c} = 0.9 \frac{\text{moles of 18CR6}}{\text{mole of cation}}.$$ (3.16)

The above calculation shows that %90 of cations are embraced by crown ether. Therefore, the rest of the cations (%10) and all the anions are surrounded by the glycerol through their salvation shell. A similar procedure for 12CR4 and 15CR5 yields

$$\frac{y_G}{x_c} = \frac{8 \text{ moles of glycerol}}{\text{mole of cation}}, \quad \frac{y_{15CR5}}{x_c} = 0.9 \frac{\text{moles of 15CR5}}{\text{mole of cation}},$$ (3.17)

$$\frac{y_G}{x_c} = \frac{8 \text{ moles of glycerol}}{\text{mole of cation}}, \quad \frac{y_{12CR4}}{x_c} = 0.9 \frac{\text{moles of 12CR4}}{\text{mole of cation}}.$$ (3.18)

Let $CN$ be the static solvation shell of the cation (which equals its corresponding coordination number), $m_w$ be the number of moles of solvent per mole ion (cation and anion) within a cluster, and note that
\[ m_w = \frac{E W_{\text{ion}} w}{M_{\text{solute}} \rho_b v}, \quad (3.19) \]

We use \( \nu = 2 \) for water, ethylene glycol, and glycerol, but we use \( \nu = 1.1 \) for crown ether solutions, since, in those cases, only 10\% of the cations are solvated by glycerol.

Hence, when the amount of solvent (in moles) per ion within a cluster, is less than the coordination number, \( CN \), of that ion, we set \( \kappa_e = \varepsilon_i \kappa_0 \), where \( \kappa_0 = 8.85 \times 10^{-12} \text{F/m} \) is the electric permittivity of the free space. On the other hand, when \( m_w \geq CN \) then we calculate \( \kappa_e = \kappa_e(w) \) as follows [see Nemat-Nasser (2002) for details]:

\[
\kappa_e = \frac{\kappa_2 + \kappa_1 + f (\kappa_2 - \kappa_1)}{\kappa_2 + \kappa_1 - f (\kappa_2 - \kappa_1)} \kappa_1, \quad \kappa_1 = \varepsilon_i \kappa_0, \quad \kappa_2 = \varepsilon_e \kappa_0, \quad f = \frac{m_w - CN}{m_w}, \quad (3.20)
\]

To estimate the parameter \( \alpha^2 \) in (3.4), first we assume that it varies linearly with \( w \) for \( m_w < CN \), i.e., we set

\[
\pm \alpha^2 = a_1 w + a_2, \quad (3.21)
\]

and estimate the coefficients \( a_1 \) and \( a_2 \) from the experimental data, using two measured values of the stiffness. The results are listed in Tables 2-A to 2-C. For \( m_w \geq CN \), furthermore, we assume that the pseudo-dipole length is controlled by the electric permittivity of its environment, given by (in m²)
\[
\alpha^2 = 10^{-20} \left( \frac{\kappa_2}{\kappa_1} \right)^2 (a_1 w + a_2). \tag{3.22}
\]

In a series of experiments, the extensional Young’s modulus, \(Y_B\), of strips of bare Nafion in various cation forms, has been measured as a function of the solvent uptake, \(w\). The solvated membrane is assumed to be incompressible. For small axial strains (i.e., less than 1%) therefore the Young modulus, \(Y_B\), of the solvated strip of bare polymer relates to the stiffness \(K\), by

\[
Y_B = 3K. \tag{3.23}
\]

Figures 3.2 to 3.12 show the experimentally measured Young’s modulus, \(Y_B\), for \(Li^+\), \(Na^+\) and \(K^+\)-form Nafion 117 ionomer with various solvents. In these figures, the results of the model are shown by solid curves. An initial porosity of \(n_0 = 0.01\) is used for the calculations. For crown ethers (last column of the tables), \(CN = 3\) represents the static solvation shell of sulfonate [Paddison, 2004]
Table 3.3. Parameters, initial data, and other results used for stiffness modeling of bare Nafion ionomer and Nafion-based IPMC in Li$^+$-form

<table>
<thead>
<tr>
<th></th>
<th>Li$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EG</td>
</tr>
<tr>
<td>$FW_{ion}$ [g/mol]</td>
<td>6.95</td>
</tr>
<tr>
<td>$CN$</td>
<td>6</td>
</tr>
<tr>
<td>$\varepsilon_1$</td>
<td>7.7</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>41</td>
</tr>
<tr>
<td>$\rho_B$ [g/cm$^3$]</td>
<td>2.01</td>
</tr>
<tr>
<td>$w$ (wet) [%]</td>
<td>85.0</td>
</tr>
<tr>
<td>$w$ (dry) [%]</td>
<td>3.8</td>
</tr>
<tr>
<td>$Y_B$ (wet) [MPa]</td>
<td>85</td>
</tr>
<tr>
<td>$Y_B$ (dry) [MPa]</td>
<td>756</td>
</tr>
<tr>
<td>$\phi$</td>
<td>1</td>
</tr>
<tr>
<td>$a_1$ $[10^{-20}$m$^2$]</td>
<td>4.1500</td>
</tr>
<tr>
<td>$a_2$ $[10^{-20}$m$^2$]</td>
<td>-0.1870</td>
</tr>
<tr>
<td>$A_B$</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Table 3.4. Parameters, initial data, and other results used for stiffness modeling of bare Nafion ionomer and Nafion-based IPMC in Na\(^+\)-form

<table>
<thead>
<tr>
<th></th>
<th>Na(^+)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EG</td>
<td>G</td>
<td>15CR5</td>
<td>18CR6</td>
</tr>
<tr>
<td>(FW_{ion} \text{ [g/mol]})</td>
<td>23.0</td>
<td>23.0</td>
<td>23.0</td>
<td>23.0</td>
</tr>
<tr>
<td>(CN)</td>
<td>5</td>
<td>5</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(\varepsilon_1)</td>
<td>7.7</td>
<td>9.4</td>
<td>9.4</td>
<td>9.4</td>
</tr>
<tr>
<td>(\varepsilon_2)</td>
<td>41</td>
<td>46.5</td>
<td>46.5</td>
<td>46.5</td>
</tr>
<tr>
<td>(\rho_B \text{ [g/cm}^3)</td>
<td>2.02</td>
<td>2.02</td>
<td>2.02</td>
<td>2.02</td>
</tr>
<tr>
<td>(w \text{ (wet) [%]})</td>
<td>146.1</td>
<td>53.8</td>
<td>70.0</td>
<td>120.0</td>
</tr>
<tr>
<td>(w \text{ (dry) [%]})</td>
<td>7.4</td>
<td>3.9</td>
<td>5.1</td>
<td>4.8</td>
</tr>
<tr>
<td>(Y_B \text{ (wet) [MPa]})</td>
<td>40</td>
<td>65</td>
<td>75</td>
<td>40</td>
</tr>
<tr>
<td>(Y_B \text{ (dry) [MPa]})</td>
<td>388</td>
<td>600</td>
<td>455</td>
<td>485</td>
</tr>
<tr>
<td>(\phi)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(a_1 \text{ [10}^{-20}\text{m}^2)</td>
<td>1.8530</td>
<td>1.3397</td>
<td>2.6924</td>
<td>2.0312</td>
</tr>
<tr>
<td>(a_2 \text{ [10}^{-20}\text{m}^2)</td>
<td>-0.1955</td>
<td>-0.1157</td>
<td>-0.2143</td>
<td>-0.0326</td>
</tr>
<tr>
<td>(A_B)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Table 3.5. Parameters, initial data, and other results used for stiffness modeling of bare Nafion ionomer and Nafion-based IPMC in K⁺-form

