Ionic polymer–metal composites (IPMCs) are commonly used as soft actuators due to their electromechanical response. However, the reverse phenomenon, i.e. IPMC’s ability to generate charge on application of mechanical strain (mechanoelectric response), is not very well understood. The concept of mechanoelectric transduction and its dependence on complex IPMC architecture comprising of electrode, polymer and composite layer is illustrated with a phenomenological model. The impedance model takes into account the charge transport inside the polymer and layer properties in terms of their impedances. The model lucidly indicates the significance of capacitance in IPMC transduction. The impedance model is used for studying IPMC step and frequency response and the effect of IPMC capacitance on its application as energy harvester.

**Keywords:** ionic polymer–metal composite; capacitance; impedance; mechanoelectric response

**Introduction**

The electroactive response of ionic polymer–metal composites (IPMCs) and their ability to produce current makes them viable for soft actuator and sensor development. IPMCs consist of bulk polymer layer, coated with metal electrodes on two sides using the electroless deposition technique, first reported by Millet et al. in 1989 [1]. Fabrication steps are illustrated in Figure 1. During electroless deposition process, Nafion® membrane is cleaned and hydrated in deionised water for 24 h. The cleaned membrane is immersed in a platinum salt solution for at least 2 h. The reduction process using ammonia and sodium borohydride added every half an hour follows, with the bath temperature increasing from 40°C to 70°C. The reduction process is repeated to achieve surface resistivity less than 10 Ω/sq. The resulting thickness of 0.17 mm to 0.20 mm has been reported using this process.

The polymer membrane allows selective ions to pass through while blocking others. Since the cations are cross-linked to polymer chains, in the dry state, they are not free to move. However, on hydration, water molecules surround the cations; this makes the entire entity mobile. Nafion is the commonly used polymer for manufacturing IPMC. The electrodes deposited using electroless deposition technique (or any variations of it) are mechanical and chemically very stable. However, the complex architecture that is the result of this chemical deposition process adds difficulty in understanding IPMCs in general [2].

* Email: rt275@cornell.edu
In the past, many models have been developed to provide an insight into material response both in the actuator as well as sensor state. These models can be broadly classified into three major categories: black-box model, grey-box model and physics model. Black-box models are used for empirically deriving relation between the input and the output [3–6]. These models are based on system identification and curve fitting and are useful for understanding the macroscopic electromechanical behaviour of IPMC [7]. Black-box models can be effectively applied for direct material control. However black-box models do not provide insight into the physical phenomenon associated with IPMC. On the other hand, grey-box models are developed by using the fundamental principle while experimentally deriving values for some of the material parameters. These material parameters either represent complex physical phenomenon or process; or describe material property that cannot be measured directly [3,8,9]. Lastly, physical models are based on the physical principle of transduction [10,11]. These models consider the ion transport and pendent structure to study the transduction in IPMC. Both material linearity and non-linearity are incorporated in the formulated models. Any of the above modelling techniques could be employed based on the need and application.

The sensing nature of IPMCs is of particular interest for the design and development of smart sensors [12,13,19] in applications such as energy harvesting [14–17,21], structural health monitoring [18], integrated sensor and actuator system [20], vibration control, tactile sensor [22,23] and impact sensors [24]. IPMCs as sensors have the advantages of compliance, long operating life, underwater applications, fast response and low maintenance. However, applications are limited due to low current output, material nonlinearity and poor understanding of mechanoelectric transduction of IPMCs. There is a particular need to understand the effect of each layer of IPMC architecture on the overall response.

This paper reports a phenomenological model that aims to provide an understanding of the layered structure of IPMCs. Each layer is represented in terms of its resistance and its capacitance. Incorporating impedance improves the adaptability of the model to different manufacturing techniques as any variation in the fabrication process affects the impedance of different layers. Hence, a parametric study illustrating the effect of layer impedance on the mechanoelectric output and energy harvesting application of IPMC is also presented.
IPMC impedance model

Each IPMC layer contributes to the overall behaviour of the material. Porous nature of the surface electrodes and the gradual decrease in the particle dispersion in the polymer and the pendent like structure of the Nafion itself, all contribute to the nonlinearity in IPMC. How these layers effect the current generation and transmission in IPMC is still not clear. Majority of research has been performed to study the effect of electrode properties like thickness [25–27], resistivity [28], type of electrode metal [29–39] and morphology [40–43] on IPMC response, mainly as an actuator. However, it is still ambiguous which IPMC layer and what properties have profound effect on the mechanoelectric response. Also it should be noted that each layer and its properties are coupled to each other, thus making it difficult to independently evaluate the effect of each layer on the mechanoelectric transduction. Conversely, any variation in the IPMC layer can be related to the respective change in its impedance. Thus an impedance-based model is fabricated to understand the role that each layer plays in IPMC transduction, particularly sensing.

