Analytical optimization of porous electrodes

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Introduction

Using electrodes or catalytic layers that are porous increases the reactive surface area but also the distance that ions and electrons have to travel, resulting in an optimal electrode thickness. Analytical current-voltage relations have been derived that allow for analytical optimization.

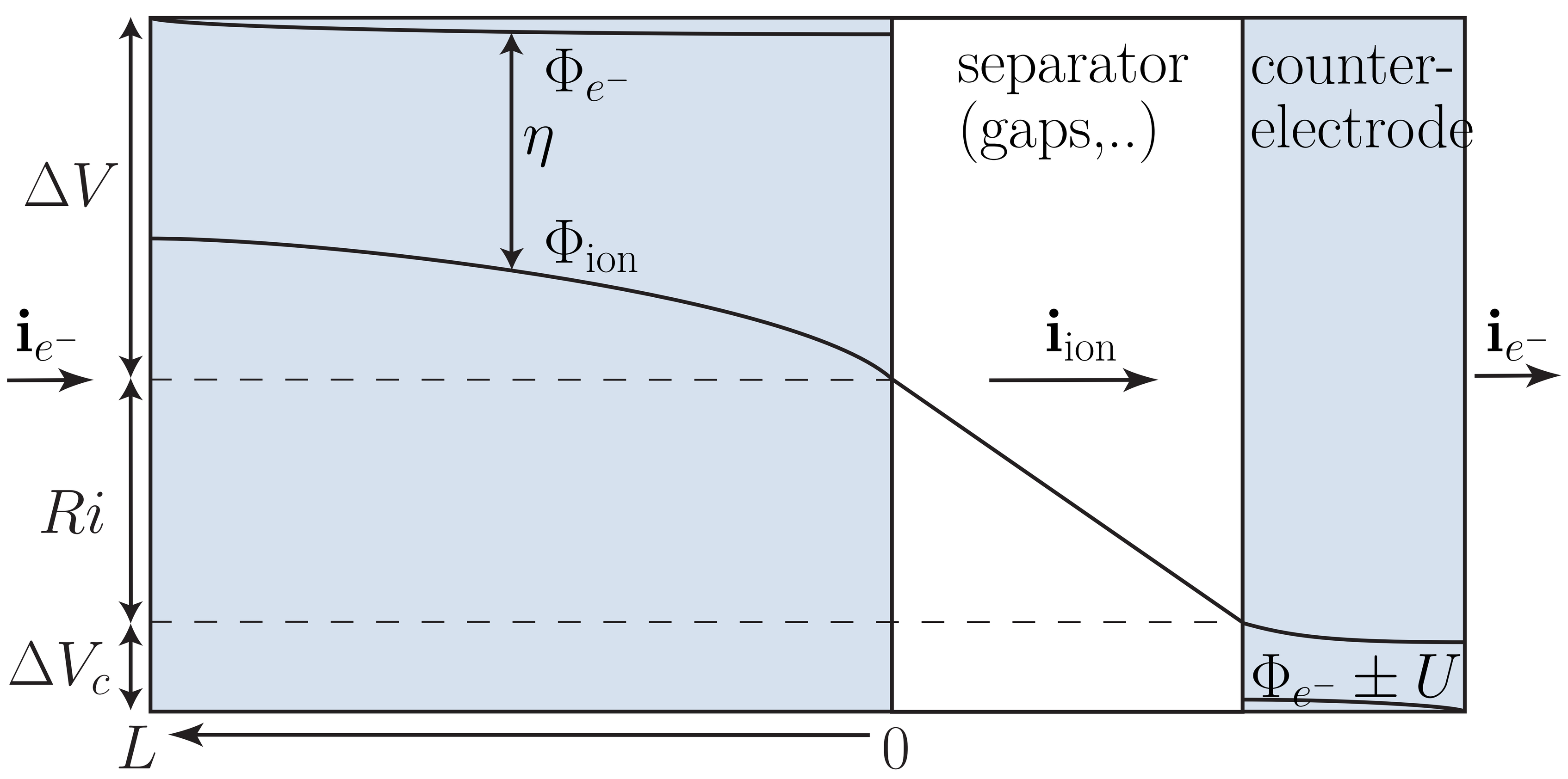

Figure 1: We consider a porous electrode with ionic and electronic currents satisfying Ohm's law and entering and leaving from opposite sides. The cell voltage reads $U \pm (iAR + \Delta V + \Delta V_c)$ for an electrolytic (+) or Galvanic (-) cell, respectively. Mass transfer limitations are neglected.

Results

For Tafel kinetics, the *electrode overpotential* can be written as

$$\Delta V = b \ln\left(\frac{i}{aLi_*\mathcal{E}}\right) + \frac{iL}{\sigma + \kappa} \tag{1}$$

with σ the electronic and κ the ionic conductivity. Here i is the current density, i_* the exchange current density, a the volumetric surface area, and b the Tafel slope.

