Current-Induced Membrane Discharge

Andersen, Mathias Bækbo; van Soestbergen, M.; Mani, A.; Bruus, Henrik; Biesheuvel, P. M.; Bazant, M. Z.

Published in:
Physical Review Letters

Link to article, DOI:
10.1103/PhysRevLett.109.108301

Publication date:
2012

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Selective ion transport across charged, water-filled membranes plays a major role in ion exchange and desalination [1,2], electrophysiology [3], fuel cells [4,5], and lab-on-a-chip devices [6–10], but is not yet fully understood. A long-standing open question has been to explain the experimentally observed overlimiting current (OLC), exceeding classical diffusion limitation [11]. Possible mechanisms include the role of electro-osmotic instability (EOI) and water splitting in the bulk solution [12–15], as well as surface conduction and electro-osmotic flow in microchannels [16]. Vortices consistent with EOI have recently been observed under OLC conditions [7,17,18], although the theory of Rubinstein and Zaltzman [19–21] remains to be tested quantitatively. The water splitting mechanism, either catalyzed by membrane surface groups or through the second Wien effect, has not yet been conclusively tied to OLC [15,22–27].

In this Letter, we propose a chemical mechanism for OLC, “current-induced membrane discharge” (CIMD), resulting from membrane (de)protonation and water self-ionization, even in the absence of fluid vortices due to EOI, in ion-exchange membranes much thicker than the Debye screening length. The amphoteric nature of the charge of ion-exchange membranes (i.e., sensitivity to pH and other stimuli) is well known [5,28–33], but not in response to a large applied current. The basic physics of CIMD is illustrated in Fig. 1 for an anion-exchange membrane. During OLC, a large electric field develops on the upstream, salt-depleted side of the membrane, which expels H\(^+\) and attracts OH\(^-\), which have an association equilibrium with the charged groups of the membrane, causing the membrane to lose its positive charge (effectively, to deprotonate, as we will consider below) thereby allowing salt co-ions to pass and producing large pH gradients. The upstream solution becomes more acidic (low pH), while the downstream, salt-enriched solution and the membrane become more basic (high pH).

The local charge of an aqueous membrane strongly depends on the local pH. In our examples below, we consider an anion-exchange membrane with fixed surface groups of volumetric concentration \(c_{\text{mem}}\), which selectively allows negatively charged anions (counterions) to pass, while largely blocking cations (co-ions) [34]. Depending on \(pH = \log_{10}(c_H)\), where \(c_H\) is the proton concentration (\(H^+\) or \(H_2O^+\)) in M, the membrane can discharge (deprotonate):

\[
\text{RH}^+ \Leftrightarrow K \cdot R + H^+.
\]

In terms of non-deprotonatable surface groups, such as quaternary amine groups in anion exchange membranes, the above reaction is equivalent to the \(OH^-\) association reaction: \(R^+ + OH^- \Leftrightarrow ROH\). The ratio of product to reactant concentrations in equilibrium is the dissociation constant \(K\) in M (\(pK = -\log_{10}(K)\). Assuming a classical Langmuir adsorption isotherm [28–32,35,36], the ionization degree of the membrane,
with dissociation constant

\[ K_w = c_{\text{H}^+}c_{\text{OH}^-}, \]  

(4)

where \( K_w = 10^{-14} \) M\(^2\) at \( T = 25^\circ C \). Although kinetics can be included [5,24-26,37], the reactions (1) and (3) are typically fast, so we assume local quasiequilibrium.

We now develop a membrane model (seemingly the first) including all of these effects: (i) transport of four ionic species, including co-ions and water ions (\( \text{H}^+ \) and \( \text{OH}^- \)) along with majority anions, (ii) water self-ionization, and (iii) \( pH \)-dependent membrane charge.

We consider the prototypical 1D electrodialysis geometry in Fig. 1, consisting of a planar ion-selective membrane of thickness \( L_{\text{mem}} \) between two well-stirred reservoir compartments of salt ion concentration \( c_{\text{res}} \) and \( pH \) of \( pH_{\text{res}} \). We adopt the simplest and most commonly used model of diffusion limitation [11], in which ion concentrations vary across “stagnant diffusion layers” (SDLs) of thickness \( L_{\text{SDL}} \).

(5)

where \( \Delta \phi = \Delta E = 0 \) and \( \Delta \phi = 8 \) (corresponding to NaCl), \( \Delta c = 0 \) and \( \Delta c = 6 \) (corresponding to HCl), and \( \Delta c = 0 \) and \( \Delta c = 10 \) (corresponding to KOH).