As mentioned earlier, when IPMC sample is exposed to a stress it produces charge. This can be partially due to the internal motion of ions [10]. The charge density on the polymer composite surface is assumed to be linearly proportional to the stress on the beam [44,45]:

\[ \rho = \psi \sigma, \quad (1) \]

where \( \rho \) is charge density, \( \sigma \) is stress on the beam and \( \psi \) is the coupling coefficient.

In order to understand the effect of ions on the mechanoelectric property of IPMC, it is important to understand the ion transport phenomenon using the continuity equation which has been described elsewhere [44,45].

Charge density, \( \rho \), electric field, \( E \), electric displacement, \( D \), and potential \( \phi \) are:

\[ \rho = \nabla \cdot D = F \left( C^+ - C^- \right) \]
\[ D = k_e E \]
\[ E = -\nabla \phi \quad (2) \]

where \( k_e \) is the dielectric constant of the polymer and the characteristic equation of IPMC can be derived as:

\[ \frac{\partial \rho}{\partial t} - d\nabla^2 \rho + \frac{dF^2 C^-}{RTk_e} \left( 1 - C^- \Delta V \right) \rho = 0, \quad (3) \]

where the initial boundary condition was \( \rho(x,0) = \rho_0 \), the initial charge density at the electrode faces. Initially when the IPMC is not bent, there is no current flowing and the potential at the surface is assumed zero. This initial condition makes the following derivation different from the actuator mode when a voltage is applied at the IPMC surface and there is a resulting displacement. Thus the potential at the clamp initially is also zero because there is no potential at the surface.

On bending the charge on the two electrodes is assumed to be equal in magnitude. Equation (3) was employed to study the step response by Farinholt and Leo [46]. An approximate analytical solution to the above equation was obtained based on the assumption that the equation was separable in spatial and temporal domain. Above equation
was employed to study the material output to dynamic input by transforming the equations in Laplace domain [45]. Though the work by Farinholt and Leo [46] and Chen et al. [45] formed the basis of this research, the reported research differs in the following ways. First of all, material response to dynamic input can be studied. Secondly, both surface and intermediate layer impedances were incorporated into the impedance model in order to address the effect of surface and polymer nonlinearity. Lastly, the model can be employed to study the effect of electrode properties (like electrode thickness, morphology and surface area) on the mechatronic response of IPMC.

With no surface impedance

For further analysis, Equation (3) was transformed into the frequency domain. The charge density is dependent on the membrane thickness, length and time. The following solution has been described in [45,47,48] and hence the derivation is not included here.

\[ s \rho(x,y,s) - d \nabla^2 \rho(x,y,s) + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \rho(x,y,s) = 0. \]  

(4)

The electric field, \( E(x,y,s) \), and potential, \( \Phi(x,y,s) \), for an IPMC sample can be described as:

\[
E(x,y,s) = \frac{2C_1}{k_e} \cosh \left( \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) x \right) - \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) + A_1, \\
\Phi(x,y,s) = \frac{2C_1}{k_e} \sinh \left( \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) x \right) - \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \left[ \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right]^2 - A_1 x + A_2,
\]

(5)

(6)

where, \( A_1 \) and \( A_2 \) are constants of integration:

\[
A_2 = 0 \\
A_1 = -\frac{2C_1}{k_e} \sinh \left( \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right) \left[ \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right]^2 - \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \left[ \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right]^2.
\]

(7)

The potential at the surface is assumed to be zero. Thus short-circuit current at \( y = 0 \) can be derived as: Hence, the current generated is:

\[
i(s) = \frac{3sY}{\psi w} \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \cdot \coth \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right) - 1 \right) u(s) \\
2L_{free} \left( \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right)^2
\]

(8)
Since electrode property affects the overall output from the IPMC samples, it was important to incorporate this effect into the model.

