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Supplementary material for “A multi-cation model for the actuation of ionic membranes with ionic liquids”

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A System of equations in the numerical solution

The collocation of the constant electrochemical potentials gives $3N$ equations,

$$\bar{\mu}_+ = \mathcal{RT} \log \left(\frac{C_{+,j}}{C_{+,j} + C_{+,j}^{\text{IL}} + C_{-,j}^{\text{IL}}} \right) + \mathcal{V}_+ \pi_j + \mathcal{F} \phi_j, \quad (1a)$$

$$\bar{\mu}_+^{\text{IL}} = \mathcal{RT} \log \left(\frac{C_{+,j}^{\text{IL}}}{C_{+,j} + C_{+,j}^{\text{IL}} + C_{-,j}^{\text{IL}}} \right) + \mathcal{V}_+^{\text{IL}} \pi_j + \mathcal{F} \phi_j, \quad (1b)$$

$$\bar{\mu}_-^{\text{IL}} = \mathcal{RT} \log \left(\frac{C_{-,j}^{\text{IL}}}{C_{+,j} + C_{+,j}^{\text{IL}} + C_{-,j}^{\text{IL}}} \right) + \mathcal{V}_-^{\text{IL}} \pi_j - \mathcal{F} \phi_j, \quad (1c)$$

for $j = 1, \dots, N$.

Similarly, by collocating the incompressibility constraint, we obtain N equations,

$$\begin{aligned} \mathcal{V}_+(C_{+,j} - \bar{C}_+) + \mathcal{V}_+^{\text{IL}}(C_{+,j}^{\text{IL}} - \bar{C}_+^{\text{IL}}) + \mathcal{V}_-^{\text{IL}}(C_{-,j}^{\text{IL}} - \bar{C}_-^{\text{IL}}) = \\ \frac{1}{\lambda_L + 2\mu_L} \left[2\mu_L(-kX_j + \varepsilon_0) - \frac{\varepsilon}{2} \xi_j^2 + \pi_j \right]. \end{aligned} \quad (2)$$

for $j = 1, \dots, N$, where

$$\varepsilon_0 = \frac{\varepsilon}{8\mu_L H} \text{trapz}(\xi^2), \quad (3a)$$

$$\begin{aligned} k = - \frac{3}{8\mu_L(\lambda_L + \mu_L)H^3} \left[(\lambda_L + \mu_L) \varepsilon \text{trapz}(\xi^2 X) \right. \\ \left. + 2\mu_L \text{trapz}(\pi X) \right]. \end{aligned} \quad (3b)$$

Herein, $\text{trapz}(\cdot)$ indicates an integral approximated via the trapezoidal rule. In other words, for a function f known at the nodes,

$$\text{trapz}(f) = \sum_{j=1}^{N-1} \frac{f_{j+1} + f_j}{2} \Delta X_{j+\frac{1}{2}}. \quad (4)$$

The discretized version of the Poisson equation provides $N - 1$

equations,

$$\begin{aligned} -\varepsilon \frac{\xi_{j+1} - \xi_j}{\Delta X_{j+\frac{1}{2}}} \\ = \mathcal{F} \left[\frac{(C_{+,j+1} + C_{+,j+1}^{\text{IL}} - C_{-,j+1}^{\text{IL}}) + (C_{+,j} + C_{+,j}^{\text{IL}} - C_{-,j}^{\text{IL}})}{2} - \bar{C}_-^* \right], \end{aligned} \quad (5)$$

for $j = 1, \dots, N - 1$.

Similarly, by imposing that $\xi = d\phi/dX$, we find other $N - 1$ equations,

$$\frac{\phi_{j+1} - \phi_j}{\Delta X_{j+\frac{1}{2}}} = \frac{\xi_{j+1} + \xi_j}{2}, \quad (6)$$

for $j = 1, \dots, N - 1$.

