Applied Physics Letters

RESEARCH ARTICLE | MARCH 27 2013

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Appl. Phys. Lett. 102, 123903 (2013)
https://doi.org/10.1063/1.4798496

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APPLIED PHYSICS LETTERS **102**, 123903 (2013)

Mechanoelectric transduction in ionic polymer-metal composite

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(Received 2 January 2013; accepted 12 March 2013; published online 27 March 2013)

The ability of ionic polymer-metal composite (IPMC) to generate current on mechanical deformation, defined as mechanoelectric transduction, can be exploited for design and development of numerous sensors and energy harvesters. However, sensor application of IPMC is currently limited due to the lack of understanding of the transduction mechanism. This paper presents a physics-based mechanoelectric model that takes into account material properties, electrostatic phenomenon, and ion transport in the IPMC. Experimental verification of the model predictions is also reported. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798496]

Ionic polymer-metal composites (IPMC) have shown great applicability as sensors and actuators[1–15] due to its electromechanical or mechanoelectrical transduction.[16–18] Despite research being reported on understanding IPMCs transduction mechanism, there is a need to understand the underlining principle of mechanoelectric response in IPMC. Understanding the mechanoelectric behavior would help in tailoring IPMC properties during manufacturing and enhance its applicability as well. IPMCs are typically manufactured using chemical deposition technique that results in a layered IPMC architecture.[19,20] Metallic electrodes form the outer most layers, followed by the intermediate layer. The intermediate layer comprises the metal particles dispersed inside the polymer matrix.[19] This intermediate layer gradually transforms into the polymer layer. Nafion is the most commonly used membrane for IPMC fabrication. All layers contribute to the complex transduction mechanism.

Currently, two mechanoelectric transduction principles have been reported: ion transport in the constitutive membrane[21–24] and electrostatic effect[21,25] resulting from cation and anion location forming a cluster (see supplemental material for cluster details[35]). In this paper a model that takes into account the combined effect of ionic motion and electrostatic effects is discussed. It is important to take into account both these effects because unlike the electromechanical transduction that can only occur when the IPMC is hydrated, the mechanoelectric transduction can be observed in poorly hydrated samples or dry membranes. Any of the existing models do not account for these observations.

Thus the mechanoelectric output voltage across IPMC is

$$V = V_{dp} + V_{ion}, \tag{1}$$

where V_{dp} is the voltage due to electrostatics effect and V_{ion} is voltage due to ionic effect in IPMC. A combination of the two voltages (V_{dp} and V_{ion}) was considered assuming that no phase shift exists between the two signals. Both voltages were measured across the thickness of the IPMC. Same vector direction convention has been used for deriving these voltages.

In dry membrane the voltage across the IPMC was assumed to be dependent on electrostatic effect ($V_{ion} = 0$). However, both ionic and electrostatic effects were considered in hydrated sample. It has been previously reported that clusters in Nafion are more spheroidal than spherical.[26] Membrane hydration was assumed to affect the electrostatic effect in terms of cluster geometry. It has been shown that on hydration, water molecules penetrate into the spheroidal cluster changing it to be spherical,[27] due to decrease in electrostatic energy of spherical cluster. For the sake of simplicity, the effect due to the electrode and intermediate layer was restricted to the study of impedance of this layer. This was because metal particles dispersed in the polymer matrix improve its conductivity[28] due to an increase in double layer capacitance.

It has been observed that in dry state there is no current flow due to ionic motion since the ions inside IPMC are dependent on water molecules for motion. Despite the suppressed ionic motion in dry polymer, voltage may be measured across the thickness of IPMC. This could be explained due to the existence of electrostatic effect in the base polymer membrane. The model formulation is based on the assumption that the shape of the cluster in Nafion in dry state to be spheroidal.[26] However, on hydration it was prudent to take a combination of both spherical and spheroidal clusters, as spheroidal clusters tend to become spherical on absorbing water molecules (Figure 1).

