Qualitative Regime Behaviour in 1D Models for Redox- flow Cells

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Introduction

Because many cell parameters are uncertain, detailed simulations often become expensive fitting. Minimal 1D models with effective closures, and dimensional analysis allow us to sweep broad parameter ranges and map polarization regimes and scalings. This **dimensionless regime map allows rapid identification of the polarization regime** corresponding to a given operating point.

1D Binary Electrolyte Membrane Model

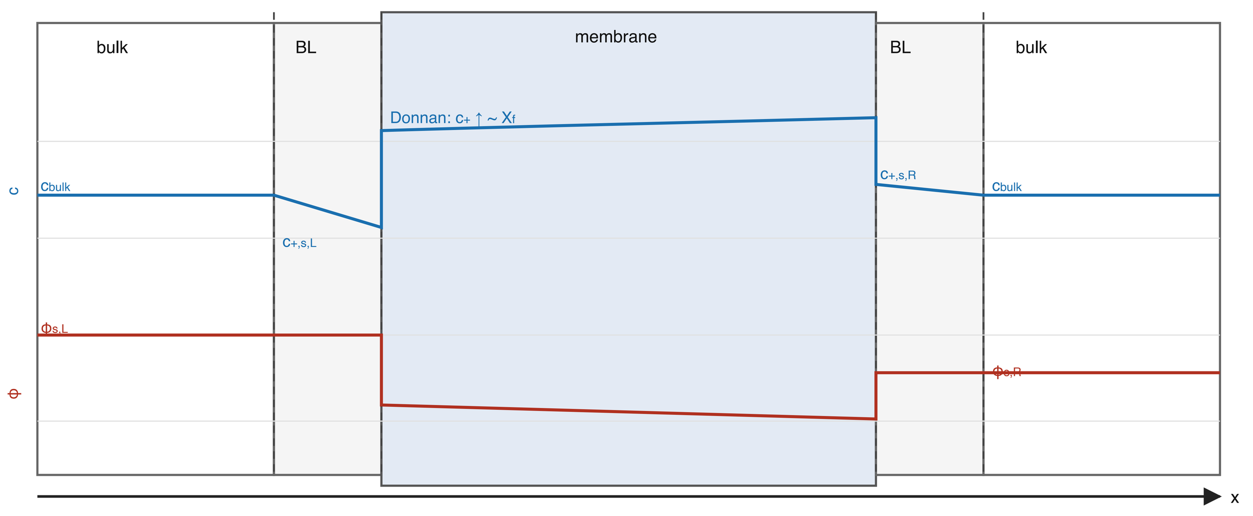

Figure 1. We use a reduced 1D steady model of the membrane and its boundary layers that captures the essential polarization mechanisms of ion-exchange membranes. The reduction assumes dilute concentrations and no strong streamwise depletion. We draw a regime map of qualitative behaviour and derive analytical polarization expressions in the typical operating range. Given that the 2D diffusive boundary layer in the range of interest is larger than the Darcy–Brinkman screening length, we use a bulk-flow scaling for mass-transfer averaging.

$$N^m_\pm = -D^m_\pm\left(\frac{dc^m_\pm}{dx} \pm \frac{F}{RT}c^m_\pm\frac{d\phi_m}{dx}\right)$$
$$c^m_+ - c^m_- + X_f = 0, \qquad i = F(N^m_+ - N^m_-)$$
$$N_{\text{neut}} = k_m(c_{b,1} - c_{s,1}) = k_m(c_{s,2} - c_{b,2})$$
$$N^s_\pm = N_{\text{neut}} \pm \frac{t_\pm}{F}i, \qquad N^m_\pm = N^s_\pm$$
$$c_{\pm,m,k} = c_{s,k}\exp\left(\mp\frac{F\Delta\phi_{D,k}}{RT}\right), \qquad k_m = 2\sqrt{\frac{D_sU_{\text{bulk}}}{L}}$$

$$\Longrightarrow \quad \beta = \frac{c_b}{|X_f|} < 1, \quad i \ll i_{\text{lim}}$$
(permselective, non-depleted)