**With intermediate and electrode impedance**

Though the density of particles in the surface electrode is high, the electrode displays capacitive impedance. Let the impedance per unit length be represented as (Figure 2):

$$ Z = \frac{Z_0}{w}, $$

where $Z_0$ is the surface impedance per unit length and width. For every section of length, $\Delta y$, a current, $i_p \Delta y$, is generated inside the polymer. This current adds to the surface current, $i_s$.

In addition to the surface electrode impedance, the polymer and the intermediate layer contribute to the overall impedance of IPMCs. In Figure 3, $i_p$ represents the current in a unit length due to ion movement in the top half of the polymer membrane.

Let intermediate layer impedance per unit length be:

$$ r_p = \frac{r_p'}{w}, $$

where $r_p'$ is the intermediate layer impedance per unit length and width. The potential at the electrodes near the clamp ($y = 0$) was assumed to be zero. Hence:

![Figure 2. Ionic polymer–metal composite with surface impedance due to porous electrode. The surface impedance results due to porous metal electrode dispersed in the polymer matrix [15].](image)
Figure 3. Ionic polymer–metal composite surface ($Z_0$) and intermediate layer ($r_p$) impedance due to the porous electrode [15,16].

$$\varphi(h, y, s) = \int_{0}^{\gamma} \frac{Z_0 i_s(\bar{y}, s)}{w} d\bar{y} + \frac{r_p'}{w} i_p(y, s)$$

(11)

$$\varphi(-h, y, s) = \int_{0}^{\gamma} - \frac{Z_0 i_s(\bar{y}, s)}{w} d\bar{y} - \frac{r_p'}{w} i_p(y, s)$$

Substituting Equation (11) in Equation (6) and solving for coefficients:

$$A_1 = -\frac{\int_{0}^{\gamma} \frac{Z_0 i_s(\bar{y}, s)}{w} d\bar{y}}{h} - 2C_1 \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right) \frac{\sinh \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right)}{hk_e \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right)^2} - \frac{r_p'}{hw} i_p(y, s)$$

(12)

$$A_2 = 0$$

Thus:

$$\frac{\partial i_s(y, s)}{\partial y} = -j_1 \int_{0}^{\gamma} i_s(\bar{y}, s) d\bar{y} + j_2 (L - y)$$

$$j_1 = \frac{sZ_0 k_e}{h + sk_e r_p'}$$

$$j_2 = \frac{3sYw \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right) \cdot \coth \left( \frac{h}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right) - 1}{\psi L_{free}^3 \left( \frac{1}{d} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right)^2 (h + sk_e r_p')}$$

(13)
Table 1. Comparing the variables, $j_1$ and $j_2$, in the model with and without intermediate layer impedance in Equations (40) and (35), respectively.

| Without intermediate layer impedance | With intermediate layer impedance |
|--------------------------------------|----------------------------------|
| $j_1 = \frac{sZ_0 k_e}{h + sk_c r_p}$ | $j_1 = \frac{sZ_0 k_e}{h + sk_c r_p}$ |
| $j_2 = \frac{3sY w \left( \frac{h}{2} (\varepsilon) \cdot \coth \left( \frac{h}{2} (\varepsilon) \right) - 1 \right)}{u(s)}$ | $j_2 = \frac{3sY w \left( \frac{h}{2} (\varepsilon) \cdot \coth \left( \frac{h}{2} (\varepsilon) \right) - 1 \right)}{u(s)}$ |

Solving for $i_4(y;s)$

$$i_4(0,s) = i(s) = \frac{j_2}{\cosh \left( \sqrt{j_1 y} \right)} \left( 1 - \cosh \left( \sqrt{j_1 y} \right) \right) + \frac{L \sinh \left( \sqrt{j_1 y} \right)}{\sqrt{j_1}}$$ \hspace{1cm} (14)

where

$$j_1 = \frac{sZ_0 k_e}{h + sk_c r_p'}$$

$$j_2 = \frac{3sY w \left( \frac{h}{2} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \cdot \coth \left( \frac{h}{2} \left( s + \frac{dF^2C^-}{RTk_e} (1 - C^- \Delta V) \right) \right) - 1 \right)}{u(s)}$$ \hspace{1cm} (15)

Equation (40) can be simplified to the model considering only surface by considering $r_p' = 0$. The intermediate layer impedance could be considered purely resistive or capacitive for convenience (Table 1). The value of $r_p'$ if assumed to be purely resistive is in the order of $10^{-5} \Omega \cdot m$. This value can be determined using impedance spectrometry (see supplementary material for impedance data).