Electrostatic field due to oblate dipolar charge at an arbitrary point external to the distribution was calculated as Ref. 29. The number of clusters per unit volume, N_p, for 1100 EW membrane was calculated using the work reported by Manley *et al*. The radius of the spherical cluster was calculated to be around 2 nm, which is coherent with the values reported in the literature.[30] Based on the study performed by James *et al.*[27] on the effect of hydration on the shape of the cluster, it was assumed that 75% of the total voltage was because of the spherical cluster. Thus in dry IPMC, the voltage across the membrane was due to electrostatic effect because of spheroidal clusters is

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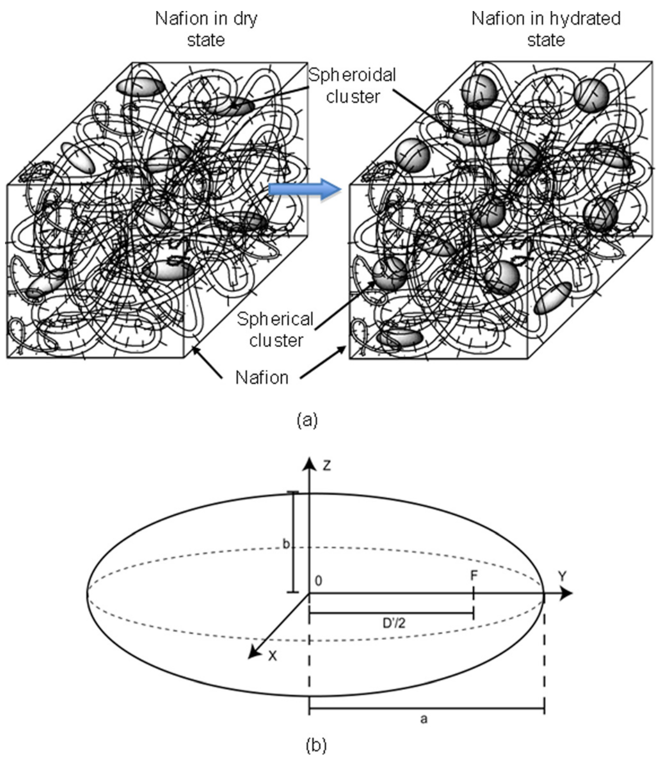

FIG. 1. Illustration of spheroidal cluster in Nafion® in dry state and a mixture of spheroidal and spherical cluster on hydration (a) and an oblong cluster structure of ionic polymer metal composites showing major axis, a, minor axis, b, and focus, F (b).

$$V(s)=\frac{4.8\times10^{-9}D'C^{-}Fh}{L^2+u(s)^2}\times\sum_{n=0}^{20}\frac{(a+10^{-9})^3}{\left(4(2n+1)^3\pi\left(\frac{a+10^{9}}{2}\right)^3 K_W\left(2\frac{K_p}{K_W}+1\right)\right)}u(s). \tag{2}$$

The value of negative ions concentration, C^-, is 1091 (mol/m^3), Faraday's constant, F, is 96487 (C/mol), K_0 is 8.85×10^{-12}, K_w is 78 K_0, and K_p is 3 K_0. The input displacement is defined as u, and distance between the foci in spheroidal cluster is defined as D'. The values of different variable and their definition are given in supplementary material.[35]

On the other hand hydrated IPMC produced output due to electrostatic and ionic effect.[19,31,32] The electrostatic effect in this case was the result of both spherical and spheroidal clusters

$$V_{dp}(s)=\frac{9.6\times10^{-9}hC^{-}F}{\pi(2K_p+K_w)\left(L^2+u(s)^2\right)}\times\left[\sum_{n=0}^{20}\frac{D(a+10^{-9})^3}{\left((2n+1)(a+10^{-9})\right)^3}+\frac{r(2r+10^{-9})^3}{\left((2n+1)(2r+10^{-9})\right)^3}\right]u(s), \tag{3}$$

$$V_{ion}(s)=\frac{\sqrt{A1}\left(1-\cosh(\sqrt{A1}y)\right)+A1L\sinh(\sqrt{A1}y)}{\sqrt{A1}^3\cosh(\sqrt{A1}y)}\times\frac{3sYwR(hA2-1)}{\psi L_{free}^3(A2)^2}u(s) \tag{4}$$

$$A1=\frac{sZ_0\kappa_e}{h};\quad A2=\frac{1}{d}\left(s+\frac{dF^2C^-}{RT\kappa_e}\right),$$