Reduced polarization law
$$\Delta\phi_s \approx -\,i\,\text{ASR}_{\text{tot}}$$
$$\text{ASR}_{\text{tot}} \approx \frac{RT}{F^2}\left[\underbrace{\frac{L_m}{D^m_+|X_f|}}_{\text{ASR}_m} + \underbrace{\frac{2(1-t_+)}{k_mc_b}}_{\text{ASR}_{D+f}}\right]$$
$$i_{\text{lim}} \sim \frac{F\,k_m\,c_{b,1}}{1-t_+}, \qquad k_m = 2\sqrt{\frac{D_sU_{\text{bulk}}}{L}}$$

$$\hat{i} = \frac{iL_m}{FD^m_+|X_f|}, \quad \beta_k = \frac{c_{b,k}}{|X_f|}, \quad \text{Da}_f = \frac{k_mL_m}{D^m_+}, \quad \delta = \frac{D^m_-}{D^m_+}, \quad t_\pm = \frac{D^s_\pm}{D^s_+ + D^s_-}$$

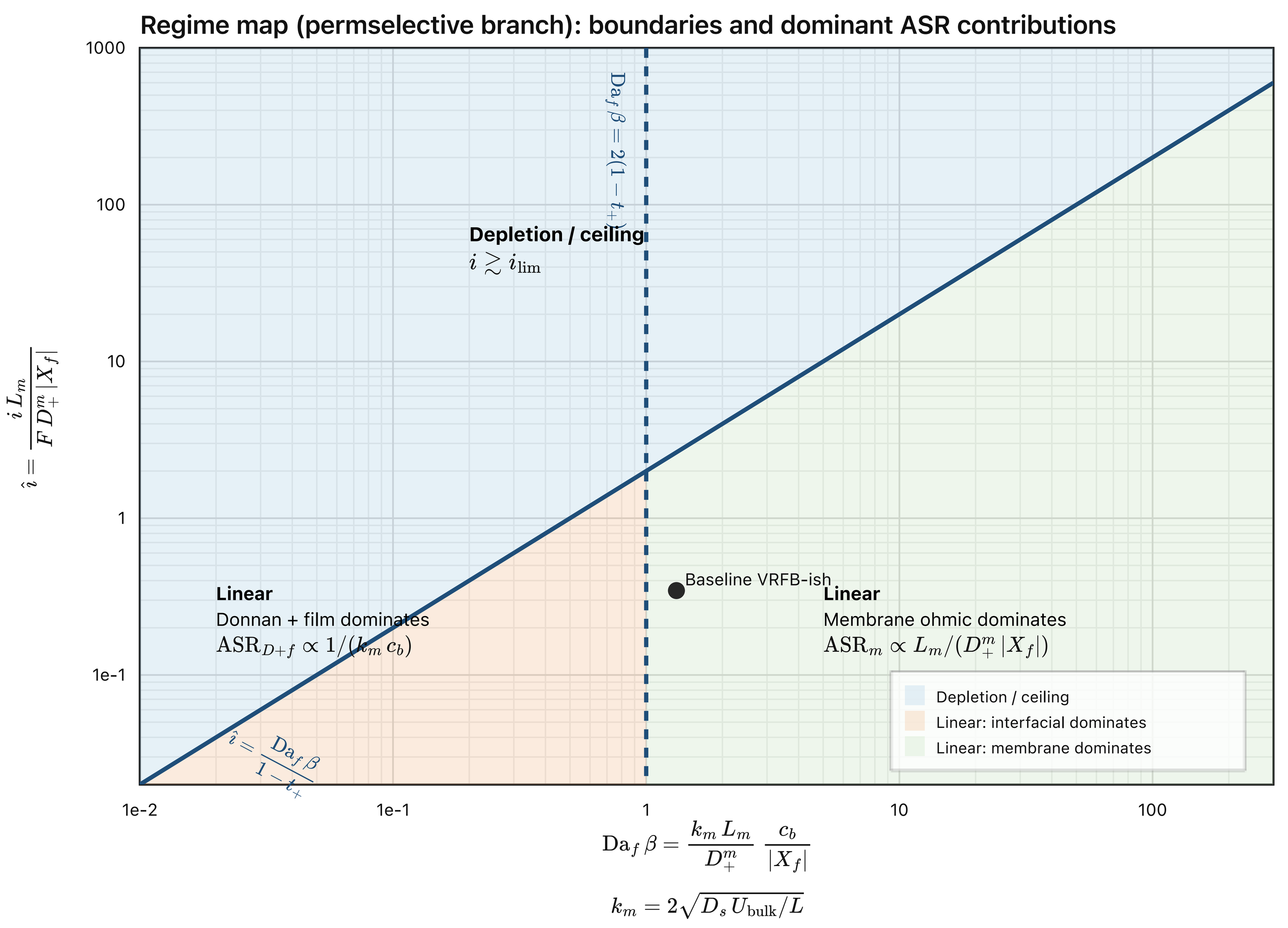

Figure 2. Regime map ($\hat{i}$ vs. $\text{Da}_f\beta$) showing distinct polarization behaviours of the 1D membrane+film model.