We impose the boundary conditions at the Stern layers to obtain two equations as

$$\phi_1 = -\frac{V}{2} + \lambda_s \xi_1, \quad (7a)$$

$$\phi_N = \frac{V}{2} - \lambda_s \xi_N. \quad (7b)$$

Last, we impose charge conservation (three equations),

$$\text{trapz}(C_+) = 2H\bar{C}_+, \quad (8a)$$

$$\text{trapz}(C_+^{\text{IL}}) = 2H\bar{C}_+^{\text{IL}}, \quad (8b)$$

$$\text{trapz}(C_-^{\text{IL}}) = 2H\bar{C}_-^{\text{IL}}. \quad (8c)$$

B Estimation of material parameters

B.1 Estimation of equilibrium concentrations

We seek to estimate equilibrium concentrations $\bar{C}_+^{\text{max}} = \bar{C}_-$ and $\bar{C}_+^{\text{IL,max}} = \bar{C}_-^{\text{IL}}$ in the case in which all charges are mobile (apart from membrane coions). Note that \bar{C}_+^{max} and $\bar{C}_+^{\text{IL,max}}$ are the maximum values of \bar{C}_+ and \bar{C}_+^{IL} , whereby part of the counterions and IL-cations can be bonded to the membrane coions. All concentrations will be estimated through

$$\bar{C}_i = \frac{N_i}{V}, \quad (9)$$

where V is the total volume of the membrane and N_i the number of moles of component i .

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Given the dry volume of the membrane, V_{dry} , and the density of dry Nafion™ $\rho_{\text{dry}} = 1580 \frac{\text{kg}}{\text{m}^3}$, we can compute the mass of the dry membrane $m_{\text{dry}} = \rho_{\text{dry}} V_{\text{dry}}$. Given the equivalent weight $\text{EW} = 1.1 \frac{\text{kg}}{\text{mol}}$, which represents the mass of dry Nafion per unit mole of sulfonate group, we can compute the number of moles of sulfonate groups in the membrane, $N_- = m_{\text{dry}}/\text{EW}$. This number will not change when the ionic liquid is added.

The dry volume of the membrane V_{dry} does not account for potential changes in volume that are associated to exchanged counterions. The volume of counterions in the membrane is $N_+ \mathcal{V}_+ = N_- \mathcal{V}_-$, where we have used $N_+ = N_-$ for electroneutrality before the soaking in IL. The molar volume of counterions can be estimated from their molar mass \mathcal{M}_+ and density ρ_+ as $\mathcal{V}_+ = \frac{\mathcal{M}_+}{\rho_+}$. Herein, we assume that the density of ions is the same as the metallic form of the counterion. For lithium, we find $\mathcal{V}_+ = 1.30 \times 10^{-5} \frac{\text{mol}}{\text{m}^3}$.

Once counterions are exchanged, an IL is added to the membrane. The volumetric uptake η of IL in the membrane per unit volume of dry membrane is commonly found in the literature^{3,4}. We consider a volumetric uptake $\eta = 0.5$, which is standard in the literature and close to the critical uptake of ILs for different membranes⁴. The total volume of the membrane after IL uptake is $V = (1 + \eta)(V_{\text{dry}} + N_- \mathcal{V}_-)$. Thus, we find

$$\bar{C}_+^{\text{max}} = \bar{C}_- = \frac{N_-}{V} = \frac{N_-}{(1 + \eta)(V_{\text{dry}} + N_- \mathcal{V}_-)} \quad (10)$$

For a Nafion™ membrane with lithium counterions, $\bar{C}_+^{\text{max}} = \bar{C}_-$ for electroneutrality, as both ionic species have unit valence.