**Experimental set-up**

Experiments were performed for model validation. IPMCs electroded with platinum on both sides were used for experimental purposes. The dimensions of the samples used were 50 mm (length) × 10 mm (width) × 0.2 mm (thickness). For energy harvesting experiments, a shaker assembly (TIRA Vibration System, TV52110) was used as the source of mechanical input. The shaker was programmed using a VR8500 controller, to produce a sinusoidal mechanical vibration at a frequency of 10 Hz. The shaft displacement was controlled at 0.5 inch (pk–pk). One end of the sample was clamped while the other end was pinned to the shaker shaft to have a better control on the sample motion. The experimental set-up is illustrated in Figure 4.

Under dynamic excitation, IPMC produced a sinusoidal waveform. In order to store the sensor output on a battery, the signal was converted to DC using a full bridge rectifier. The rectified signal was used for charging a capacitor, typically $>1000 \mu F$, followed by
a 40 mAh rechargeable NiMH battery (VARTA). Battery voltage was recorded using a IOTech Personal Daq 56 data acquisition system.

For determining the frequency response the sample was vibrated, in closed loop, using the shaker with the frequency ranging from 1 Hz to 25 Hz. The amplitude of vibration was fixed to 0.5 inch (Figure 5). A data acquisition system purchased from National Instruments (SCB 68) was employed for the measurement of the voltage on the sample.

The impedance of the sample was measured using a universal electrochemical laboratory system (VoltaLab80 PGZ402). Electrochemical impedance spectroscopy (EIS) was performed in deionised water using a two-electrode system and a conductivity cell purchased from BekkTech LLC (BT-112). The frequency was scanned between 100 mHz to 100 Hz. The conductivity cell performed in-plane measurement to calculate surface impedance. Scanning electron microscopy (SEM) was performed using a Hitachi S-4700 equipped with an Oxford energy dispersive spectroscopy (EDS) system. The samples were dried to obtain the micrographs. Simulations were performed in MATLAB/SIMULINK software.

The tensile modulus of the IPMC samples was measured using a universal testing machine (Instron 5565, USA). Fabricated IPMCs were punched out using a dog-bone shaped punch mould, their size followed by ASTM 638 and 882 and excess water on the surface was removed by pressing them on tissue paper right before the experiment. The strain was applied at a rate of 10 mm/min.
Results

Step response

The impedance model can be employed to study the step response, as shown in Figure 6. The voltage output from the IPMC shows an exponential decay with time. This could be because ions move back to their original position to achieve equilibrium (back diffusion). As shown in the graph, the charge density is zero inside the polymer. This value increases towards surface electrodes. The plots show the same trend as that reported by Farinholt and Leo [46].

Frequency response

Frequency response analysis can be performed using the impedance model by simplifying Equations (8) and (14) using the following assumption (see Table 2 for definitions):

\[
\coth \left( \frac{1}{d} \left( s + \frac{dF^2C^-}{RT\kappa_e} \left( 1 - C^- \Delta V \right) \right) h \right) \approx 1
\]

\[
|C^- \Delta V| \ll 1
\]

\[
\therefore 1 - C^- \Delta V \approx 1
\]

Figure 6. Simulated charge density (a) and surface potential (b), from a 10 mm × 50 mm × 0.17 mm IPMC under 0.5 inch step deformation.

Table 2. Definition of parameters used in the model.

| Parameter | Definition                | Units     | Value    |
|-----------|---------------------------|-----------|----------|
| \(F\)     | Faraday’s constant        | C/mol     | 96,487   |
| \(R\)     | Gas constant              | J/mol/K   | 8.3143   |
| \(Y\)     | Young’s modulus           | Pa        | 50 \(\times\) 10^6 |
| \(h\)     | Thickness                 | \(\mu m\) | 100      |
| \(D\)     | Ionic diffusivity         | \(m^2/s\) | 3.32 \(\times\) 10^{-11} |
| \(C^-\)   | Anion concentration       | mol/m^3   | 1091     |
| \(k_e\)   | Dielectric permittivity   | F/m       | 1.88 \(\times\) 10^{-3} |
| \(\Psi\)  | Coupling constant         | J/C       | 104      |
The final equations without and with IPMC impedance are:

\[
i(s) = \frac{3sYw}{2\psi L_{\text{free}} \left( \frac{1}{\alpha} \left( s + \frac{dF^2 C^-}{RTk_e} \right) \right)^2} \left( \frac{h + sk_e r_p'}{sZ_0 k_e} \right) \left( 1 - \cosh \left( \sqrt{\frac{sZ_0 k_e}{h + sk_e r_p'}} \right) \right) \times \frac{L}{\sinh \left( \sqrt{\frac{sZ_0 k_e}{h + sk_e r_p'}} \right)} (17)
\]

\[
i(s) = \frac{3sYw}{\psi L_{\text{free}}^3} \left( \frac{1}{\alpha} \left( s + \frac{dF^2 C^-}{RTk_e} \right) \right)^2 \left( h + sk_e r_p' \right) u(s) (18)
\]

The model can also be used for determining some material properties like diffusion, anion concentration, coupling coefficient and dielectric constant by data fitting (Table 3).

The estimated values were close to those reported in the literature [45]. The model was employed to predict the frequency response for IPMC samples with different lengths. Predictions were compared with the experimentally measured data, as shown in Figure 7. The sample width and thickness were 10 mm and 290 µm, respectively.

**Parametric study**

**Impedance**

Surface electrodes could play an important role in the overall mechanoelectric response. Impedance spectrometry was performed to analyse both surface electrodes as well as polymer impedance. The results of the impedance spectroscopy are shown in Figure 8.

The plot of Figure 8a depicts the porous nature of the electrode. Also the real component of the impedance had lower values due to the higher density of metal particles on the surface. The analogous electric circuit for the spectroscopy consists of resistance and capacitance in parallel. On the contrary, the impedance for the polymer showed higher values. This was due to the decrease in metal particles inside the membrane. Also both cases showed the dependence of impedance on frequency. The capacitance of the IPMC

| Model          | \(D\) (m²/s) | \(C^-\) (mol/m³) | \(k_e\) (F/m) | \(\Psi\) (J/C⁻¹) |
|---------------|-------------|-----------------|--------------|----------------|
| No impedance  | \(6.11 \times 10^{-11}\) | 1891.10         | 0.0062       | 308.82         |
| With impedance| \(6.91 \times 10^{-11}\) | 2308.90         | 0.0018       | 328.98         |
| Literature [45]| \(3.32 \times 10^{-11}\) | 1091.00         | 0.0018       | 104–550        |
Figure 7. Comparing frequency response of IPMC using impedance model with and without surface impedance with experimental results. Response of samples with length 70 mm (a) and 50 mm (b) vibrated at frequency ranging from 1–25 Hz with vibration amplitude at 0.5 inch (pk–pk) are plotted.

Figure 8. EIS to measure surface impedance (a) and membrane impedance (b) of IPMC.
exponentially decreased with increase in frequency, as capacitive impedance is inversely proportional to the frequency.

From the impedance model the dependence of mechanoelectric output on polymer impedance through permittivity (Figure 9) was observed. The model predicted an increase in output current with increase in permittivity. The capacitance of IPMC is directly proportional to the permittivity and hence as permittivity increases the capacitance increase and hence the output from the polymer increases. Increasing the metal inside the polymer membrane could increase the permittivity of IPMC. Besides, the permittivity was also affected by membrane hydration.

The model was also employed to test the dependence of IPMC output on the surface resistance and capacitive reactance in the IPMC, as shown in Figure 10. The model predicts that as the surface resistance is increased, the output of the IPMC decreases. This could be due to fact that poor surface conductivity leads to signal transmission losses. Similarly, low capacitance (i.e. higher capacitive reactance) also leads to decrease signal conduction and hence lower output from the IPMC.

**Temperature effect**

The effect of temperature on the mechanoelectric properties of the IPMCs was studied. The electrostatic–ionic model was employed for predicting the temperature effect. The glass transition temperature of IPMC was measured to be around $105^\circ$C and the melting temperature was around $210^\circ$C (Figure 11a). The mechanoelectric output from an IPMC, for a small temperature, is shown in Figure 11b. The model did not predict any phase changes that occurred after the glass transition temperature.

As shown in Figure 11b, the ionic effect increases with increase in temperature whereas the electrostatic effect reduces with increase in temperature. The decrease in electrostatic output with increase in temperature might be due to the loosening in the polymer chain forming the clusters. Conversely, the clusters in the polymeric membrane swell according to the water content. This in turn resulted in the change in mechanical and chemical property
Figure 10. Dependence of mechanoelectric output on surface resistance and capacitive reactance as predicted by the impedance model.