(6)

and satisfying Poisson’s equation

\[ \frac{d \phi}{dx} = \frac{\Delta E}{e} \]

(5a)

\[ J_\pm = f_rD_\pm \left( \frac{dc_\pm}{dx} \pm c_\pm \frac{d \phi}{dx} \right) \]  

(5b)

\[ J_w = -f_rD_w \left( \frac{dp_w}{dx} + (\Delta c_\text{M} + P_w \Delta c_{\text{H}_{\text{OH}}} \text{OH}) \right) \]  

(5c)

where \( J_i \) is the ionic current density of species \( i \) and \( f_r \) is a correction factor for the ion diffusion coefficient in the membrane, taking into account geometrical and chemical effects which effectively retard ion transport (\( f_r = 1 \) in the SDLs). Here, \( \phi \) is the dimensionless mean electrostatic potential scaled to the thermal voltage \( V_T = k_B T/e = 25.7 \text{ mV} \) and satisfying Poisson’s equation

(6)

and

(7)

where \( \lambda_B = e^2/(4\pi e r_j \varepsilon_0 k_B T) \) is the Bjerrum length, and

\[ \rho_{\text{ions}} = e(c_+ - c_- + c_{\text{H}^+} - c_{\text{OH}^-}) \quad \text{and} \quad \rho_{\text{mem}} = \alpha e c_{\text{mem}} \]

are charge densities due to the ions and the immobilized charges in the membrane, respectively. The porosity \( \varepsilon \) of the membrane appears because concentrations \( c_i \) are defined with respect to the interstitial, not total, volume \( (\varepsilon = 1) \) in the SDLs. In our simulations below, we choose the following typical parameters: \( c_{\text{mem}} = 5 \text{ M} \), \( pK = 9.5 \), \( L_{\text{mem}} = L_{\text{SDL}} = 100 \mu \text{m} \), \( \varepsilon_{\text{res},\text{SDL}} = 78, \varepsilon_{\text{res},\text{mem}} = 29, \varepsilon = 0.4 \), \( f_r = 0.02 \) [39], \( D_\pm = 1.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) and \( D_w = 2.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) (corresponding to NaCl), \( D_{\text{H}^+} = 9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \), and \( D_{\text{OH}^-} = 5.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \). We also use \( pH_{\text{res}} = 7 \) and \( \beta = 2c_{\text{res}}/c_{\text{mem}} = 0.02 \), unless otherwise noted. The voltage difference across the system is \( \Delta \phi \). At the reservoir-SDL boundaries we set \( c_{\pm} = c_{\text{res}} \) and relate \( P_w \) to \( pH_{\text{res}} \).

In spite of neglecting fluid flow, the model still predicts OLC, as shown in Fig. 1. The classical ion concentration polarization phenomenon is apparent in panel (b) with salt depletion where counterions (anions) enter the membrane \( (x = x_2) \) and enrichment where they leave \( (x = x_3) \). Within the membrane, however, anion depletion and cation (co-ion) enrichment reveal a significant loss of selectivity due to CIMD. At the same time, panel (c) shows large, order-of-magnitude variations in \( c_{\text{H}^+} \), “mirrored” by \( c_{\text{OH}^-} \).
through the equilibrium Eq. (4), with proton enrichment (acidity) in the left SDL and proton depletion (basicity) in both the membrane and the right SDL. The existence of such pH variations has been confirmed experimentally in similar systems [40–43].

Motivated by this observation, we analyze the pH gradients perturbatively in the full CIMD model. We consider underlimiting currents, assume thin, quasiequilibrium double layers (Donnan approximation) at the SDL–membrane interfaces, and solve the leading-order problem for $c_\text{H}$, $c_\text{OH}$ and $\phi$ with small perturbations in $c_\text{H}$ and $c_\text{OH}$, valid when $(c_\text{H} + c_\text{OH})/(c_+ + c_-) \ll 1$. The resulting semianalytical model suffices to predict CIMD (variations of membrane charge with local pH) via Eq. (2). Numerical calculations show that pH and $\alpha$ are nearly constant across the membrane, so the water charge density is averaged between positions $x_2$ and $x_3$ (see below) to calculate the membrane charge and midplane pH [Fig. 2(b)] to be used in Eq. (2) to calculate $\alpha$.