<table>
<thead>
<tr>
<th></th>
<th>K⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>EG</td>
</tr>
<tr>
<td>$FW_{ion}$ [g/mol]</td>
<td>39.1</td>
</tr>
<tr>
<td>$CN$</td>
<td>4</td>
</tr>
<tr>
<td>$\varepsilon_1$</td>
<td>7.7</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>41</td>
</tr>
<tr>
<td>$\rho_B$ [g/cm³]</td>
<td>2.07</td>
</tr>
<tr>
<td>$w$ (wet) [%]</td>
<td>32.0</td>
</tr>
<tr>
<td>$w$ (dry) [%]</td>
<td>4.0</td>
</tr>
<tr>
<td>$Y_b$ (wet) [MPa]</td>
<td>148</td>
</tr>
<tr>
<td>$Y_b$ (dry) [MPa]</td>
<td>748</td>
</tr>
<tr>
<td>$\phi$</td>
<td>1</td>
</tr>
<tr>
<td>$a_1$ [$10^{-20}$ m²]</td>
<td>3.9657</td>
</tr>
<tr>
<td>$a_2$ [$10^{-20}$ m²]</td>
<td>-0.1817</td>
</tr>
<tr>
<td>$A_B$</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Figure 3.2. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Li$^+$ form vs. solvation; Ethylene glycol as solvent; $FW_{\text{ion}} = 6.95$, $\rho_b = 2.01$, $a_1 = 4.1500$, $a_2 = -0.1870$, $CN = 6.0$, $\phi = 1.0$

Figure 3.3. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Li$^+$ form vs. solvation; Glycerol as solvent; $FW_{\text{ion}} = 6.95$, $\rho_b = 2.01$, $a_1 = 2.3991$, $a_2 = -0.1664$, $CN = 6.0$, $\phi = 1.0$
Figure 3.4. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Li$^+$ form vs. solvation; 12-Crown-4 as solvent; $FW_{ion} = 6.95$, $\rho_B = 2.01$, $a_1 = 3.4368$, $a_2 = -0.0970$, $CN = 3.0$, $\phi = 1.0$

Figure 3.5. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Na$^+$ form vs. salvation; Ethylene glycol as solvent; $FW_{ion} = 23$, $\rho_B = 2.02$, $a_1 = 1.8530$, $a_2 = -0.1955$, $CN = 5.0$, $\phi = 1.0$
Figure 3.6. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Na⁺ form vs. salvation; Glycerol as solvent; $FW_{ion} = 23$, $\rho_B = 2.02$, $a_1 = 1.3397$, $a_2 = -0.1157$, $CN = 5.0$, $\phi = 1.0$

Figure 3.7. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Na⁺ form vs. salvation; 15-Crown-5 as solvent; $FW_{ion} = 23$, $\rho_B = 2.02$, $a_1 = 2.6924$, $a_2 = -0.2143$, $CN = 3.0$, $\phi = 1.0$
Figure 3.8. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in Na\(^+\) form vs. salvation; 18-Crown-6 as solvent; \(FW_{ion} = 23, \; \rho_B = 2.02, a_1 = 2.0312, a_2 = -0.0326, CN = 3.0, \phi = 1.0\)

Figure 3.9. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in K\(^+\) form vs. salvation; Ethylene glycol as solvent; \(FW_{ion} = 39, \; \rho_B = 2.07, a_1 = 3.9657, a_2 = -0.1817, CN = 4.0, \phi = 1.0\)
Figure 3.10. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in $\text{K}^+$ form vs. salvation; Glycerol as solvent; $FW_{\text{ion}} = 39$, $\rho_B = 2.07$, $a_1 = 1.3016$, $a_2 = -0.1498$, $CN = 4.0$, $\phi = 1.0$

Figure 3.11. Uniaxial stiffness (Young’s modulus) of bare Nafion 117 and IPMC (data points and the solid curve, model) in $\text{K}^+$ form vs. salvation; 15-Crown-5 as solvent; $FW_{\text{ion}} = 39$, $\rho_B = 2.07$, $a_1 = 2.8069$, $a_2 = -0.0246$, $CN = 3.0$, $\phi = 1.0$
3.5. IPMC ACTUATION

3.5.1. Tip Displacement

We assume that, in response to changes in the clusters effective pressure, the solvent will diffuse into and out of the clusters until the elastic resistance of the matrix polymer in the boundary layers balances the internal cluster pressure. The resulting strains are called eigenstrains. For a cantilevered sample in pure bending, the radius of curvature, $R_b$, is related to the maximum bending strain, $\varepsilon_{\text{max}}$, by

$$
\varepsilon_{\text{max}} \approx \pm \frac{H}{R_b},
$$

(3.24)
where $H$ is the half of IPMC sample thickness (see Figure 3.13).

![Figure 3.13. Schematic of the cross section of an IPMC](image)

The volumetric strain, $\varepsilon_v$, is given by

$$\varepsilon_v = \ln (1 + w(x,t)).$$

(3.25)

Relating the bending due to the volumetric strain to the bending resistance of the sample, the radius of curvature, $R_b$, as a measure of actuation, becomes

$$\frac{L}{R_b} = \frac{L}{2H^3(3Y_{IPMC} - 2Y_h)} \int h Y_{BL}(w(x,t)) x \ln (1 + w(x,t)) dx,$$

(3.26)

where $h$ is the thickness of the bare ionomer, $L$ is the cantilever's length, $Y_{BL}(w(x,t))$ is the boundary layer's Young modulus, $x$ measures distance along the cross section of the strip from its mid-point, as shown in Figure 3.13, and a strip of unit width is considered.
3.5.2. Voltage induced Cation Redistribution

The redistribution of cations under an applied potential is modeled using the coupled electrochemical equations that characterize the net flux of the species, caused by the electrochemical potentials (chemical concentration and electric field gradients). The total flux consists of cation migration and solvent transport. Cation migration is assumed to occur first, followed by the diffusion-controlled solvent transport. The flux, \( J_i \), of species \( i \) is characterized by [Bockris and Reddy (1998), Shewmon (1989), and Eikerling et al. (1998)],

\[
J_i = -\frac{C_i D_i \partial \mu_i}{RT} + C_i \nu_i, \tag{3.27}
\]

where \( D_i \) is the diffusivity coefficient, \( \mu_i \) is the chemical potential, \( C_i \) is the concentration, \( \nu_i \) is the velocity of species \( i \). The chemical potential is defined by

\[
\mu_i = \mu_{i0} + RT \ln(\gamma_i C_i) + z_i \phi F, \tag{3.28}
\]

where \( \mu_{i0} \) is the reference chemical potential, \( \gamma_i \) is the affinity of species \( i \), \( z_i \) is the species charge, and \( \phi \) is the electric potential. We assume an ideal solution where \( \gamma_i = 1 \), and, since there are only one type of cations, drop the subscript \( i \) and rewrite (3.27) as

\[
J = -D \frac{\partial C}{\partial x} - \frac{zDF}{RT} \frac{\partial \phi}{\partial x} + CV, \tag{3.29}
\]
where \( D \), \( C \), and \( z \) are the ionic diffusivity coefficient, concentration, and charge of the cations, respectively. The variation in electric potential field, \( \phi = \phi(x,t) \), in the membrane is governed by the basic Poisson's electrostatic equations [Jackson (1962) and Cheston (1964)],

\[
\frac{\partial (\kappa E)}{\partial x} = z(C - C^-)F, \quad E = -\frac{\partial \phi}{\partial x},
\]

(3.30)

where \( E \) and \( \kappa \) are the electric field and the electric permittivity, respectively. Now, since the solvent velocity is very small, we may neglect the last term in (3.29), and in view of (3.30) and continuity, obtain

\[
J(x,t) = -D \left[ \frac{\partial C(x,t)}{\partial x} - zC(x,t) \left( \frac{F}{RT} \right) E(x,t) \right],
\]

(3.31)

\[
\frac{\partial C(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x},
\]

(3.32)

\[
\frac{\partial E(x,t)}{\partial x} = z \left( \frac{F}{\bar{\kappa}} \right) (C(x,t) - C^-).
\]

(3.33)

Here \( \bar{\kappa} \) is the overall electric permittivity of the solvated IPMC sample that can be estimated from its measured effective capacitance. The above system of equations can be directly solved numerically, or they can be solved analytically using approximations. In
the following sections, both methods are considered and the results are presented and compared.

