Electroactuation with Single Charge Carrier Ionomers

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A simple theory of electromechanical transduction for single-charge-carrier double-layer electroactuators is developed, in which the ion distribution and curvature are mutually coupled. The obtained expressions for the dependence of curvature and charge accumulation on the applied voltage, as well as the electroactuation dynamics, are compared with literature data. The mechanical- or sensor-performance of such electroactuators appears to be determined by just three cumulative parameters, with all of their constituents measurable, permitting a scaling approach to their design.

Electro-mechanical materials have long intrigued physicists. Such materials can serve as sensors and transducers (where mechanical stimulation generates a voltage) or can function as electroactuators where voltage generates a mechanical response (for review see [1-3]). A class of such materials, called Ionomeric Polymer Metal Composites (IPMC), is based on the motion of ions of one sign in an elastic polymer membrane enclosed between two bendable electrodes. Applied voltage causes mobile ions to accumulate near the oppositely charged electrode, forming an electrical double layer that expands the membrane and a depletion layer at the opposite electrode that contracts the membrane, causing bending (Fig. 1).

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across the plates. The second term accounts for the electrostatic energy of all ions interacting with each other and with the external field. The third term (see Eq. 2) is the entropy of the standard “lattice-gas model” [19], including the volume of ions [20]. The fourth term is the pressure-volume work that provides the coupling between mechanical bending and the ion concentration profile. Indeed, \( Kv \) is the pressure exerted by ions and \( \kappa x \) the elongation of the device due to curvature at a distance \( x \) away from the centre (\( x > 0 \) in extension; \( x < 0 \) in compression). This effective pressure-volume work characterises ion-induced swelling. This term is proportional to the sum of first moments of the charge distributions at each electrode, reflecting the fact that the more polarized charge distribution, the more favourable bending is. The fifth term, outside the integral, is the energetic cost of bending an Euler-Bernoulli beam.\[21\]

Note that the beam is assumed to be much longer than its width, precluding Gaussian curvature with only 1-dimensional bending.

All in all, Eqs. 12 describe several competing physical effects: the electrostatic and entropic costs of building up ions near one electrode and depleting them at the other. Bending relieves the energy of charge accumulation but the extent of bending is inhibited by the mechanical energy needed to deform the material.

Minimising the free energy functional (Eqs. 12) with respect to \( \rho \), constraining the total number of ions, gives the electrochemical potential of the mobile ions \( \mu_+ = e\psi + k_BT \ln[c_+/(c_{\text{max}} - c_+)] - K\kappa e\kappa x.\) By equating \( \mu_+ \) to its value in the bulk, \[22\] \( \mu_0 = k_BT \ln[c_0/(c_{\text{max}} - c_0)] \), we obtain the cation distribution (Fermi-like if \( \kappa = 0 \)) \[13\]

\[
c_+ = \frac{c_{\text{max}} - c_0}{c_{\text{max}} - c_0 - 1} \exp\left[\frac{e\psi - K\kappa e\kappa x}{k_BT}\right] + 1.
\]

Consequently, minimisation of Eqs. 1 and 2 gives a (dimensionless) modified Poisson-Fermi equation

\[
d^2y/dX^2 = \frac{(1 - \gamma)(e^y - 1)}{(1 - \gamma)e^y + \gamma}, \tag{4}
\]

with dimensionless variables \( X \equiv x/l_D, \ y \equiv e\psi/k_BT - p\kappa X l_D \) where \( p \equiv K\kappa /k_BT \), ion crowding parameter \( \gamma \equiv c_0/c_{\text{max}} \), Debye length \( l_D = (4\pi l_B c_0)^{-1/2} \) and Bjerrum length \( l_B = e^2/ek_BT \). Equation 4 is solved with boundary conditions \( y = 0 \) at \( x = 0 \), corresponding to vanishing electric field and potential in the bulk. These conditions are true for widely separated electrodes, so that the electrical double layer does not overlap the depletion layer, maintaining electroneutrality in the bulk; warranted unless the membrane is nanoscale thin. One can then combine two semi-infinite solutions corresponding to the anode and cathode. Taking the first integral of Eq. 4 gives the expression for the electric field:

\[
\frac{dy}{dX} = \sqrt{\frac{y + 1}{\gamma} \ln(\gamma e^{-\psi} - \gamma + 1)} \tag{5}
\]