Figure 11. Measured glass transition ($T_g$) and melting temperature ($T_m$) of IPMC (a) and the effect of temperature studied using the electrostatic–ionic model (b).

The ionic effect increased due to increase in diffusion coefficient with increase in temperature:

$$D = D_0 \exp \left( -\frac{E_A}{RT} \right)$$

(19)

where $D$ is the diffusion coefficient, $D_0$ is the initial diffusion coefficient, $E_A$ is the activation energy for diffusion, $T$ is the temperature and $R$ is the gas constant. An equation of this form is known as the Arrhenius equation. Besides, an increase in ionic conductivity of the polymer, $\sigma$ [49] with temperature was also observed:

$$\sigma = (0.005139\gamma - 0.00326) e \left[ 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right],$$

(20)
where \( e \) is the charge on electron and \( \gamma \) is the water molecules per sulphonic acid group in the membrane. Water molecules in the membrane are in turn dependent on the temperature.

The temperature also affected the electrochemical properties of the IPMCs. Hence experiments were performed to conduct electrochemical analysis at different temperatures. Deionised water was used as the solvent. The sample used was Pt-IPMC of dimensions 10 mm × 10 mm. The temperature was increased from 18°C to 60°C. The voltage was changed from –1 V to 1 V at 10 mV/s for voltammetry. For deriving impedance spectrometry, the frequency was controlled to change from 100 mHz to 100 KHz. The results of the three experiments are shown in Figures 12–14.

The voltammograms obtained at different temperatures showed an increase in the hysteresis with increase in temperature. Oxidation and reduction peaks became prominent with increase in temperature in anodic and cathodic scans. In addition, an increase in the rate of reaction both in forward and backward scan was observed with increase in temperature [50]. Similar observations could be made from EIS data plotted in Figure 13. The graph shows that there is an increase in impedance with an increase in temperature. This increase was due to the imaginary component of impedance. This was reconfirmed through capacitance data that showed an increase in capacitance with temperature (Figure 14).

The other effect on polymer property due to temperature was on the material modulus (Figure 15). The temperature was scanned between 10°C to 100°C with frequency of 0.2 Hz, 0.5 Hz, 1 Hz, 2 Hz, 5 Hz and 10 Hz under tensile loading.

Storage modulus decreased with increase in temperature. This drop was larger for temperatures above 70°C. Above this temperature the viscous flow increased to reduce the modulus. It could be anticipated that the absence of water in the cluster leads to an increase in intermolecular forces and ionic interaction. Increase in temperature reduces the cluster dimension in the IPMC thus increasing the mobility of polymeric chain and hence decreasing the storage modulus and increasing loss modulus. Tan \( \delta \) did not change drastically between 20°C to 50°C. This rise becomes more prominent with further increase in temperature.

Figure 12. Voltammogram at different temperatures.
Recently, IPMCs have been used in energy harvesting applications. However, due to the low current output from an IPMC, the design of energy harvesting circuits becomes difficult. Thus, there is a definite need to improve the output from the IPMC. The model shows that IPMC capacitance is critical parameter in improving IPMC output in sensor mode. The model predictions were confirmed with the experimental data on the impedance of the IPMC samples fabricated by changing electrode and interfacial or composite layer.

**Effect of capacitance on energy harvesting**

IPMC samples were manufactured by inducing: (1) cracks across the length of IPMC (Sample 1), (2) cracks along the length of IPMC (Sample 2) using sandpaper size 320 and
(3) randomly perforating both sides of Nafion® using needle of tip diameter 300 µm (Sample 3). IPMC samples of size 10 mm × 50 mm were prepared from Nafion® 117. Electroless deposition was employed for depositing platinum electrodes on Nafion samples. Samples 1, 2, 3 and typical IPMC were prepared at the same time in the same hot bath using same chemical deposition method. The electrode morphology was examined using SEM, as shown in Figure 16. Sample 1 and 2 are similar except in the direction of the surface roughness. Sample 1 is with roughness across the length and Sample 2 is along the length. The reason for different cross-sectional view (SEM) is based on the sample placement in the machine. Surface morphology is included in the supplementary material.

All the samples used in the following experiments were 100% hydrated (i.e. the samples were soaked in water for at least 24 h). The experiments were performed with samples in water so that effect of water loss may be neglected.