3.5.2.1. Finite-difference Solution of Cation Transport

An efficient finite-difference simulation procedure for the solution of the steady-state and transient versions of the Nernst-Plank and Poisson system of equations is used, following Brumleve and Buck [1978]. This allows for both spatial and temporal variations. The resulting implicit and non-linear equations are solved using an iterative Newton-Raphson technique [Carnahan et al., 1969]. Equation (3.31) to (3.33) are converted into finite difference form, as follows:

\[
J_j = -D \left[ \frac{C_{j+1} - C_j}{\Delta XM_j} - z \frac{C_{j+1} + C_j}{2} \left( \frac{F}{RT} \right) E_j \right], \quad 1 \leq j \leq N-1, \quad (3.34)
\]

\[
C_j - C_j^0 = -\frac{\Delta t}{\Delta XB_j} (J_j - J_{j-1}), \quad 1 \leq j \leq N, \quad (3.35)
\]

\[
\frac{\partial E_j}{\partial x} = \frac{z}{K} \left( C_j - C^- \right), \quad 1 \leq j \leq N, \quad (3.36)
\]

\[
\Delta t = t_{k+1} - t_k, \quad \Delta XB_i = \frac{x_2}{2}, \quad \Delta XB_N = \frac{x_N - x_{N-1}}{2}, \quad (3.37)
\]

\[
\Delta XM_j = x_{j+1} - x_j, \quad 1 \leq j \leq N-1, \quad (3.37)
\]

\[
\Delta XB_j = \frac{x_{j+1} - x_{j-1}}{2}, \quad 2 \leq j \leq N-1,
\]

\[N = \text{Total number of spatial elements.}\]
The physical parameters in equations (3.34) to (3.36) are rendered dimensionless, as
follows:

\[ J'(x,t) = J(x,t) \ell / D_0 C^- \quad x = x/\ell \quad \text{and} \quad E'(x,t) = E(x,t) \ell F / RT, \]
\[ \phi'(x,t) = \phi(x,t) F / RT \quad D = D / D_0 \quad C(x,t) = C(x,t)/C^- \quad (3.38) \]
\[ K = \kappa RT / C^- \ell^2 F^2 \quad t = tD_0 / \ell^2. \]

Substituting (3.34) in (3.35) and using (3.30) to relate the electric field to the electric
potential, we obtained,

\[ C_j - C_j^0 = \frac{\Delta t}{\Delta X \beta_j} \left[ D \left( \frac{C_2 - C_1}{\Delta X M_j} - \frac{C_2 + C_1}{\Delta X M_j} \frac{\phi_j' - \phi_j}{2} \right) \right] = 0, \quad j = 1, \quad (3.39) \]

\[ C_j - C_j^0 = \frac{D \Delta t}{\Delta X \beta_j} \left[ C_{j+1} - C_j - \frac{C_j - C_{j-1}}{\Delta X M_j} \right. \]
\[ \left. - \frac{z}{2} \left[ (C_{j+1} + C_j) \frac{\phi_{j+1}' - \phi_j}{\Delta X M_j} + (C_j + C_{j-1}) \frac{\phi_j' - \phi_{j-1}}{\Delta X M_{j-1}} \right] \right] = 0, \quad 2 \leq j \leq N - 1, \quad (3.40) \]

\[ C_N - C_N^0 = \frac{\Delta t}{\Delta X \beta_N} \left[ -D \left( \frac{C_N - C_{N-1}}{\Delta X M_1} - \frac{C_N + C_{N-1}}{\Delta X M_{N-1}} \frac{\phi_N' - \phi_{N-1}}{2} \right) \right] = 0, \quad j = N, \quad (3.41) \]

\[ \frac{\phi_{j+1}' - \phi_j}{\Delta X M_j} - \frac{\phi_j' - \phi_{j-1}}{\Delta X M_{j-1}} - \frac{K}{\Delta X M_j} \left[ (C_j) - 1 \right] = 0, \quad 2 \leq j \leq N - 1. \quad (3.42) \]

To improve efficiency, the resulting equations are solved using smaller time-steps, \( \Delta t \),
at the start of the actuation, and larger \( \Delta t \) at later time. Similarly, smaller grid spacing is
used close to the electrodes, and larger ones near the center of the membrane. The values
of the ion concentration and the electric potential are defined at the center of the grids (separated by $\Delta XB$), while those of the electric field are defined at their boundaries (separated by $\Delta XM$). The finite-difference spatial mesh is illustrated in Figure 3.14. To simulate the transient response, very small time steps are used.

![Figure 3.14. Typical simulation grid showing the location of the concentration, electric potential, and electric field; $E_0$, $\phi_1$, and $C_1$ are defined at the left interface, and $E_n$, $\phi_n$, and $C_n$ at the right interface. Throughout the rest of the grid, the concentration and electric potential are defined at the center of each volume element and electric fields are defined at its boundaries.](image)

Equations (3.39) and (3.41) guarantee zero cation flux into and out of the membrane. Also, the electric potential at the two ends are prescribed by,

$$
\phi_1 = -\left(\frac{\varphi_0}{2}\right), \quad \phi_n = \left(\frac{\varphi_0}{2}\right).
$$

(3.43)
where $\varphi_0$ is the applied potential. To apply Newton-Raphson method to the problem at hand, we recast equations (3.39) to (3.42) in the following difference form:

$$a_j = -\frac{D\Delta t}{\Delta X B_j} \left[ \frac{1}{\Delta X M_j} - \frac{z}{2} \left( \frac{\phi'_{j+1} - \phi'_{j-1}}{\Delta X M_{j-1}} \right) \right], \quad 2 \leq j \leq N,$$

$$b_j = 1 + \frac{D\Delta t}{\Delta X B_j} \left[ \left( \frac{1}{\Delta X M_j} + \frac{1}{\Delta X M_{j-1}} \right) - \frac{z}{2} \left( \frac{\phi'_{j+1} - \phi'_{j-1}}{\Delta X M_{j-1}} \right) \right], \quad 2 \leq j \leq N - 1,$$

$$c_j = \frac{D\Delta t}{\Delta X B_j} \left[ -\frac{z}{2} \left( \frac{\phi'_{j+1} - \phi'_{j}}{\Delta X M_j} \right) - \frac{1}{\Delta X M_j} \right], \quad 1 \leq j \leq N - 1,$$

$$d_j = -\frac{D\Delta t}{\Delta X B_j} \left[ \frac{C_j + C_{j-1}}{\Delta X M_{j-1}} \right], \quad 3 \leq j \leq N,$$

$$f_j = -\frac{D\Delta t}{\Delta X B_j} \left[ \frac{C_{j+1} + C_j}{\Delta X M_j} \right], \quad 3 \leq j \leq N,$$

$$y_j = -\frac{K}{\Delta X M_j} \left[ \frac{1}{\Delta X M_j} + \frac{1}{\Delta X M_{j-1}} \right], \quad 2 \leq j \leq N - 1,$$

$$x_j = z, \quad 2 \leq j \leq N - 1,$$

$$s_j = \frac{K}{\Delta X M_j} \left[ \frac{1}{\Delta X M_{j-1}} \right], \quad 3 \leq j \leq N - 1,$$

$$w_j = \frac{K}{\Delta X M_j} \left[ \frac{1}{\Delta X M_j} \right], \quad 2 \leq j \leq N - 1,$$

$$t_j = \frac{D\Delta t}{\Delta X B_j} \left[ \frac{z}{2} \left( \frac{C_{j+1} + C_j}{\Delta X M_j} + \frac{C_j + C_{j-1}}{\Delta X M_{j-1}} \right) \right], \quad 2 \leq j \leq N - 1,$$

$$g_1 = C^*_1 - C^*_0 = \frac{1}{\Delta X B_1} \left[ D\Delta t \left( \frac{C^*_1 - C^*_0}{\Delta X M_1} - \frac{z}{2} \frac{\phi'_{2} - \phi'_{1}}{\Delta X M_1} \right) \right], \quad j = 1,$$
The results for cation transfer for a Nafion-based IPMC in Li⁺-form and with water as solvent, under DC electric potential, $\varphi_0$, of 1.25V are shown in Figures 3.15 and 3.16 which show the variation of the normalized charge density, $Q(x,t)$, through the thickness of the IPMC sample at indicated instants.