Minimising Eq. 4 with respect to \( \kappa \) with \( H \equiv h/l_D \) and \( \tilde{\rho} \equiv (c_+/c_0) - 1 \), gives the dimensionless curvature:

\[
\kappa \equiv \kappa h = \frac{3eK}{2Eh^2} \frac{S}{S_0} l_D^2 c_0 \left(\int _{-H}^{H} \tilde{\rho} dX + \int _{0}^{H} \tilde{\rho} dX\right).
\]

The approximate equality is justified as the range of the charge density variation is much shorter compared to the separation between the electrodes [23]. Hence, \( \kappa \sim Q \) where \( Q \) is the charge per unit cross-section area stored in both the double layer and depletion layer, consistent with experimental results [3]. The integrals in Eq. 6 can then be evaluated using the Gauss law [24] which relates surface charge densities at each of the electrodes to electric inductions. Since the electrical induction (Eq. 5) contains itself \( \kappa \) through the definition of \( y \), a transcendental equation for \( \kappa \) emerges:

\[
\kappa = \alpha \left\{ \frac{1}{2} \left[ V_1 - p\kappa + \frac{1}{\gamma} \ln(\gamma e^{-V_1 + p\kappa} - \gamma + 1) \right] \right. \\
+ \left. \frac{1}{2} \left[ -V_2 + p\kappa + \frac{1}{\gamma} \ln(\gamma e^{V_2 - p\kappa} - \gamma + 1) \right] \right\} \tag{7}
\]

Here \( \alpha \), the dimensionless electroactuation number, is the key cumulative parameter for the actuation strength [25].

\[
\alpha \equiv \frac{3K}{2Eh} \frac{l_D S}{S_0 c_0} \frac{v}{\gamma} \equiv \frac{3K}{4\sqrt{\pi}} \frac{S}{S_0} \frac{v}{h} \frac{c_0^{1/2}}{l_B^{1/2}} \tag{8}
\]

The response vanishes when the membrane is soft or the plates are rigid (\( K/E \to 0 \)). Here, the dimensionless potential drops \( V \), \( V_1 \) and \( V_2 \) are, respectively, the total voltage, and the potential drops near the positive and negative electrodes, all normalized to \( k_BT/e \), obtained via equating the induction, thus the surface charge density, on both electrodes (this transforms the system into a constant voltage ensemble):

\[
V_1 = V - V_2 = p\kappa + \ln \frac{1 - \exp((1 - \gamma)(V - 2p\kappa))}{(1/\gamma - 1) \exp(-\gamma(V - 2p\kappa) - 1)} \tag{9}
\]

Expanding Eq. 7 in the low voltage regime gives \( V_1 \approx V_2 \approx V/2 \) and \( \kappa \approx \alpha \sqrt{(1 - \gamma)V} \). In the opposite large voltage limit, \( V_1 \approx (1 - \gamma)V \) and \( \kappa \approx \alpha \sqrt{8(1 - \gamma)V} \).

Figure 3 shows the full numerical solution of Eq. 7 where these two limits are recovered. This solution is replicated by the interpolation formula

\[
\kappa = \alpha \sqrt{1 - \gamma} \frac{V}{\sqrt{\frac{8}{\gamma} + 1}} \tag{10}
\]

matching the two limits. As seen from Eq. 10 the crossover from linear to non-linear regimes occurs at
When $V = 8$. At 300K, this corresponds to 0.2 Volts (see Fig. 3). This crossover has been observed experimentally in single-mobile-charge systems \[26, 27\] and was rationalized in ref \[28\]. Rearranging Eq. 10 yields this membrane thickness measured in units of Debye length.

To illustrate how the full solution of Eq. 7 works, consider a simple law for the experimental data: $(V/\kappa)^2 = \alpha^2 (1 - \gamma) (1 + \frac{v}{\kappa})$ which gives a straight line plotting $(V/\kappa)^2$ vs $V$. Experimental tests of this law and its 1/8 ratio between the slope and intercept are needed.

Figure 2 shows that the effect of curvature on the concentration profile is to reduce ion polarization at the electrodes. This is expected, as bending relaxes the steric and electrostatic strain induced by the accumulation and depletion of mobile ions near the electrodes. Bending opens extra volume close to the negative electrode, lowering the local concentration of cations. Conversely at the positive electrode, bending decreases the extent of the depletion layer.

Figure 3 demonstrates that larger electrode/membrane contact area and larger volume of the charge carrier enhance bending. More charge is stored for higher surface area electrodes and crowding in the double layer increases with ion size \[33\]. To achieve a substantial curvature of $\kappa = 1 \text{ cm}^{-1}$ at an applied voltage of 4V, assuming $\gamma = 0.25$, $\alpha/h$ must be greater than 0.03cm$^{-1}$. Using the above physical characteristics, the separation between the electrodes must be less than 10$\mu$m.