Given the molar mass \mathcal{M}_{IL} of the IL, the uptake volume $V_{\text{IL}} = \eta(V_{\text{dry}} + N_- \mathcal{V}_-)$ and its density ρ_{IL} , we find the number of moles of IL in the membrane as

$$N_{\text{IL}} = \frac{m_{\text{IL}}}{\mathcal{M}_{\text{IL}}} = \frac{\rho_{\text{IL}} V_{\text{IL}}}{\mathcal{M}_{\text{IL}}} \quad (11)$$

Thus,

$$\bar{C}_+^{\text{IL,max}} = \bar{C}_-^{\text{IL}} = \frac{N_{\text{IL}}}{V} = \frac{N_{\text{IL}}}{(1 + \eta)(V_{\text{dry}} + N_- \mathcal{V}_-)} \quad (12)$$

B.2 Estimation of ions' molar volumes

We need to estimate the molar volumes of the cations and anions resulting from the decomposition of the IL. These molar volumes are not readily available from the literature. To provide an estimate, we first compute the molar volume of the IL from its molar mass and density as $\mathcal{V}_{\text{IL}} = \frac{\mathcal{M}_{\text{IL}}}{\rho_{\text{IL}}}$. We utilize the van der Waals volumes of cations ($V_{\text{w},+}^{\text{IL}}$) and anions ($V_{\text{w},-}^{\text{IL}}$)⁵ to estimate the fractions of the molar mass associated to the cations and anions as

$$\mathcal{V}_+^{\text{IL}} = \frac{V_{\text{w},+}^{\text{IL}}}{V_{\text{w},+}^{\text{IL}} + V_{\text{w},-}^{\text{IL}}} \mathcal{V}_{\text{IL}}, \quad (13a)$$

$$\mathcal{V}_-^{\text{IL}} = \frac{V_{\text{w},-}^{\text{IL}}}{V_{\text{w},+}^{\text{IL}} + V_{\text{w},-}^{\text{IL}}} \mathcal{V}_{\text{IL}}. \quad (13b)$$

For EMI-BF₄, $\mathcal{V}_{\text{IL}} = 1.597 \times 10^{-4} \frac{\text{m}^3}{\text{mol}}$, $V_{\text{w},+}^{\text{IL}} = 113.882 \text{ \AA}^3$ and $V_{\text{w},-}^{\text{IL}} = 52.006 \text{ \AA}^3$, such that $\mathcal{V}_+^{\text{IL}} = 1.096 \times 10^{-4} \frac{\text{m}^3}{\text{mol}}$ and $\mathcal{V}_-^{\text{IL}} = 5.01 \times 10^{-5} \frac{\text{m}^3}{\text{mol}}$.

B.3 Estimation of diffusivities

The diffusivity in Nafion™ of simple counterions such as lithium has been experimentally measured⁶ at different concentrations. We use an average value $\mathcal{D}_+ = 1.2 \times 10^{-10} \frac{\text{m}^2}{\text{s}}$ for lithium counterions.

To the best of our knowledge, no experimental results are available for the diffusivity of cations and anions from the dissociation of ILs in ionic membranes. Some molecular dynamics simulations have estimated the diffusivity of some widely used ILs in Nafion™^{7,8}. We estimate the diffusivity at a temperature of 298 K by fitting the molecular dynamics results in Sun and Zhou⁷ with an exponential in the form ae^{bx} . We find $\mathcal{D}_+^{\text{IL}} = 1.34 \times 10^{-12} \frac{\text{m}^2}{\text{s}}$ and $\mathcal{D}_-^{\text{IL}} = 1.12 \times 10^{-12} \frac{\text{m}^2}{\text{s}}$.

B.4 Other parameters

In all our simulations, we set $\delta = 10^{-3}$. Such a value of δ is larger than the one that would be estimated from the electric permittivity of Nafion™ membranes⁹. This choice is motivated by two considerations: 1) it facilitates numerical convergence; and 2) it accounts for high-surface electrodes that arise from electrochemical plating in IPMCs, which considerably increase the capacitance of electrode double layers^{10,11}.

The Stern layer is assumed to be a fraction of the thickness of the diffuse layer. As no numerical or experimental study has investigated the thickness of the Stern layer in the electric double layer of counterions, IL-cations and IL-anions in Nafion™, we set as a reasonable estimate $\Lambda_s/\delta = 10^{-2}$.

The Young modulus of IL-swollen Nafion™ is taken to be 250 MPa, as experimentally determined in Bennett⁴ for volumetric uptakes of around 50%. Similar to previous studies on IPMCs¹², we set $\nu = 0.45$.

Notes and references

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