where Y is the young's modulus of IPMC, $Z0$ is the surface impedance per surface area, k_e is the dielectric permittivity, R is the gas constant, d is ionic diffusivity, T is the absolute temperature, and D is the electric displacement. Length and with are defined by variables L and w, respectively. Total thickness of IPMC is given as $2h$. If there is no phase shift, the total voltage in Laplace domain was

$$V(s)=V_{dp}(s)+V_{ion}(s). \tag{5}$$

The mechanoelectric model hence could be used to study the effect of ion concentration, frequency response, temperature, surface and intermediate layer impedance, mechanoelectric coupling, and dielectric permittivity on mechanoelectric property of IPMC. However there are certain limitations associated with the model. The model assumes that the charge on the surface was linearly proportional to the stress on the surface. In reality this relationship may not be linear in nature due to the viscoelastic nature of

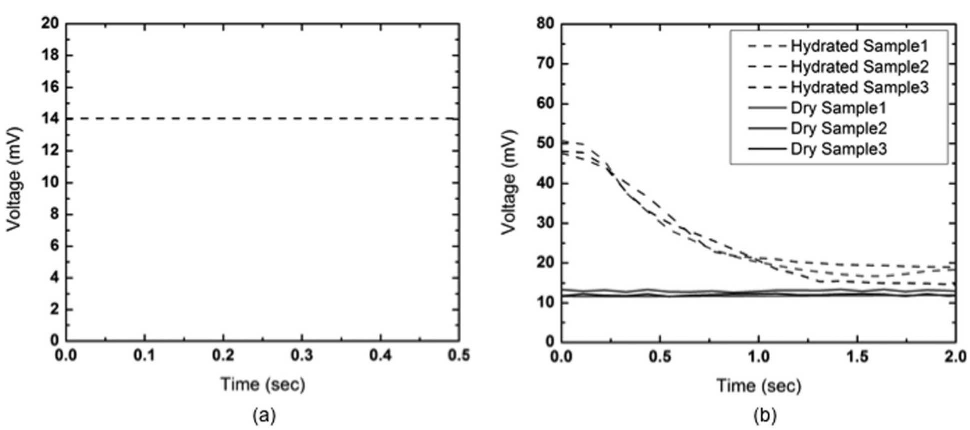

FIG. 2. IPMC response to step input because of electrostatic effect (a), and experimentally measured voltage output from a 10 mm × 50 mm × 0.17 mm IPMC under 0.5 in. step deformation (b).

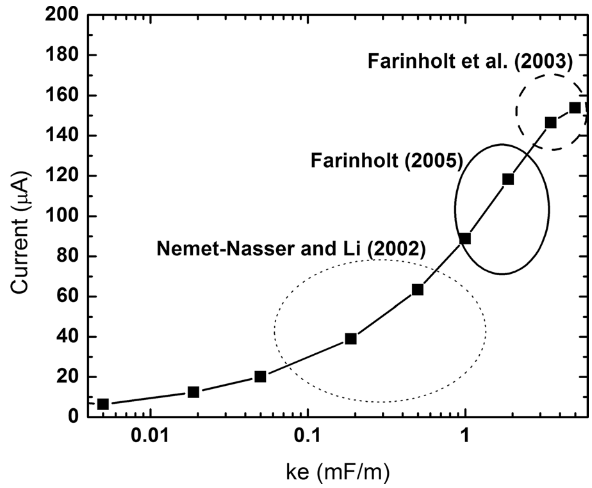

FIG. 3. Dependence of mechanoelectric output on permittivity as predicted by the electrostatic-ionic model. The values commonly used in literature are also highlighted.

IPMCs. Although the model explicitly illustrates the role of electrostatic and ionic effects in IPMC, in actuality these phenomena are tightly coupled and hence difficult to determine individually. Furthermore the model takes into account certain variables like charge concentration, coupling coefficient between charge and applied stress, diffusion constant, and dielectric permittivity, which are specific to each sample and hence must be determined for individual samples for better prediction. However, using the values of parameters from literature does give insightful results.