The final result for the most general model including membrane discharge, arbitrary values for $pH_{\text{res}}$ and $c_{\text{res}}$, and the possibility that all diffusion coefficients are different, consists of Eq. (2) together with the set of algebraic equations below (see the Supplemental Material for details [44]). First, we introduce the dimensionless salt flux variable $J_{\text{salt}} = (J_x - J_xD_x + D_x)/J_{\text{lim}}$, in which $J_{\text{lim}} = 2D_x c_{\text{res}}/L_{\text{SDL}}$ is the “classical” limiting current density [11], and obtain the salt current–voltage relation,

$$\Delta \phi = 4\tanh^{-1}(j_{\text{salt}}) + j_{\text{salt}} \frac{\beta}{\gamma} \alpha,$$

in which $\gamma = \exp(x_2 - x_1)/l_{\text{mem}}$, where $l_{\text{mem}} = L_{\text{mem}}/L_{\text{SDL}}$ is the membrane-to-SDL width ratio. The first term describes concentration polarization in the SDLs, while the second is the Ohmic response of the membrane. Next, we introduce the dimensionless water ion flux $J_w = J_w/L_{\text{SDL}}/(D_w\sqrt{K_w})$ and water ion variable $\rho_w = J_w/L_{\text{SDL}}/(D_w\sqrt{K_w})$ and obtain the following equations:

$$\rho_w(x_{\text{limit}}) = \rho_w(x_{\text{midplane}}) \times \exp[j_{\text{salt}}\beta/(\gamma\alpha)] + j_{\text{lim}}/\gamma = 0, \quad \sinh^{-1}[(\rho_w(x_{\text{limit}})/2) - \sinh^{-1}[(\rho_w(x_{\text{midplane}})/2)] = \sinh^{-1}(\rho_w(x_{\text{midplane}})/2) - \sinh^{-1}(\rho_w(x_{\text{limit}})/2)],$$

where $\rho_w(x_{\text{limit}}) = \rho_w^\text{res} + j_w + \rho_\\text{res}[1 + 2\gamma\beta/\alpha]\ln(1 + j_{\text{salt}})$, (where in these expressions $i = 2$ and $3$ corresponds to $-$ and $+$, respectively). Here, $\rho_w^\text{res}$ is related to $pH_{\text{res}}$ and $\rho_0 = [4 + (\rho_w^\text{res})^2]^{1/2}$. Note that $x_{\text{limit}}$ and $x_{\text{midplane}}$ refer to positions on either side of the equilibrium electric double layer at the membrane–SDL interfaces. In the limit of an infinite membrane charge $\beta/\alpha \to 0$ the solution to the leading order problem [Eq. (7)] is simply the “classical” result [45],

$J_{\text{salt}} = \tanh(\Delta \phi/4)$. We find the characteristic voltage factor $\phi_0$ by expanding Eq. (7) for small $j_{\text{salt}} \ll 1$ and obtain $J_{\text{salt}} = \Delta \phi/\phi_0$ in which $\phi_0 = 4 + \beta/\gamma$ assuming constant $\alpha = 1$. The voltage factor $\phi_0$ characterizes the exponential-like approach of the current density to its limiting value with applied voltage. Thus, in the classical picture, for $\Delta \phi/\phi_0 = 3$ we expect the current density to be at $\approx 95\%$ of its limiting value.

Results of the semianalytical model are compared with full numerical calculations in Fig. 2, which shows good agreement in the expected range of validity $\Delta \phi/\phi_0 \leq 1$. The pH appears to converge towards a limiting value for $\Delta \phi \to \infty$, and the jump in this limiting pH value between the left SDL and the membrane is huge, here about 5 pH units at the highest values of $\Delta \phi$ considered. We note that the deviation between the analytical and numerical solution is largest in the left SDL where electroneutrality is most strongly violated. This comparative analysis constitutes a validation of our numerics and provides further support for our conclusions regarding the role of pH in controlling the ionic transport properties of ion-selective membranes.

We now turn to a numerical analysis of the CIMD model Eqs. (2)–(6). For comparison, we also solve the classical model $M_1$ used in all prior work on EOI [17–21] in which (i) $c_+ = 0$ in the membrane, (ii) $c_{\text{H}} = c_{\text{OH}} = 0$ everywhere, and (iii) $\alpha = 1$ for all conditions. Additionally, we solve two intermediate models which include co-ions in the membrane with $\alpha = 1$ and either exclude (M2) or include (M4) water ions, i.e., taking 2 or 4 ions into account in the membrane, respectively. The total current density is $J_{\text{tot}} = J_+ + J_- + J_w$.

Figure 3(a) shows the significant decrease in the ionization degree $\alpha$ predicted by the CIMD model, in contrast to the constant $\alpha = 1$ in the $M_1$ model. Moreover, $\alpha$ decreases with decreasing $\beta$ (due to the increasing Donnan potential) and decreases with $pH_{\text{res}}$ (due to decreasing $c_{\text{H}}$ in the membrane). A striking, and yet unexplained prediction is that for $\Delta \phi/\phi_0 \leq 3$ and $pH_{\text{res}}$ larger than 7 the ionization degree is almost constant until the curve hits that for $pH_{\text{res}} = 7$ after which the curves follow each other. In general we find beyond a few times $\phi_0$ that reservoir pH has a very small influence on membrane charge, fluxes, and currents [see also Figs. 3(b)–3(d)]. A more in-depth analysis of the effect of reservoir pH and the inclusion of additional chemical species is left for future work. Figure 3(b) shows the significant increase of co-ion flux $J_+$, thus loss
of membrane selectivity, with increasing voltage, as predicted by the CIMD model, for all values of pH and β, while Fig. 3(d) shows likewise the increase in current density \( J_w \) due to water ions. Still, these contributions do not sum to the increased current during OLC, as shown in Fig. 3(c), the difference being due to increased counterion flux \( J_+ \).