In the simulation, it is assumed that $\Delta X M_j = \Delta X B_j$, $j = 2, 3, ..., N - 1$, and 40 elements are used within $1/7$ of the sample thickness at each ends. For the rest of the ionomer cross-section close to the center, we have used 40 elements. For the time steps, we have used 1ms for $t < IT$ and 1s thereafter until the steady-state solution is reached; for the simulation results that are discussed in what follows, $IT = 150$ has been used.
Figure 3.15. Anode boundary layer cation depletion over time; Nafion-based IPMC in Li$^+$-form with water as solvent, 1.25V DC electric potential

Figure 3.16. Numerical results for the anode and cathode cation distribution at equilibrium; Nafion-based IPMC in Li$^+$-form with water as solvent, 1.25V DC electric potential
Figure 3.17. Numerical results for the anode and cathode boundary layer formation; Nafion-based IPMC in Li\(^+\)-form with water as solvent, 1.25V DC electric potential

The results suggest that the boundary layers initially form anti-symmetrically, and then become non-symmetric. The anode boundary layer forms gradually although the timescale for this formation is small (0.25 seconds for the example discussed). This matches the experimental results shown in Figure 3.19. The effective permittivity, \( \varepsilon_r \), is calculated to be 0.0269F/m, based on the measured effective capacitance of 11.9mF/cm\(^2\); and \( C^- \) is calculated to be 1,185mol/m\(^3\), based on the solvent uptake of 53% for the bare ionomer.

Nemat-Nasser and Li [2000] assumed an anti-symmetric cation distribution along the sample and showed that it then must have the following form:
Nemat-Nasser [2002] has shown that the final steady-state cation distribution is not anti-symmetric, but, rather, it is completely non-symmetric. Numerical results show that the cation distribution along the sample starts from an anti-symmetric solution, but it then becomes non-symmetric as the cations of the clusters in the anode boundary layer are depleted.

### 3.5.2.2. Approximate Solution with One Timescale

Ignoring small terms in equations (3.31) to (3.33) we obtain the following expression [Nemat-Nasser, 2002]:

\[
\frac{\partial}{\partial \chi} \left[ \frac{\partial (\kappa E)}{\partial t} - D \left( \frac{\partial^2 (\kappa E)}{\partial \chi^2} - \frac{C^{-2} F^2}{\kappa RT} (\kappa E) \right) \right] = 0. \tag{3.46}
\]

This equation provides a natural length scale, \( \ell \), defined by (3.45)\(_2\), and a natural timescale, \( \tau \), given by

\[
\tau = \frac{\ell^2}{D}. \tag{3.47}
\]

\[
C(x) = C^- + \frac{\kappa \varphi_0}{2F\ell^2 \sinh(h/\ell)} \sinh(x/\ell), \quad \ell = \left( \frac{\kappa RT}{C^- F^2} \right)^{1/2}. \tag{3.45}
\]
The final (equilibrium) length of the anode boundary layer that is completely depleted of its cations is give by

\[ \ell' = \left( \frac{2\phi_0 F}{RT} - 2 \right) \ell. \]  
(3.48)

Nemat-Nasser [2002] shows that the final (equilibrium) cation concentration, the electric field, and the electric potential within the anode boundary layer, \(-h < x \leq -h + \ell'\), are given by

\[ C = 0, \quad E^{(1)}(x) = \frac{1}{\ell} (\Delta \left. \frac{x}{\ell} + E_0\right), \quad \phi^{(1)}(x) = K_0 \left( \frac{x}{\ell} \right)^2 - E_0 \frac{x}{\ell} + A_0, \]

\[ K_0 = \frac{C^{-} F \ell^2}{k} = \frac{RT}{F}. \]  
(3.49)

Similarly, in the cathode boundary layer, \(-h + \ell' < x \leq h\), Nemat-Nasser [2002] has obtained,

\[ E^{(2)}(x) = \frac{1}{\ell} \left[ B_0 \exp(x/\ell) + B_1 \exp(-x/\ell) \right], \]
\[ \phi^{(2)}(x) = -B_0 \exp(x/\ell) + B_1 \exp(-x/\ell) + B_2, \]
\[ \frac{C(x) - C^{-}}{C^{-}} = \frac{F}{RT} \left( B_0 \exp(x/\ell) - B_1 \exp(-x/\ell) \right). \]  
(3.50)
where $E_0$, $A_0$, $B_0$, $B_1$ and $B_2$ are the integration constants, to be fixed using the boundary and continuity conditions, leading to the following expressions:

\[
E_0 = K_0(1-a'), \quad A_0 = \frac{\varphi_0}{2} - K_0\left(1 + \frac{\ell'}{\ell} - 2a\right),
\]
\[
B_0 = \exp(-a)\left(\frac{\varphi_0}{2} + B_1\exp(-a) + B_2\right), \quad B_1 = K_0\exp(-a'), \quad B_2 = \frac{\varphi_0}{2} - \frac{1}{2}K_0\left(1 + \frac{\ell'}{\ell}\right)^2 + 1,
\]

where $a \equiv h/\ell$ and $a' \equiv h'/\ell$ are generally very small. Using this fact, the above constants are obtained from the following boundary conditions:

\[
C(-h') = 0, \quad h' = h - \ell', \quad E^{(1)}(-h') = E^{(2)}(-h'), \quad \phi^{(1)}(-h') = \phi^{(2)}(-h'), \quad \int_{-h}^{h}(C(x,t) - C^-)dx = 0.
\]

As an example, the equilibrium charge distribution across the Nafion-based IPMC in Li$^+$-form with water as solvent, under DC electric potential, $\varphi_0 = 1.25V$ and after 300 seconds, using the approximate solution (ignoring small terms) is shown in Figure 3.18. This distribution is attained gradually over time. Thus, it is necessary to also estimate the temporal charge variation. Nemat-Nasser [2002] shows that, with good accuracy, the (equilibrium) spatial variation of the charge distribution can be modified to include the temporal effect using the following form:
\[
\frac{C(x) - C^-}{C^-} = g(t) \left[ \frac{F}{RT} \left( B_0 \exp(x/\ell) - B_1 \exp(-x/\ell) \right) \right], \quad g(t) = 1 - \exp(-t/\tau). \quad (3.53)
\]

Figure 3.18. Variation of the normalized charge density, \( Q(x,t) \), through the thickness of a Nafion-based IPMC in Li\(^+\)-form with water as solvent; with \( a = h/\ell = 136, \ \phi_0 = 1.25 \text{V} \)

Figure 3.19. Comparison between various approaches for the solution of cation transport over time; Nafion-based IPMC in Li\(^+\)-form with water as solvent, 1.25V DC electric potential
3.5.2.3. Approximate Solution with Two Timescales

