

An alternative explanation of back-relaxation in ionic polymer metal composites



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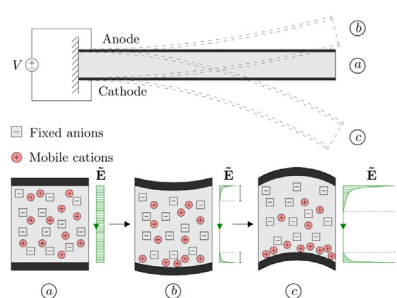
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HIGHLIGHTS

- We theoretically investigate actuation of ionic polymer metal composites.
- Electric polarization, ion mixing, and mechanical stretching are modeled.
- Back-relaxation is explained without reversing the cations' motion.
- Cations' motion breaks the symmetry of the electric field at the electrodes.
- Maxwell stress could be the critical explaining variable for back-relaxation.

GRAPHICAL ABSTRACT



At the onset of double layers' formation, the moment produced by the osmotic pressure will cause the IPMC to bend toward the anode. As time progresses, a wider region of the ionomer is depleted of cations in the vicinity of the anode. The increasing thickness of the cation-depleted region will cause a difference in the intensity of the electric fields at the double layers, modulating the moment generated by Maxwell stress. Maxwell stress will finally dominate the osmotic pressure, causing the IPMC to exhibit back-relaxation.

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ABSTRACT

The phenomenon of back-relaxation in ionic polymer metal composites (IPMCs) has attracted the interest of the scientific community for two decades, but its physical origins largely remain elusive. Here, we propose an explanation of this phenomenon based on Maxwell stress. From first principles, we demonstrate that IPMC actuation is controlled by the nonlinear interplay between osmotic and electrostatic phenomena. While osmotic pressure tends to produce a rapid bending toward the anode, Maxwell stress generates a slow relaxation toward the cathode. The relative weight of these phenomena is determined by the applied voltage. At voltage levels comparable to the thermal voltage, IPMC actuation is dominated by osmotic effects. As the applied voltage is increased, Maxwell stress overcomes the osmotic pressure, leading to back-relaxation.

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1. Introduction

Ionic polymer metal composites (IPMCs) are an emerging class of electroactive materials, which have shown strong potential as

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soft artificial muscles in a wide range of applications across technology and life science [1]. For example, IPMCs have been utilized as propulsion systems in biologically-inspired robots, implantable heart-assist and compression devices, and tactile displays for virtual reality [2,3]. Many more applications are under way, fueled by advancements in three-dimensional printing of free-form IPMCs [4,5]. IPMCs typically consist of an ionomeric membrane, neutralized by mobile cations and plated by conductive electrodes. The application of a voltage difference across the

electrodes induces an electric field in the ionomer, which is responsible for the controlled migration of cations [6]. The accumulation and depletion of cations through the ionomer is generally regarded as the key physical driver of IPMC actuation, leading to electrostatic, osmotic, and hydraulic forces [1].

Perhaps, the least understood and most surprising physical phenomenon associated with IPMC actuation is the so-called “back-relaxation”. The phenomenon was likely discovered about twenty years ago on Nafion-based samples immersed in a mixed solution of Na_2SO_4 and H_2SO_4 by Asaka and colleagues [7], and since then a number of studies have demonstrated its ubiquity across a range of material compositions (cation and solvent type) and experimental conditions (degree of hydration, applied voltage, and in-air versus in-solvent testing) [8–13]. As described in Asaka et al. [7], “in the case of a step voltage [of 1 V], the composite quickly[, within 100 ms,] bends to the anode side and bends back to the cathode side gradually[, while still under the electric potential]”. Back-relaxation in well saturated Nafion samples was observed for a large number of alkali-metal cations, and it was found to be abolished for large, organic cations [9] at the expense of weaker and slower actuation. The level of hydration was also shown to play a central role on back-relaxation, whereby the cogent removal of a fraction of the water in the ionomer can be used to reduce the phenomenon [13].

The generally accepted view for the physical mechanisms at the basis of back-relaxation focuses on the slow water flow within the ionomer [14]. Specifically, as cations migrate toward the cathode, not only they rapidly carry water molecules attached to them, but do they drag also loose water that is in excess within the ionomer, similar to the “added mass” effect in fluid mechanics. Once carried toward the cathode, the loose water will slowly diffuse back within the ionomer, causing the IPMC to relax. While we cannot dispute or reaffirm this hypothesis, we have discovered that back-relaxation is predicted by the nonlinear balance between osmotic and electrostatic phenomena during cation migration. We argue that Maxwell stress, often neglected in IPMC models, has a central role in explaining back-relaxation. Our explanation is the direct outcome of a recently proposed physically-based model [15], which was only implemented for steady-state deformations. By simply analyzing the model in time, we unveil the rapid deformation toward the anode, followed by the slow back-relaxation.