Although the current–voltage relation in CIMD is quite complicated, our simulations and analysis suggest two general trends: (i) OLC increases with reservoir salt concentration, roughly as \( \beta^{0.65} \) for the parameters of Fig. 3; (ii) OLC is nearly independent of reservoir pH, in spite of the large pH gradients produced across the membrane.

Finally, we analyze the possible effect of CIMD on EOI. In the classical \( M_1 \) model, nonequilibrium space charge forms at the limiting current \([45–48]\), and its growing separation from the membrane reduces viscous resistance to electro-osmotic flow and destabilizes the fluid \([19–21]\). As a measure of the propensity to develop EOI we use the transverse (Helmholtz-Smoluchowski) electro-osmotic mobility \( \mu_{eo}/\mu_{eo,0} \) at the left SDL-reservoir edge, which is equal to the first moment of the charge density, \(-4\pi \alpha H \int_{\phi_0}^{\phi} x \rho_{\text{ions}} \, dx\), or the dimensionless potential difference across the left SDL, \( \phi(x_1) - \phi(x_2) \).

![Graphs showing current-voltage relations and comparison of CIMD models](image)

**FIG. 3 (color online).** Comparison of the classical \( M_1 \) model (only counterions in the membrane) with the full CIMD model for different concentration ratios \( \beta = \frac{c_{\text{res}}}{c_{\text{mem}}} = 0.004, 0.02, 0.04 \), and in the case \( \beta = 0.02 \) for \( \text{pH}_{\text{res}} = 5.5, 7, 8.5 \). (a) Membrane ionization degree \( \alpha \). (b) Co-ion current \( J_+ \). (c) Total current \( J_{\text{tot}} \). (d) Water ion current \( J_w \).

**FIG. 4 (color online).** Comparison of three fixed-charge membrane models \( M_n \) having \( n = 1, 2, 4 \) mobile ionic species and the CIMD model for (a) charge density \( \rho_{\text{ions}} \) versus distance \( x^* \) from the membrane scaled to the reservoir Debye length \( \lambda_D \), and (b) electro-osmotic mobility \( \mu_{eo} \) as a function of total current \( J_{\text{tot}} \). To further stress the effect of CIMD, the CIMD and \( M_4 \) models are shown for the higher current density \( J_{\text{tot}}/J_{\text{lim}} = 1.03 \) compared to \( J_{\text{tot}}/J_{\text{lim}} = 1.01 \) for the \( M_1 \) and \( M_2 \) models.

**Figure 4(a)** shows that slightly above the limiting current \( J_{\text{tot}}/J_{\text{lim}} = 1.01 \) the \( M_1 \) model already predicts a very significant extended space charge layer (the “shoulder”) maximum in \( \rho_{\text{ions}}/\rho_{\text{ions},0} = (\lambda_D L_{\text{SDL}}/\phi_0) d^2 \phi/dx^2 \) several hundred Debye lengths from the membrane), whereas for an even higher current \( J_{\text{tot}}/J_{\text{lim}} = 1.03 \), using the more realistic CIMD model, the extension of this layer is still very minor. The two intermediate models lie in between. Figure 4(b) shows how the transverse electro-osmotic mobility is predicted by the \( M_1 \) model to diverge at the limiting current. This divergence is significantly reduced only by the full CIMD model including simultaneously co-ion access, water ion transport, water splitting, and membrane discharge. We note that a proper analysis of EOI would be more involved, since here we have simply focused on the transverse electro-osmotic mobility as a way of illustrating the suppression of EOI due to CIMD.

In conclusion, we have theoretically demonstrated that OLC through aqueous ion-exchange membranes can result from CIMD, or loss of ion selectivity due to (de-) protonation coupled to ion transport and water self-ionization. The appearance of OLC carried partially by salt co-ions and water ions reduces separation efficiency in electrodialysis, but the associated large pH gradients and membrane discharge could be exploited for current-assisted ion exchange or pH control. In addition to the effect of the water ions, the loss of ion selectivity due to CIMD leads to a further suppression of the nonequilibrium space charge that is much larger than in any of the models \( M_1, M_2, \) and \( M_4 \), see Fig. 4(a). The nonequilibrium space charge is responsible for EOI and thus CIMD should be considered in both models and experiments on OLC with...