The approximate solution with one timescale can be improved by introducing a second timescale. To this end, we start with the basic equation (3.46), and assume that the solution is anti-symmetric in a period less than, say, $\tau_1$, given by

$$E(x) = \frac{1}{\ell} \left[ B_0 \exp\left( \frac{x}{\ell} \right) + B_1 \exp\left( -\frac{x}{\ell} \right) \right], \quad E = -\frac{\partial \phi}{\partial x},$$

$$\phi(-h) = \left( \frac{\varphi_0}{2} \right), \quad \phi(h) = -\left( \frac{\varphi_0}{2} \right), \quad \int_{-h}^{h} \left( C(x,t) - C^- \right) dx = 0,$$

where, in view of the boundary conditions (3.54), we also have

$$B_0 = B_1 = \frac{\varphi_0}{2} \exp(-a).$$

Now, we assume that for times greater than $\tau_1$, the anode boundary layer growth is governed by

$$\ell'(t) = \sqrt{\frac{2\phi_0'(t)F}{RT}} - 2,$$

where the function $\phi_0'(t)$ is chosen to have the follow form:
\[ \phi'_0(t) = \varphi_0 \left[ 1 - \exp \left( -\frac{t - \tau_1}{\tau_2} \right) \right], \]  
\[ \text{(3.57)} \]

based on the numerical results and experimental observations. Then, the final solution becomes,

\[ \frac{C(x,t) - C^-}{C^-} = \frac{F}{RT} \left[ B_0(t) \exp(x/\ell) - B_1(t) \exp(-x/\ell) \right], \]

\[ B_0(t) = \exp(-a) \left[ \frac{\phi'_0(t)}{2} + B_1 \exp(-a) + B_2(t) \right], \]

\[ B_1 = K_0 \exp(-a'), \quad B_2(t) = \frac{\phi'_0(t)}{2} - \frac{1}{2} K_0 \left[ \left( 1 + \frac{\ell'(t)}{\ell} \right)^2 + 1 \right], \]

\[ \text{(3.58)} \]

where \( B_0(t), B_1(t), \) and \( B_2(t) \) are time-dependent parameters, resulting from spatial integration of the basic equations.

The results of accumulated charge in the cathode boundary layer for various approaches are presented and compared with the experimental results in Figure 3.19. As is seen, the numerical results and the results of the approximate solution with two timescales nicely fit the experimental data. We used \( \tau_1 = 0.25 \) seconds and \( \tau_2 = 6 \) seconds in the two timescale approach to obtain the results shown in Figure 3.19.

3.5.3. Boundary Layers

As stated, the application of an electric potential produces two thin boundary layers, one near the anode and the other near the cathode electrodes, while maintaining the
overall electric neutrality in the IPMC strip. The cation imbalance within the clusters of each boundary layer 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.

3.5.3.1. Anode Boundary Layer

At equilibrium state, the total effective anode boundary layer length, $L_A$, is given by

$$L_A \equiv \ell + \ell' = \left( \frac{2\varphi_0 F}{RT} - 1 \right) \ell, \quad (3.59)$$

The normalized total ion (cation and anion) concentration within each boundary layer is

$$\nu(x,t) = \frac{C(x,t)}{\overline{C}} + 1. \quad (3.60)$$
The osmotic pressure then is

$$\Pi(x,t) = \frac{\phi Q_b K_0}{w(x,t)} \nu(x,t).$$

(3.61)

As the anode boundary layer is being depleted of its cations, electrostatic interaction forces develop among the remaining fixed anions, introducing an additional pressure, say, $p_{AA}$, within the cluster, while at the same time, the dipole-dipole interaction forces, $p_{ADD}$, are being diminished. The two effects are coupled, since the cation distribution within a cluster would depend on its concentration. Nemat-Nasser [2002] has simplified the required analysis by assuming that the two effects are uncoupled. We follow the same approach here to calculate $p_{AA}$, arriving at

$$p_{AA}(x,t) = \frac{1}{18\kappa(x,t)} Q_b^2 \frac{R_0^2}{[w(x,t)]^{4/3}} \left( \frac{C(x,t)}{C^-} + 1 \right),$$

(3.62)

where $\kappa(x,t)$ is the effective electric permittivity of the clusters, $R_0$ is the initial (dry) cluster size; for the definition and derivation of various parameters, see Nemat-Nasser [2002]. Similarly, the corresponding $p_{ADD}$ is estimated from

$$p_{ADD}(x,t) = \frac{1}{3\kappa(x,t)} Q_b \left( \frac{\alpha(x,t)}{w(x,t)} \right)^2 \left( \frac{C(x,t)}{C^-} \right).$$

(3.63)
The total pressure within a typical anode boundary layer cluster hence is

\[ p_c(x,t) = \Pi(x,t) + p_{AA}(x,t) + p_{ADD}(x,t). \]  

\[ (3.64) \]

### 3.5.3.2. Cathode Boundary Layer

Consider now the clusters within the cathode boundary layer. Unlike the anode boundary layer, the clusters in the cathode boundary layer are filled with additional cations. Distribution of cations inside the cathode boundary layer is not uniform. The normalized total ion concentration and the osmotic pressure within the cathode boundary layer are defined by (3.60) and (3.61).

In the cathode boundary layer, we identify two forms of electrostatic interaction forces. One is repulsion due to the cation-anion pseudo-dipoles already present in the clusters, and the other is due to the extra cations that migrate into the clusters and interact with the existing pseudo-dipoles. The additional stresses produced by this latter effect may tend to expand or contract the clusters, depending on the distribution of cations relative to fixed anions. We again model each effect separately, although in actuality they are coupled. The dipole-dipole interaction pressure in the cathode boundary layer clusters is estimated as follows:

\[ p_{CDD}(x,t) = \frac{1}{3\kappa(x,t)} Q^2 \left( \frac{\alpha(x,t)}{w(x,t)} \right)^2 \left( \frac{C(x,t)}{C^-} \right). \]

\[ (3.65) \]

We represent the interaction between the pre-existing dipoles and the additional cations that move into a cluster under the action of an applied voltage, by dipole-cation interaction stresses defined by,
For sulfonates in Nafion-based IPMC, we expect extensive restructuring and redistribution of the extra cations. It appears that this process underpins the observed reverse relaxation of the Nafion-based IPMC strip. In fact this redistribution of the cations within clusters in the cathode boundary layer may quickly diminish the value of \( p_{DC} \) to zero or even render it negative. To represent this, equation (3.66) is modified by a relaxation factor, \( g_1(t) \), and rewritten as

\[
p_{DC}(x,t) = \frac{2Q_b^{-2}}{9k(x,t)} \frac{R_0 \alpha(x,t)}{[w(x,t)]^{5/3}} \left( \frac{C(x,t)}{C^-} + 1 \right) g_1(t),
\]

(3.67)

\[
g_1(t) = [r_0 + (1-r_0) \exp(-t/\tau')] \quad r_0 < 1,
\]

where \( \tau' \) is the relaxation time, and \( r_0 \) is the equilibrium fraction of the dipole-cation interaction forces.

Total pressure inside the cathode boundary layer cluster hence is

\[
p_c(x,t) = \Pi(x,t) + p_{DC}(x,t) + p_{CDD}(x,t).
\]

(3.68)

### 3.5.4. Variation in Solvent Uptake

Pressure inside the clusters within the backbone ionomer, \( p_c(x,t) \), is resisted by the elastic stress \( \sigma_r \), at the cluster boundary, \( a_0 \):
\[ \sigma_r(a_0, t) = -p_0(t) + K(t) \left( \frac{w(x, t)}{w_0} \right)^{-4/3}, \quad (3.69) \]

As a result, the net pressure, \( t_c \), on the solvent inside the cluster can be defined as

\[ t_c(x, t) = -\sigma_r(a_0, t) + p_c(x, t), \quad (3.70) \]

where (3.64) and (3.68) define the corresponding \( p_c(x, t) \). The ion flux must satisfy continuity equation (3.22). For the solvent, we have

\[ \frac{\dot{w}(x, t)}{1 + w(x, t)} + \frac{\partial v(x, t)}{\partial x} = 0. \quad (3.71) \]

The solvent exchange in the clusters should be calculated using the diffusion equation and the initial boundary conditions. Since the anode boundary layer is rather thin, we may assume a uniform \( w(x, t) \) and \( t_c \) across this boundary layer. So in the anode and cathode boundary layers, (3.71) is approximated by

\[ \frac{\dot{w}(x, t)}{1 + w(x, t)} = D_{bl} t_c(x, t), \quad (3.72) \]

where \( D_{bl} \) is introduced to include the effect of the anode and cathode boundary layer thickness in hydraulic permeability. We have assumed that this value is constant across the anode and cathode boundary layers.
3.5.5 Response upon Shorting

Shorting refers to the state when the electric potential is removed and the two faces of the sample are electrically connected. In this case, experiments suggest that some cations transport relatively rapidly into the cation-depleted anode boundary layer while a fraction of cations within the cation-rich cathode boundary layer transport back into the interior of the IPMC. The remaining extra cations in the cathode boundary layer then move slowly out into the interior region till the equilibrium condition (a uniform charge distribution) is eventually achieved; which may take a rather long time depending on the cations and the nature of the solvent. To model this phase of actuation, it is assumed that the equations governing the discharge process are similar to those of the charging process but now we start with a set of initial conditions that characterize the state just prior to shorting.