The real impedance values for different IPMC samples might also shed some light onto the resistance due to interfacial layer. Poor harmony between the polymer membrane and electrode results in higher impedance value. The higher value of this impedance leads to poor electromechanical property and hence lowers output from the IPMC. Figure 17a shows the impedance spectroscopy for the different samples. The curves depicted capacitive-resistive behaviour as mentioned before. The impedance for Sample 1 was higher than the other samples. This was believed to be due to more number of
peaks and valleys formed due to surface roughening. The capacitance of IPMC decreased with increase in frequency because capacitance is inversely proportional to the frequency (Figure 17b). This decrease with frequency was in accordance with the typical behaviour of a capacitor. The capacitance value of Sample 3 was higher than other types of IPMC sample hence producing larger mechanoelectric output signal. Various capacitance values have been reported in the literature ranging from 0.1 mF/cm² to 100 mF/cm² [10,28,46,51].

Electrodes might be affected by the charge on the surface. Hence, cyclic voltammetry was performed using a three-electrode system. Figure 17c compares cyclic voltammograms of IPMC samples after 3-time reduction. No distinct electrochemistry was expected to occur between the scanning potential of –1 V to 1 V. As the signal generated by IPMC falls in low voltage range we believe that it did not lead to oxidation-reduction on the electrode surface. The $I-V$ curve in Figure 17c also illustrates that Sample 3 did not show any significant hysteresis. On the other hand, Sample 1 showed maximum hysteresis followed by Sample 2 and typical IPMC, in that order.

In another set of experiments the tensile modulus of IPMC samples was measured. Any loss of water during the course of the experiment was neglected. As shown in Figure 18, Sample 3 showed highest modulus followed by Samples 1 and 2. Typical IPMC demonstrated lowest modulus. According to the law of mixtures, IPMC stiffness may be calculated by incorporating metal electrode stiffness in stiffness of Nafion. Platinum reduction inside IPMC could have caused increase in modulus in case of Sample 3.

Results of the above experiments are summarised in Table 4. An improvement in mechanoelectric property of Sample 3 was observed based on experimental results.
Figure 17. Impedance spectroscopy (a), capacitance (b) and voltammogram (c) of IPMC samples after 3-time electroless deposition. The size of the samples was 10 mm × 50 mm × 0.20 mm.

Figure 18. Young’s modulus for different samples.
Table 4. Summary of the properties of IPMC samples with different surface impedance.

| Properties                     | Sample 1 | Sample 2 | Sample 3 | Typical |
|--------------------------------|----------|----------|----------|---------|
| Average resistivity ($\Omega$/sq) | 13.50    | 17.50    | 7.96     | 8.22    |
| Average hysteresis             | High     | Moderate | Very low | Low     |
| Average capacitance (mF)       | 20       | 50       | 170      | 30      |
| Average Young’s modulus (MPa)  | 38.00    | 36.00    | 52.50    | 33.50   |

Figure 19. Voltage on the battery as measured using different samples with modified IPMC impedance.

In order to verify the hypothesis that reduction in surface impedance leads to an improvement in IPMC output, an energy harvesting experiment was conducted to charge a battery using the shaker assembly. The result is shown in Figure 19.

It is clear that an increase in capacitance and reduction in surface resistivity positively affects IPMC output and hence battery charging. Despite of the fact that only electrode roughness and surface area was modified for manufacturing Samples 1, 2 and 3, the modifications also affects the material stiffness. Though the overall result is an improvement in the IPMC output, it is very difficult to individually change each layer property without affecting other properties.

Conclusion

The dependence of IPMC output on its impedance is evident. Polymer layer coated with metal electrodes, and the dispersion of metal particles into the polymer membrane forming the composite layer in IPMC and the conductivity of the polymer membrane itself contributes to the overall impedance of IPMCs. A phenomenological model that not only takes into account the charge transport in an IPMC but also the impedance of each layer to predict the mechanoelectric output is reported. The impedance model provides a tool to understand the role played by individual layers of an IPMC. The model is used to predict the frequency
response of IPMCs with increasing length. In addition, a parametric study using the model is conducted that concludes that increasing capacitance and decreasing surface resistance can improve IPMC output. Based on the parametric study, IPMC samples with different surface electrode properties were fabricated and used for energy harvesting applications. Battery charging using different IPMC samples also shows that capacitance plays a key role in IPMC transduction.

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