Mechanoelectric model was employed to study the step response of IPMC. A displacement of 0.5 in. was used as the input. Experimental setup is reported in the supplementary material.[35] Since the spheroidal geometry was dependent on the curvature of the sample, the electrostatic output remained constant as long as the curvature was unchanged as shown in Figure 2(a). The values of the parameters used are in the supplementary material.[35] Since the total output from IPMC was assumed to be a combination of the electrostatic and ionic effect, the overall IPMC output would show an exponential decay with time in hydrated form. Figure 2(b) shows the experimentally measured voltage across IPMC. The decay was observed to be slower than that predicted by the model. This could be due to the fact that ionic motion inside IPMC is slower than that predicted by the model.

From the mechanoelectric model the dependence of IPMC output on permittivity (Figure 3) was observed. The electrostatic-ionic model predicted an increase in output current with increase in permittivity. The capacitance of IPMC is directly proportional to the permittivity, and as permittivity increases the capacitance 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. It should be noted that layered IPMC architecture makes it very difficult to exclusively study the effect of one particular property on IPMC output both in sensor and actuator cases. However, it has been reported in literature that IPMC capacitance is predominantly affected by effective electrode area in actuator mode.[33] Another work[31,34] reported elsewhere by the author also studies the effect of impedance (resistance and capacitance) on IPMC sensing output. IPMCs with different surface electrode morphology were fabricated using electroless deposition technique. Different electrode morphology in turn was observed to affect IPMC capacitance and hence permittivity and ultimately IPMC output.

Figure 4 compares the output predicted from the model with the experimentally measured output, combining the electrostatic and ionic effect in dry and hydrated samples, respectively.

The graphs show a phase shift between the experimental and the simulated data. It is believed that the ionic motion inside the IPMC is slow. The model, however, did not account for this delay in ionic motion. Ionic effect was predicted to produce higher mechanoelectric output than the electrostatic effect. Also, an increase in the voltage was observed with frequency.

The mechanoelectric model presented here is different from previously reported models in literature.[1,10,17,19] First of all, the model due to ionic effect was added to the electrostatic model discussed previously to incorporate both ionic and electrostatic effect in IPMC. On one hand, the electrostatic effect accounts for the functioning of the material in dry conditions, due the presence of spheroidal clusters. The equations were extended to incorporate the presence of spherical clusters on hydration. Second, material response to dynamic input was studied. Lastly, both surface and intermediate layer impedances were incorporated into the ionic model in order to address the effect of surface and polymer

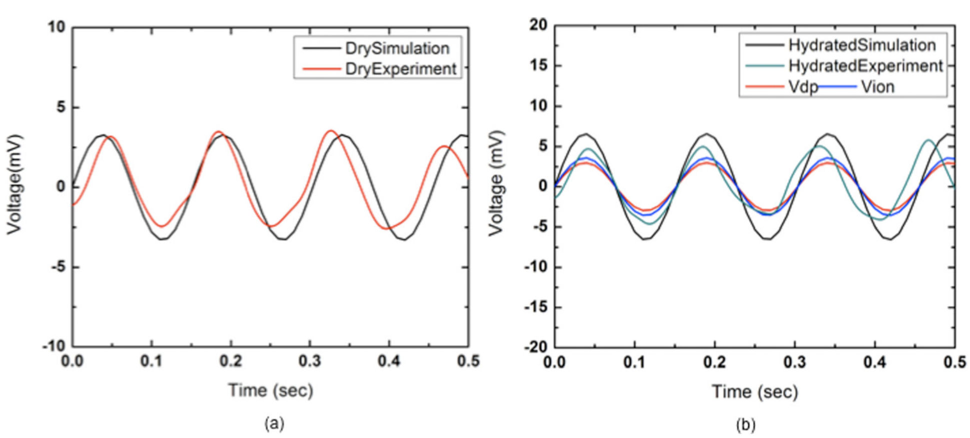

FIG. 4. Comparison of mechanoelectric model prediction with experimentally measured voltage output in dry (a) and hydrated (b) IPMC sample at 7 Hz vibration.

non-linearity. The model was employed to study the effect of electrode properties (like electrode thickness, morphology, and surface area) on the mechanoelectric response of IPMC. This model aims to provide a framework and can be extended further to incorporate more detailed study on the interfacial layer, both in dry and hydrated state. This would be particularly beneficial for improving IPMC signal generation to input stimuli.

The authors acknowledge the partial financial support of the U.S. National Science Foundation (IIS #0713075) and the Nevada System of Higher Education.

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