Assume that the shorting occurs at \( t = T_s \). Let \( \tau'' \) define the time scale for the discharge process. Furthermore, assume that a fraction, \( r \), of the extra cations remain in the cathode boundary layer, i.e., within this time scale. Thus, in the anode boundary layer we have, for \( t \geq T_s \),

\[
p_{ADD}(x,t) = \frac{1}{3\kappa(x,t)} Q^2 \left( \frac{\alpha(x,t)}{w(x,t)} \right)^2 \left( \frac{C(x,t)}{C^-} \right)^2 \left[ 1 - g_2(t) \right], \tag{3.73}
\]

\[
p_{AA}(x,t) = \frac{1}{18\kappa(x,t)} Q^2 R_0 \left( \frac{C(x,t)}{C^-} + 1 \right)^{1/3} g_2(t), \tag{3.74}
\]

\[
g_2(t) = r + (1 - r) \exp \left[ -\frac{t + T_s}{\tau''} \right]. \tag{3.75}
\]
In addition, Eq. (3.60) for total ion concentration is modified to read

\[ \nu(x,t) = \frac{C(x,t)}{C^-} + 1 - g_2(t). \]  \tag{3.76} 

The above equations are obtained by simply assuming that the discharge is the reverse of the charging process, although in reality the various involved processes are coupled. In the cathode boundary layer, for \( t \geq T_s \), we set:

\[ p_{CDD}(x,t) = \frac{1}{3 \kappa(x,t)} Q_0^2 \left( \frac{\alpha(x,t)}{w(x,t)} \right)^2 \left( \frac{C(x,t)}{C^-} \right) \left[ 1 - g_2(t) \right], \]  \tag{3.77} 

\[ p_{DC}(x,t) = \frac{2Q_0^2}{3 \kappa(x,t)} \frac{R_0 \alpha(x,t)}{[w(x,t)]^{5/3}} \left( \frac{C(x,t)}{C^-} + 1 \right) g_1(t) g_2(t). \]  \tag{3.78} 

\[ \nu(x,t) = \frac{C(x,t)}{C^-} + 1 + g_2(t). \]  \tag{3.79} 

As an example, we summarize the procedure that has been followed to model a Nafion-based IPMC sample in Na\(^+\)-form with water as the solvent, and subjected to 1.25V DC potential. Values of \( a_1 \) and \( a_2 \) are obtained from the stiffness model. The parameter \( R_0 \) must be calculated with some care. Since \( w_i \approx \left( a_i / R_0 \right)^3 \), where \( w_i \) is the initial volume fraction of solvent in the Nafion part of the IPMC, and \( a_i \) is the cluster size at solvent uptake \( w_i \), we may set \( R_0 \approx w_i^{-1/3} a_i \). The cluster size, \( a_i \), is obtained from the Gierke cluster size model [Gierke and Hsu, 1982], as modified by Li and Nemat-
Nasser [2000]; a summary is given in Appendix 3.7. Based on that model, a cluster size, \( a_i = 1.8 \text{ nm} \), is calculated and assumed to exist prior to the application of the potential.

Table 3.6 gives the values of various parameters used for the purpose of modeling of the actuation response. As discussed earlier, two different timesteps are used to reduce the simulation time as noted in Table 3.6. It is noteworthy to mention that the value for the effective capacitance used for the modeling of the actuation is different than that which would be obtained from the effective capacitance measurements. The value used here is based on the experimentally measured charge transfer.

Figure 3.20 shows the charge transfer over time for the strip of Nafion-based IPMC in Na⁺-form with water, subjected to a 1.25V step potential for 46.7sec and then shorted. In the figure, the heavy solid curve represents the model and the geometric symbols connected by solid curve represent the experimental results. The model in this case predicts faster charge transfer than that observed experimentally, as is seen in Figure 3.20. Figure 3.21 shows the corresponding variation of the normalized curvature with time.

The same procedure is used to model Nafion-based IPMCs in other cation forms with other solvents [Nemat-Nasser and Zamani, 2005]. For solvents such as glycerol or crown ethers, the sensitivity of our measurement devices was insufficient to discern in certain cases the necessary signals from that of the background noise. So for the purpose of modeling, the measured effective capacitance is used. Tables 3.7 to 3.9 represent various values of the model parameters for Nafion-based IPMCs with indicated cations and solvents. The corresponding actuation graphs are given in Figures 3.22 to 3.33.
Figure 3.20. Charge transfer over time for a strip of Nafion-based IPMC in Na⁺-form with water, subjected to a 1.25V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 46.7sec.

Figure 3.21. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Na⁺-form with water, subjected to a 1.25V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 46.7sec.
Table 3.6. Parameters used for actuation response modeling; Nafion-based IPMC in Na\(^+\) form and water as solvent, subjected to a step potential and then shorted

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Na(^+) - Water</th>
</tr>
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<tr>
<td>(\Delta t) [seconds]</td>
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</tr>
<tr>
<td>(N)</td>
<td>100</td>
</tr>
<tr>
<td>(a_f) [nm]</td>
<td>1.8</td>
</tr>
<tr>
<td>(D_{bl.}) ([m^2/\text{sec}])</td>
<td>5.0(\times10^{-2})</td>
</tr>
<tr>
<td>(2h) [(\mu)m]</td>
<td>192</td>
</tr>
<tr>
<td>(2H) [(\mu)m]</td>
<td>204</td>
</tr>
<tr>
<td>(L) [mm]</td>
<td>28.6</td>
</tr>
<tr>
<td>(w_f) [%]</td>
<td>50</td>
</tr>
<tr>
<td>(\varphi_0) [V]</td>
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</tr>
<tr>
<td>(r_0)</td>
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</tr>
<tr>
<td>(\overline{\kappa}) [F/m]</td>
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</tr>
<tr>
<td>(\tau) [seconds]</td>
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</tr>
<tr>
<td>(\tau') [seconds]</td>
<td>0.1</td>
</tr>
<tr>
<td>(r)</td>
<td>0.1</td>
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<tr>
<td>(\tau'') [seconds]</td>
<td>0.001</td>
</tr>
</tbody>
</table>
Table 3.7. Parameters used for actuation response modeling; Nafion-based IPMC in Li$^+$ form and various solvents, subjected to a step potential and then shorted.