Our hypothesis is motivated by experimental observations [11,16], indicating that: (i) replacing the step input with a slow ramp that stabilizes at the same step voltage does not mitigate back-relaxation and (ii) reducing the intensity of the step input below 1 V hinders back-relaxation. Both these observations do not seem to favor the claim that back-relaxation is a manifestation of an added mass effect. The former evidence suggests that back-relaxation is attained under slowly-varying applied voltages, which would abate inertia. The latter evidence points at an explanation of back-relaxation where physical nonlinearities are at the core of the phenomenon, beyond linear processes associated with added mass. The possibility that the origins of back-relaxation are beyond hydraulic effects was also put forward in the technical literature [10–12,17–19], through a detailed analysis of the ionomer microstructure. These theories are construed upon an ionic cluster model, whose complexity may challenge the physical interpretation of the phenomenon and the calibration of simulation parameters from experimental data.

In contrast, the model proposed by Cha and Porfiri [15] is formulated within a continuum framework for the study of IPMCs, grounded on the thermodynamically rigorous theory proposed by Hong et al. [20] to study polyelectrolyte gels. Electrostatic and osmotic forces are not quantified from a microscopic analysis of cluster deformation and dipole–dipole interactions. Instead, they naturally stem from a free energy density, which accounts for mechanical stretching, ion mixing, and electric polarization at a macroscopic level. Our approach is based on a minimalistic treatment

of the mechanics and electrochemistry of IPMCs, which deliberately neglects viscoelasticity, solvent flow, redox reactions, steric effects, and diffusion processes at the electrodes to establish a first understanding of the possibility that back-relaxation may be simply caused by Maxwell stress.

2. Modeling framework

We start by concisely summarizing the model proposed in Cha and Porfiri [15] in the absence of steric phenomena and diffusion processes at the electrodes. For clarity, we adopt the same notation presented therein, which applies to large deformations. Briefly, we describe the state of the ionomer through the deformation gradient with respect to the initial stress-free configuration \mathbf{F} , the concentration of mobile cations per unit undeformed ionomer C , and the nominal electric displacement $\tilde{\mathbf{D}}$. The free energy density is expressed as the sum of three contributions

$$W(\mathbf{F}, \tilde{\mathbf{D}}, C) = W_{\text{mec}}(\mathbf{F}) + W_{\text{ion}}(\mathbf{F}, C) + W_{\text{pol}}(\mathbf{F}, \tilde{\mathbf{D}}), \quad (1)$$

where W_{mec} is the contribution from mechanical stretching of the ionomer, W_{ion} is associated with mixing of mobile cations and fixed anions, and W_{pol} is related to electric polarization of the ionomer. We hypothesize that the mechanical response is well approximated by a Saint Venant–Kirchhoff constitutive model, such that

$$W_{\text{mec}}(\mathbf{F}) = \frac{\lambda_L}{2}(\text{tr}\mathbf{L})^2 + \mu_L \text{tr}(\mathbf{L}^2), \quad (2)$$

where $\mathbf{L} = \frac{1}{2}(\mathbf{F}^T\mathbf{F} - \mathbf{I})$ is the Green–Lagrange strain tensor and λ_L and μ_L are Lamé parameters. With respect to ion mixing, we simply consider a solution of two dilute species, such that

$$W_{\text{ion}}(\mathbf{F}, C) = RT \left[C \left(\ln \frac{C}{C_0 \det \mathbf{F}} - 1 \right) - C_0 \left(\ln \frac{1}{\det \mathbf{F}} - 1 \right) \right], \quad (3)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, T is the absolute temperature, and C_0 is the fixed anion concentration. Finally, we assume that the ionomer is dielectrically isotropic, such that

$$W_{\text{pol}}(\mathbf{F}, \tilde{\mathbf{D}}) = \frac{1}{2\varepsilon} \frac{\mathbf{F}^T \tilde{\mathbf{D}} \cdot \tilde{\mathbf{D}} \otimes \tilde{\mathbf{D}}}{\det \mathbf{F}}, \quad (4)$$

where ε is the permittivity.

The nominal stress in the ionomer \mathbf{s} is simply computed by taking the derivative of (1) with respect to the deformation gradient, resulting into three distinct contributions, associated with mechanical elasticity ($\partial W_{\text{mec}}/\partial \mathbf{F}$), osmotic pressure ($\partial W_{\text{ion}}/\partial \mathbf{F}$), and Maxwell stress ($\partial W_{\text{pol}}/\partial \mathbf{F}$). Similarly, the nominal electric field is obtained by differentiating (1) with respect to $\tilde{\mathbf{D}}$ ($\tilde{\mathbf{E}} = \partial W_{\text{pol}}/\partial \tilde{\mathbf{D}}$), and the electrochemical potential is given by $\mu = \mathcal{F}\psi + \partial W_{\text{ion}}/\partial C$, where ψ is the electric potential ($\tilde{\mathbf{E}} = -\nabla\psi$) and $\mathcal{F} = 96485 \text{ C mol}^{-1}$ is the Faraday constant. The last element of the constitutive theory is to ensure that the free energy never increases, which we fulfill by hypothesizing that the cation flux is isotropic with diffusivity \mathcal{D} . By using Gauss law, mechanical equilibrium, and mass continuity, one can systematically obtain the governing equations for the ionomer; a detailed derivation is given in the Supplementary material (see Appendix A).

In this study, we focus on a thin IPMC of length L and thickness $2H \ll L$ undergoing in-plane deformations, such that a beam-like theory applies. By assuming that the curvature k is much smaller than $1/H$, the electrochemistry is governed by a Poisson–Nernst–Planck (PNP) system along the through-the-thickness

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