This simple model has no hysteresis or dissipation effects; the electroactuator response is fully reversible. Experimentally, hysteresis may occur due to non-idealities such as Joule heating, leakage of solvent outside the electrode, irreversible mechanical deformation of the ionic polymer metal composite \[36, 37\] and the current from trace water hydrolysis. Nanoporous electrodes \[38, 39\] are also not considered; surface roughness is assumed to occur on a scale much larger than the Debye length.

**Dynamics** - The simplest results can be obtained assuming: (i) the mechanical response time of the polymer is much faster than the charging of the double layer, (ii) the height of the electrode roughness is much smaller than the electrode-electrode separation and (iii) the dimensions of all channels are much larger than both the hydrated ion size and the Debye length. In this case, the response dynamics are solely determined by the migration of ions through the bulk and an equilibrium-like charging of the electrical double layers. The theory of double layer charging in single-mobile-charge-carrier systems has been considered in detail \[19, 40\]. Applying this to the case of electro-actuation, in response to a dimensionless step potential $U_0(=eV_0/k_BT)$ imposed at $t = 0$, we find an equation for $\kappa(t)$ \[41\],

$$ t = \frac{\tau}{\alpha} \int_0^{\kappa(t)} \frac{d\kappa}{U_0 - V(\kappa)}. $$

Here $\tau = R_0C_0$; $R_0 = 2h/(S_0\sigma) = 2h_{\text{ion}}T/(S_0\text{ohm}e^2D)$ is the resistance of the bulk ($\sigma$ is the ionic conductivity and $D$ is the diffusion coefficient of the ion); $C_0 = \varepsilon S/(8\pi l_D)$ is the linear Debye capacitance, giving

$$ \tau = \frac{h_{\text{ion}}}{D} \frac{S}{S_0}. $$

Equation 11 is solved analytically in the limits of linear response ($U_0 < 8\sqrt{U_0}$) and strongly nonlinear response:

$$ \kappa(t) = \alpha \sqrt{1 - \gamma} \left\{ U_0 \left(1 - \exp \left[ -\frac{t}{\sqrt{1 - \gamma}} \right] \right) \right\} \quad \text{for} \ U_0 < 8\sqrt{U_0} \text{tanh} $$

$$ (13) $$
The two forms coincide at short times, where the initial rate of bending \(aU_0/\tau\) is independent of \(\gamma\), since crowding of ions requires time to develop. The maximum final bending (Eq. 10) scales as \(a\sqrt{1 - \gamma}\) which is maximal at \(c_0 = c_{\text{max}}/2\) (or \(\gamma = 1/2\)). Hence, a vital prediction of our model is that single-ion actuators could be improved by roughly doubling the ion exchange capacity \([42]\) of Nafion ionomers. The relation between excess ion volume and actuation rate can be obtained by noting that in the linear response regime, \(x \sim vt/R_0\) with \(R_0 \sim v^{1/3}\) \([43]\). This gives the counter-intuitive prediction \(x \sim v^{2/3}t\) that the actuation becomes more rapid with larger ions! In the main part of Figure 4, the full \(x(t)\) curve, calculated via Eq. 13, is compared with experimental data \([6, 14]\).

**Conclusion** - A self-consistent theory of single-ion conducting electroactuators is presented, in which the curvature is considered on the same footing as the concentration profiles, modelling both actuation and sensing. The model assumes a strong coupling of ion build-up and depletion with local volume that forces bending. The theory reveals the roles of all physical characteristics but most importantly, they group themselves into three cumulative parameters: (i) dimensionless response coefficient - the electroactuation number \(\alpha\) (Eq. 8), (ii) ion crowding parameter \(\gamma\) and (iii) the relaxation time \(\tau\) for dynamics (Eq. 12). These three parameters have clear constituents, each of which can be independently measured or estimated. Other results are as follows:

- At large voltages, both curvature and charge accumulation increase as \(\sqrt{V}\), owing to ion crowding.
- For a given voltage, increasing the surface roughness, volume of ion and decreasing the electrode-electrode separation all increase bending.
- Plotting experimental data as \((V/\kappa)^2\) vs. \(V\) is predicted (Eq. 10) to give a straight line with a slope 8 times smaller than the intercept.
- The dynamic response is described by simple analytical formulae (Eqs. 12 and 13).
- Electroactuation number \(\alpha\) allows a scaling approach for rational design of electroactuators \([44]\).

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