<table>
<thead>
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<th>Parameters</th>
<th>Ethylene Glycol</th>
<th>Glycerol</th>
<th>12CR4</th>
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</thead>
<tbody>
<tr>
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<td>0.001 / 5</td>
<td>0.001 / 10</td>
</tr>
<tr>
<td>$N$</td>
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<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$a_i$ [nm]</td>
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<td>2.3</td>
<td>2.0</td>
</tr>
<tr>
<td>$D_{Bl}$ [m$^2$/sec]</td>
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<td>1.0×10$^{-6}$</td>
<td>5.0×10$^{-4}$</td>
</tr>
<tr>
<td>$2h$ [µm]</td>
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<td>212</td>
<td>285</td>
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<tr>
<td>$2H$ [µm]</td>
<td>309</td>
<td>232</td>
<td>306</td>
</tr>
<tr>
<td>$L$ [mm]</td>
<td>40.4</td>
<td>30.8</td>
<td>28.6</td>
</tr>
<tr>
<td>$w_i$ [%]</td>
<td>271</td>
<td>125</td>
<td>145</td>
</tr>
<tr>
<td>$\varphi_0$ [V]</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$r_0$</td>
<td>0.9</td>
<td>0.02</td>
<td>0.95</td>
</tr>
<tr>
<td>$\bar{\kappa}$ [F/m]</td>
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<td>1.38×10$^{-1}$</td>
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</tr>
<tr>
<td>$\tau$ [seconds]</td>
<td>4.0</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>$\tau'$ [seconds]</td>
<td>1.0</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>$r$</td>
<td>0.99</td>
<td>0.1</td>
<td>0.95</td>
</tr>
<tr>
<td>$\tau''$ [seconds]</td>
<td>1000</td>
<td>100</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Table 3.8. Parameters used for actuation response modeling; Nafion-based IPMC in Na$^+$ form and various solvents, subjected to a step potential and then shorted.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ethylene Glycol</th>
<th>Glycerol</th>
<th>15CR5</th>
<th>18CR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta t$ [seconds]</td>
<td>0.001 / 1</td>
<td>0.001 / 5</td>
<td>0.001 / 10</td>
<td>0.001 / 10</td>
</tr>
<tr>
<td>$N$</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$a_f$ [nm]</td>
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<td>2.8</td>
<td>3.45</td>
</tr>
<tr>
<td>$D_{BL}$ [m$^2$/sec]</td>
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<td>$5.0 \times 10^{-5}$</td>
<td>$3.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>$2h$ [$\mu$m]</td>
<td>290</td>
<td>212</td>
<td>285</td>
<td>248</td>
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<td>309</td>
<td>232</td>
<td>306</td>
<td>264</td>
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<tr>
<td>$L$ [mm]</td>
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<td>30.8</td>
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<td>28.6</td>
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<td>$w_i$ [%]</td>
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<td>67</td>
<td>181</td>
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<td>$\varphi_0$ [V]</td>
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<td>2.0</td>
<td>2.0</td>
<td>3.0</td>
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<td>0.72</td>
<td>0.94</td>
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<tr>
<td>$\tilde{\kappa}$ [F/m]</td>
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<td>$1.38 \times 10^{-1}$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>$8.0 \times 10^{-3}$</td>
</tr>
<tr>
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<td>5.0</td>
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<td>1</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>$r$</td>
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<td>0.1</td>
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</tr>
<tr>
<td>$\tau''$ [seconds]</td>
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<td>100</td>
<td>50</td>
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</tr>
</tbody>
</table>
Table 3.9. Parameters used for actuation response modeling; Nafion-based IPMC in K$^+$ form and various solvents, subjected to a step potential and then shorted

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ethylene Glycol</th>
<th>Glycerol</th>
<th>15CR5</th>
<th>18CR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta t$ [seconds]</td>
<td>0.001 / 5</td>
<td>0.001 / 5</td>
<td>0.001 / 10</td>
<td>0.001 / 1</td>
</tr>
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<td>$N$</td>
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<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$a_i$ [nm]</td>
<td>4.0</td>
<td>0.5</td>
<td>1.8</td>
<td>2.0</td>
</tr>
<tr>
<td>$D_{BL}$ [m$^2$/sec]</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>$2h$ [$\mu$m]</td>
<td>185</td>
<td>178</td>
<td>255</td>
<td>285</td>
</tr>
<tr>
<td>$2H$ [$\mu$m]</td>
<td>206</td>
<td>196</td>
<td>274</td>
<td>306</td>
</tr>
<tr>
<td>$L$ [mm]</td>
<td>28.6</td>
<td>28.0</td>
<td>30.2</td>
<td>28.6</td>
</tr>
<tr>
<td>$w_i$ [%]</td>
<td>45</td>
<td>36</td>
<td>124</td>
<td>145</td>
</tr>
<tr>
<td>$\varphi_0$ [V]</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>$r_0$</td>
<td>0.99</td>
<td>0.95</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>$\bar{\kappa}$ [F/m]</td>
<td>$1.38 \times 10^{-1}$</td>
<td>$1.38 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\tau$ [seconds]</td>
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<td>3</td>
<td>0.019</td>
<td>0.1</td>
</tr>
<tr>
<td>$\tau'$ [seconds]</td>
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<td>0.01</td>
<td>1</td>
<td>0.1</td>
</tr>
<tr>
<td>$r$</td>
<td>0.99</td>
<td>0.25</td>
<td>---</td>
<td>0.1</td>
</tr>
<tr>
<td>$\tau''$ [seconds]</td>
<td>1000</td>
<td>0.1</td>
<td>---</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 3.22. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Li\(^{+}\)-form with ethylene glycol (EG), subjected to a 2.0V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 199.2sec

Figure 3.23. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Li\(^{+}\)-form with glycerol (G), subjected to a 2.0V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 2,611.1sec
Figure 3.24. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Li$^+$-form with 12CR4, subjected to a 2V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 8,514.0sec

Figure 3.25. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Na$^+$-form with ethylene glycol (EG), subjected to a 2.0V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 281.1sec
Figure 3.26. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Na⁺-form with glycerol, subjected to a 2V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 2,610.0 sec

Figure 3.27. Variation of normalized curvature over time for a strip of Nafion-based IPMC in Na⁺-form with 15CR5, subjected to a 2V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 1,837.0 sec
Figure 3.28. Variation of normalized displacement over time for a strip of Nafion-based IPMC in Na\textsuperscript{+}-form with 18CR6, subjected to a 3V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results.

Figure 3.29. Variation of accumulated charge over time for a strip of Nafion-based IPMC in K\textsuperscript{+}-form with ethylene glycol, subjected to a 1.5V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 300.0sec.
Figure 3.30. Variation of normalized curvature over time for a strip of Nafion-based IPMC in K\textsuperscript{+}-form with ethylene glycol (EG), subjected to a 1.5V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 300.0sec.

Figure 3.31. Variation of normalized curvature over time for a strip of Nafion-based IPMC in K\textsuperscript{+}-form with glycerol, subjected to a 2V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 1,036.1sec.
Figure 3.32. Variation of normalized curvature over time for a strip of Nafion-based IPMC in K\(^+\)-form with 18CR6, subjected to a 2.5V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results; shorted at 669.0sec

Figure 3.33. Variation of normalized displacement over time for a strip of Nafion-based IPMC in K\(^+\)-form with 15CR5, subjected to a 2.5V step potential; the heavy solid curve is model and the geometric symbols connected by solid curve are experimental results
3.6. SUMMARY AND CONCLUSIONS

Both the initial relatively fast motion and the subsequent relaxation of Nafion-based IPMCs have been modeled based on the micromechanisms proposed by Nemat-Nasser [2002]. Remarkably, the model correctly produces both qualitatively and, with reasonable accuracy, quantitatively all observed, rather peculiar, behaviors of this class of soft actuators.

First the stiffness of the bare ionomer and the corresponding IPMC is modeled for each cation-form and various degrees of solvation, identifying and evaluating several micro-structural parameters that are also necessary for the modeling of the corresponding actuation.

To model the actuation, we assumed 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. 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 a time scale, $\tau_i$. This modifies the effective dipole-cation interaction forces, thereby contributing to the back relaxation.

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. 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 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 has been actually observed during the very slow back relaxation of IPMCs that are solvated with ethylene glycol and particularly with glycerol.

The coupled equations are solved incrementally. At each step the effective pressures in the anode and cathode clusters are calculated. 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 take into account the dependence of the stiffness of the IPMC on the volume fraction of the solvent that varies along the thickness and in time.

Based on the model and comparison with the experimental results, the following overall observations are made:

- The neutralizing cations, the nature and the degree of saturation of the solvent, the electrode morphology, and the chemical structure and characteristics of the backbone polymer are all important parameters that affect the electrical-chemical-mechanical
response of IPMCs, both quantitatively and qualitatively. IPMCs with heavier and more viscous solvents have slower actuations, higher solvent uptakes, smaller stiffness at fully solvated states, and lower overall capacitance.