- **Analytical result.** In the permselective, non-depleted regime ($\beta < 1$, $i \ll i_{\text{lim}}$), the full 1D membrane+film model reduces to a linear polarization law with two series contributions: membrane ohmic + interfacial (Donnan+film). The membrane diffusion potential scales as $O(\beta^2)$ and is typically negligible.
- **VRFB-like operating point (order-of-magnitude).** For $L_m \sim 100$–$200\,\mu$m, $U_{\text{bulk}} \sim 10^{-2}$ m/s, $|X_f| \sim 2.5$ M, $D^m_+ \sim 10^{-9}$ m²/s, $c_b \sim 1$ M, $L \sim 3.5$ cm:
  $i_{\text{lim}} \sim 4 \times 10^2$ mA/cm², $\text{ASR}_{D+f} \sim 0.125\,\Omega\cdot$cm², $\text{ASR}_m \sim 0.2\,\Omega\cdot$cm²,
  so **interfacial and membrane resistances are comparable** in practical ranges.

1D Half-Cell Porous Electrode Model

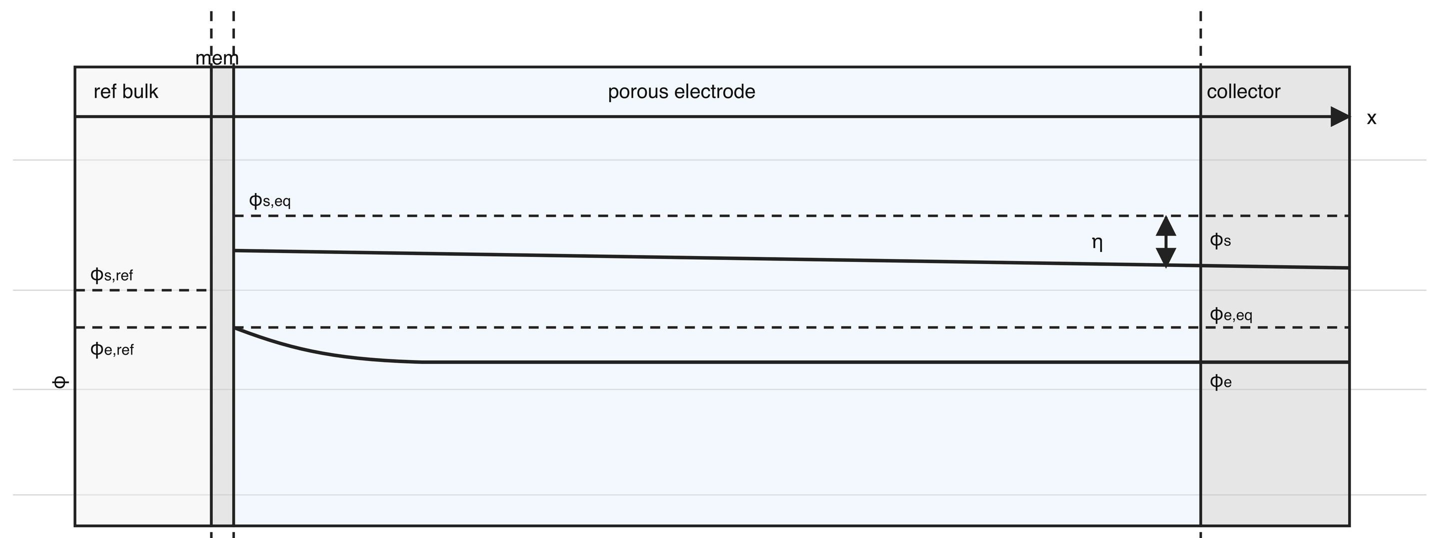

Figure 3. Neglecting concentration gradients, polarization in a porous electrode of a redox-flow half-cell reduces to a single nonlinear ODE for the local overpotential η, controlled by three dimensionless groups. A regime map identifies dominant polarization mechanisms and yields analytical asymptotic expressions for the measured polarization in each region.