Using the *implicit* analytical solution of Newman and Tobias (1962) we derived an accurate explicit approximation for the *electrode effectiveness factor*:

$$\mathcal{E} \approx \left(1 + \frac{(\sigma/\kappa)^{\frac{\sigma-\kappa}{\sigma+\kappa}}}{\sigma+\kappa}\frac{iL}{2b}\right)^{-1} \tag{2}$$

The details and various generalizations can be found in Ref. [1]. Using these relations, the electrode thickness that minimizes ΔV was derived analytically as

The optimal electrode thickness:

$$L_{opt} \approx \frac{4b}{i}\frac{\sigma\kappa}{\sigma+\kappa} \tag{3}$$

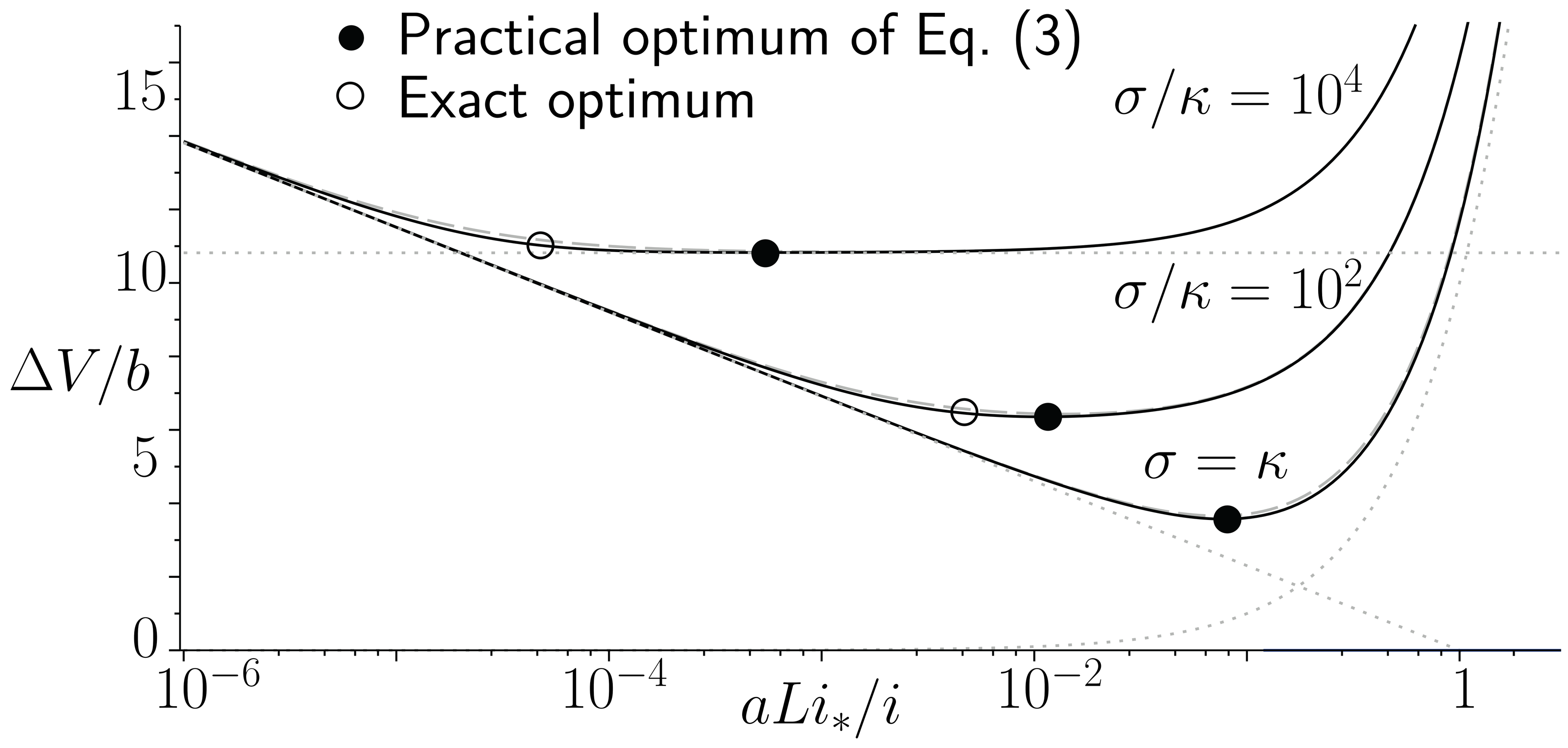

Figure 2: The dimensionless electrode overpotential vs electrode thickness. The approximation of Eqs. (1) and Eq. (2) (grey, dashed) nearly overlaps with the exact solution (solid).

- With $\kappa = \sigma = 100$ S/m, Eq. (3) gives for a typical *redox flow battery* operating at $i = 0.3$ A/cm^2 an optimal electrode thickness of about 2.5 mm.
- With $\kappa = \sigma/10^4 = 1$ S/m $L_{opt} \approx 24$ μm for a typical *fuel cell* or *electrolyzer* at $i = 1$ A/cm^2.

Highlights

- A simple *explicit* current-voltage relationship (error $\lesssim 1$ %) over full range of Butler-Volmer kinetics for arbitrary σ/κ.
- The Tafel slope doubles according to $b_{\text{eff}} \approx b\,(2 - \mathcal{E})$.
- The optimal particulate electrode porosity for $\sigma \gg \kappa$ is $n/(1+n) \approx 0.6$ for a Bruggemans exponent $n \approx 1.5$.
- For linear kinetics the optimal thickness $\sim \sqrt{L_{opt} i/ai_*}$.
- For a rapidly deeply-discharged battery, the final term in Eq. (1) is multiplied with $\frac{1}{2}\left(1 + \frac{\sigma}{\kappa_d} + \frac{\kappa}{\sigma_d}\right)$ with σ_d and κ_d the conductivities of the depleted electrode material.
- Inclusion of mass transport effects currently in progress.

References

[1] JW Haverkort. A theoretical analysis of the optimal electrode thickness and porosity. *Electrochimica Acta*, 295:846–860, 2019.