- The basic mechanism of the IPMC actuation is governed by the cation transport, which creates imbalance in electrostatic and osmotic pressures within the clusters and hence promoting solvent transport.

- The application of an electric potential produces two thin boundary layers, one near the anode and the other near the cathode electrodes. 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. Experimental results such as the ones shown in Figures 3.20 and 3.29, suggest that the continued depletion of cations from the anode and accumulation into the cathode boundary layers long after the initial fast motion and way into the period of back relaxation of the cantilever that is actuated by a DC voltage.

- Once the equilibrium is reached, most of the clusters in the anode boundary layer are completely and depleted of their cations and those in the cathode boundary layer are rich with additional cations.

- 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.
For a fully solvated IPMC membrane, the equilibrium distribution of the cations and the internal potential that develops under the action of an applied step potential of magnitude $\varphi_0$, depend on the effective permittivity, $\kappa$, the ionomer thickness, $h$, the concentration of the anions, $C^-$, and the magnitude of the applied potential, $\varphi_0$.

The effective length of the anode boundary layer at equilibrium is given by

$$L_A = \ell + \ell' = \left(\sqrt{\frac{2\varphi_0 F}{RT}} - 1\right)\ell, \quad \ell = \left(\frac{\kappa RT}{C^- F^2}\right)^{1/2}.$$ 

This has been established by Nemat-Nasser [2002] using an approximate analytical estimate and is confirmed by our numerical solution.

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

Nafion-based IPMCs that are neutralized with alkali metals show remarkably different responses when solvated with crown ethers. 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. Moreover, 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.
The variation of the response from sample to sample (or even for the same sample tested at various times) is often so great that only an approximate quantitative correspondence between the theoretical predictions and the experimental results should be expected, or reasonably required. Nevertheless, the model seems to correctly produce, both qualitatively and, with reasonable accuracy, quantitatively all the observed responses of these IPMCs.

To apply high electric potentials without electrolysis, IPMCs with other solvents such as ethylene glycol, glycerol, and crown ether solutions can be used. This enables actuating a strip of an IPMC in open air for rather long time periods, and, or at low temperatures.

To maximize the normalized curvature of a cantilevered strip with its bending stiffness held fixed, it is necessary to maximize the effective capacitance and surface conductivity of IPMC.

3.7. APPENDIX: CLUSTERS SIZE APPROXIMATION

The X-ray scanning of the Nafion membranes [Gierke et al., 1981] has shown that in process of solvent absorption, hydrophilic regions consisting of clusters are formed within the membrane. Cluster formation is promoted by the aggregation of hydrophilic ionic sulfonate group located at the terminus of vinyl ether sulfonate pendants of polytetrafluoroethylene chain. While these regions are hydrophilic, the membrane backbone is hydrophobic and it is believed that the motion of solvent takes place among

* Hydrophilicity and hydrophobicity are generally terms used for affinity or lack of affinity toward polar molecule of water. In the present work we use these terms for interaction toward any polar solvent (i.e. ethylene glycol).
these clusters via the connecting channels. The characteristic of these clusters and channels are important factors in IPMC sample behavior. The size of the solvated cluster radius \( a_i \) depends on the cation form, type of solvent used, and the amount of solvation. The average cluster size can be calculated by minimizing the free energy of the cluster formation with respect to the cluster size. The total energy for cluster formation consists of an elastic \( (U_{ela}) \), an electrostatic \( (U_{ele}) \), and a surface \( (U_{sur}) \) component. The elastic energy is given by [Li and Nemat-Nasser, 2000],

\[
U_{ela} = \frac{3NkT}{\langle h^2 \rangle} \left[ \frac{\sqrt{\langle N\cdot E\cdot W_{ion} \rangle}}{\rho^* N_A} - a_i \right]^2,
\]

where \( N \) is the number of dipoles inside a typical cluster, \( k \) is Boltzmann’s constant, \( T \) is the temperature, \( \langle h^2 \rangle \) is the mean end-to-end chain length, \( \rho^* \) is the effective density of the solvated membrane, and \( N_A \) is Avogadro’s number \( (6.023 \times 10^{23}) \), respectively. The electrostatic energy is defined by,

\[
U_{ele} = -g \frac{N^2}{4\pi \kappa_e} \frac{m^2}{a_i^5},
\]

where \( g \) is a geometric factor, \( m \) is the dipole moment, and \( \kappa_e \) is the effective permittivity within the cluster. The surface energy can be expressed as
\[ U_{\text{sur}} = 4\pi a_i^2 \gamma, \quad (3.83) \]

where \( \gamma \) is the surface energy density of the cluster. Therefore, the total energy due to the presence of clusters in the ionomer is given by

\[ U_{\text{tot}} = n(U_{\text{ele}} + U_{\text{ela}} + U_{\text{sur}}), \quad (3.84) \]

where \( n \) is the number of clusters present in the membrane. Minimizing this energy with respect to cluster size, \( \left( \frac{\partial U_{\text{tot}}}{\partial a_i} = 0 \right) \), gives the optimum cluster size at which the free energy of the ionomer is minimum. In this manner Li and Nemat-Nasser [2000] have obtained,

\[ a_i = \left\{ \frac{\gamma < h^2 > EW_{\text{ion}} (w + \Delta V)}{2RT \rho_b} \left[ 1 - \frac{4\pi \rho_b}{3\rho^*(w + \Delta V)} \right]^2 \right\}^{1/3}, \quad (3.85) \]

\[ \Delta V = \frac{N_i V_i \rho_d}{EW_{\text{ion}}}, \quad (3.86) \]

where \( V_i \) is the volume of a single ion exchange site. Assuming that \( < h^2 > = EW_{\text{ion}} \beta \) [Forsman, 1986], it can be seen that,

\[ a_i^3 = \frac{\gamma \beta}{2RT \eta}, \quad (3.87) \]
\[ \eta = \frac{EW_{\text{ion}}^2 (w + \Delta V)}{\rho_B} \left[ 1 - \frac{4\pi \rho_B}{3 \rho (w + \Delta V)} \right]^2. \] (3.88)

Figure 3.34 shows the variation of the cluster size \( a_i^3 \) in nm\(^3\) for different solvent uptakes. Data from Nafion-based IPMC samples with different cations and different solvent uptakes are considered. The model is compared with the experimental results on the cluster size based on X-ray scanning, shown as circles in Figure 3.34 for Nafion ionomer in various cation forms and with water as solvent [Gierke et al., 1981]. We have set \( \beta = 1.547 \), \( \gamma = 0.15 \), and \( V_i = 68 \times 10^{-24} \) cm\(^3\) to calculate the cluster size [Forsman, 1986].

![Figure 3.34. Cluster size in Nafion membranes with different solvent uptakes](image-url)
As can be seen from the Figure 3.34, cluster size varies linearly with $\eta$ for different solvents and cation forms. For the Nafion membrane treated with other various considered solvents, we have used the physical properties of the sample prior to the application of a potential and have estimated the cluster sized that is needed for modeling of the corresponding IPMC actuation.

3.8. REFERENCES


### 3.9. ACKNOWLEDGEMENTS

We wish to thank Drs. Steve Wax (DARPA), Len Buckley (NRL), Carlos Sanday (NRL), and Randy Sands for their initial support of this research at UCSD which has been continued now for a while without external funding at UCSD’s CEAM. We are grateful to Professor Mohsen Shahinpoor and Dr. K. J. Kim for providing the Nafion-based IPMC samples; to Dr. K. Asaka for providing the Flemion-based IPMC samples; to Dr. Yosi Bar-Cohen for his continued interest and stimulating interaction; to Mr. Jon Isaacs and Mr. Dave Lischer for developing the experimental equipment and techniques; and to Dr. Jeff McGee for helpful code to obtain the effective capacitance. This work has been supported by CEAM of the University of California, San Diego.