$$i_e + i_s = i_T$$
$$\frac{di_e}{dx} = a\,i_{BV}(\eta)$$
$$i_e = -\kappa\frac{d\phi_e}{dx}$$
$$i_s = -\sigma\frac{d\phi_s}{dx}$$
$$\eta = \phi_s - \phi_e - E_{eq}$$
$$i_e(0) = i_T, \quad i_e(L) = 0$$

$$\Longrightarrow$$

$$\frac{d^2\eta}{dx^2} = \frac{a}{\kappa_{\text{eff}}}i_{BV}(\eta)$$
$$\kappa_{\text{eff}}^{-1} = \sigma^{-1} + \kappa^{-1}$$
$$\eta'(0) = \frac{i_T}{\kappa}$$
$$\eta'(L) = -\frac{i_T}{\sigma}$$

$$\eta_{\text{meas}} = \phi_s(L) - \phi_e(0) - E_{eq} = \frac{\kappa_{\text{eff}}}{\sigma}\eta(L) + \frac{\kappa_{\text{eff}}}{\kappa}\eta(0) - \frac{i_TL}{\sigma+\kappa}$$

$$K_r = \frac{\kappa}{\sigma}, \quad L_s = \sqrt{\frac{RT\,\kappa_{\text{eff}}}{aF^2k_0C}}, \quad \Delta = \frac{L}{L_s}, \quad i_{\text{crit}} = \frac{RT\,\kappa}{FL_s}, \quad \frac{i_T}{i_{\text{crit}}}$$

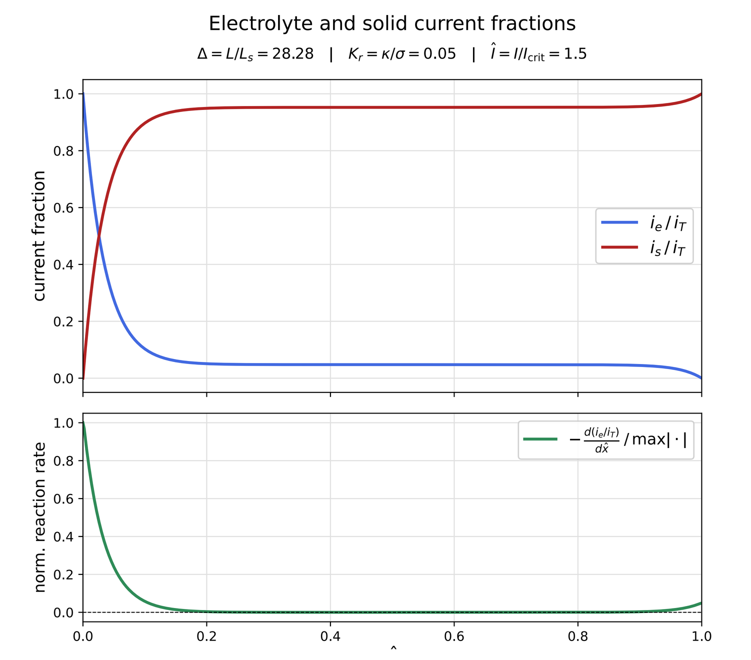

Figure: Solid and electrolyte current fractions and volumetric reaction along the normalized length.

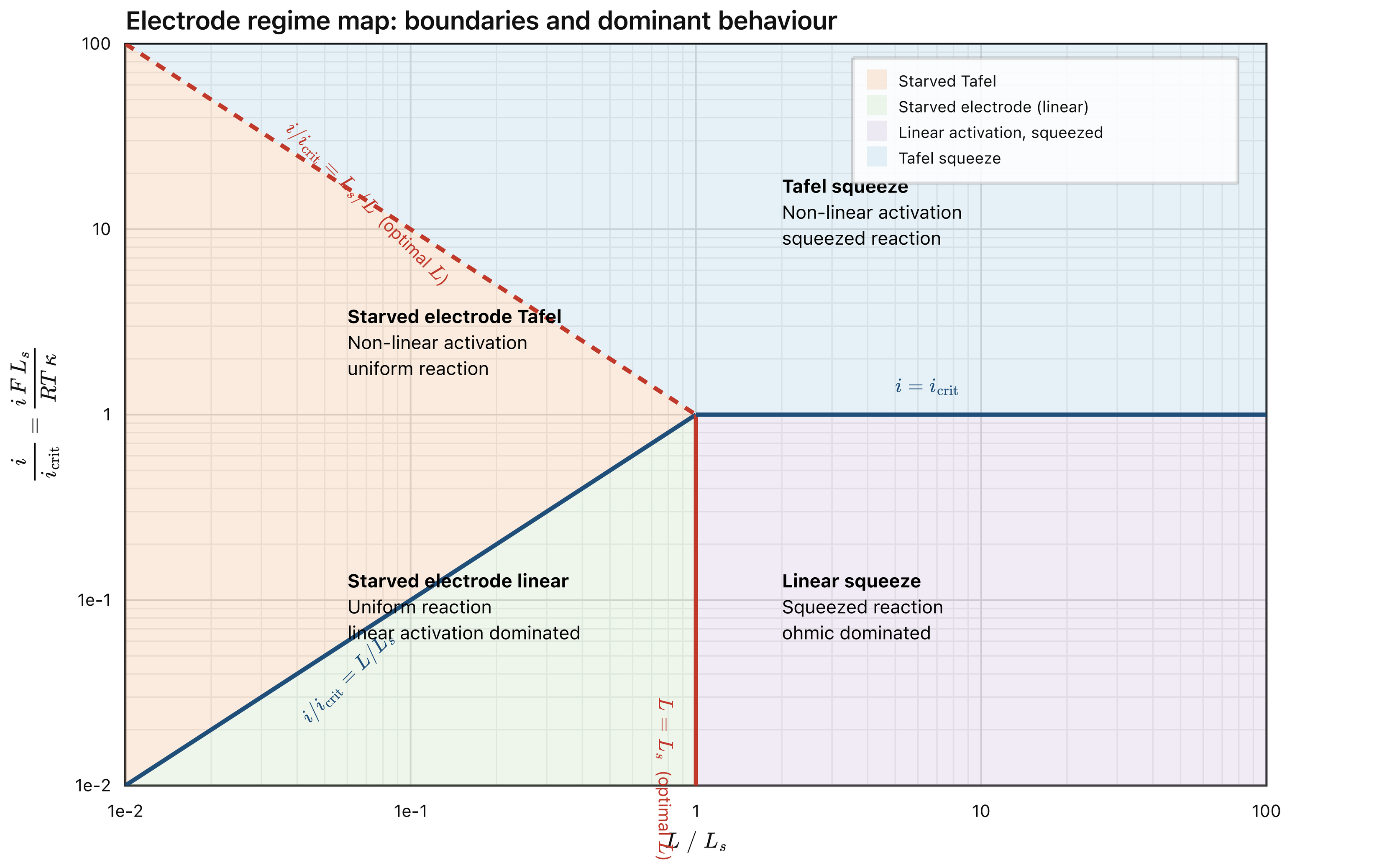

Figure 4. Electrode transport–kinetic regime map across representative operating conditions.

Analytical expressions by regime

Starved Linear
$$|\eta_{\text{meas}}| = i_T\frac{L}{\sigma} + i_T\left(\frac{RT}{aF^2k_0CL}\right)$$

Linear Squeeze
$$|\eta_{\text{meas}}| = i_T\frac{L}{\sigma} + i_T\left(\frac{L_s}{\kappa}\right)$$

Starved Tafel
$$|\eta_{\text{meas}}| = i_T\frac{L}{\sigma} + \frac{RT}{\alpha F}\ln(i_T) - \frac{RT}{\alpha F}\ln(aFk_0CL)$$

Tafel Squeeze
$$|\eta_{\text{meas}}| = i_T\frac{L}{\sigma} + \frac{2RT}{\alpha F}\ln(i_T) - \frac{RT}{\alpha F}\ln\left(\frac{2aRT\kappa k_0C}{\alpha}\right)$$

- **Low current (linear kinetics):** The optimal porous-electrode thickness is set by the natural reaction penetration length, $L \sim L_s$, balancing distributed charge-transfer and ohmic losses.
- **High current (Tafel regime):** Activation compresses the effective reaction zone ($L_{\text{dyn}} \sim 1/i_T$), leaving an increasing fraction of the electrode as an ohmic "dead" region; thus the optimal thickness decreases with operating current. In practice, hydraulic constraints such as pressure-drop scaling must also be considered.

References

[1] Newman, J., & Tiedemann, W. (1975). Porous-electrode theory with battery applications. *AIChE Journal*, 21(1), 25–41.

Newman, J., & Balsara, N. P. (2021). *Electrochemical Systems*. John Wiley & Sons.

Kontturi, Kyösti, Lasse Murtomäki, and José A. Manzanares. Ionic transport processes OUP Oxford, 2008.

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