Thermodynamically Consistent Kinetics of Electrodeposition

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Introduction

- Existing phase field models for electrodeposition typically introduce a phase field variable whose evolution is governed by the Allen-Cahn equation.
- We propose a thermodynamically consistent model for electrodeposition based on variational nonequilibrium thermodynamics of electrochemical systems[1].
- Key features are: 1. the use of the metal concentration field as the phase field variable and 2. the incorporation of Butler-Volmer kinetics into the generalized Poisson-Nernst-Planck equations.

Goals

1. Formation of electric double layers at equilibrium.
2. Satisfies the Nernst equation at equilibrium.
3. Describes morphological changes under an applied potential or current.

Theory

Chemical equation

M^{n+} (l) + (n-m)e^- (s) ⇌ M^{m+} (s)

Gibbs free energy functional

$$G = \int_V \left[g(\vec{c}) + \frac{1}{2}\left(\kappa \left|\nabla \tilde{c}\right|^2 - \varepsilon_{\mathrm{p}} \left|\nabla \phi\right|^2 \right) + \sum_{i=1}^{N} z_i e c_i \phi + \sum_{i=1}^{N} \mu_i^{\ominus} c_i \right] dV$$

- *G*: *g* (homogeneous free energy density), gradients, electrostatics and standard states.
- *g*: double well function + ideal solutions + standard chemical potential differences[2,3].

Variational framework

Electrochemical potentials: $\mu_i \equiv \frac{\delta G}{\delta c_i}$

Diffusional fluxes: $F_i \equiv -\frac{D_i c_i}{k_{\mathrm{B}} T} \nabla \mu_i$

Metal ion concentration: $\frac{\partial c}{\partial t} = R(\{\mu_j\})$

Generalized Nernst-Planck equations: $\frac{\partial c_i}{\partial t} + \nabla \cdot F_i = s_i R(\{\mu_j\})$

Poisson's equation for electrostatics: $-\nabla \cdot \varepsilon_p \nabla \phi = \sum_{i=1}^{N} z_i e c_i$

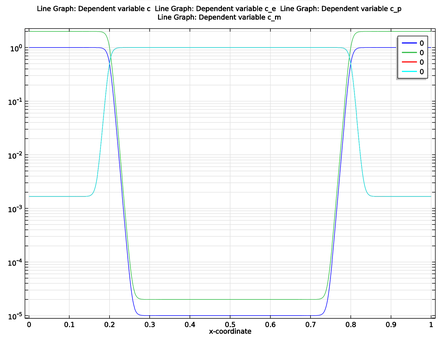
Butler-Volmer reaction kinetics

$$R = k_0 c_{\mathrm{s}} \left\{ \exp\left[\frac{\mu_+ + (n-m)\,\mu_{\mathrm{e}} - \mu_{\ddagger}^{\mathrm{ex}}}{k_{\mathrm{B}} T} \right] - \exp\left(\frac{\mu - \mu_{\ddagger}^{\mathrm{ex}}}{k_{\mathrm{B}} T} \right) \right\}$$

Numerical results for equilibrium

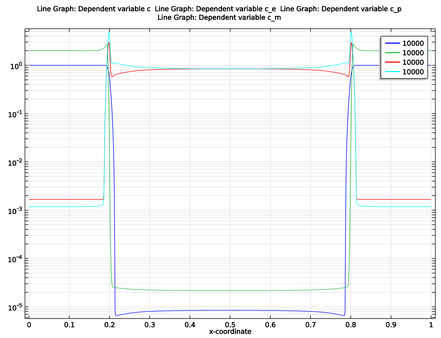
Initial concentrations

n = 2, m = 2

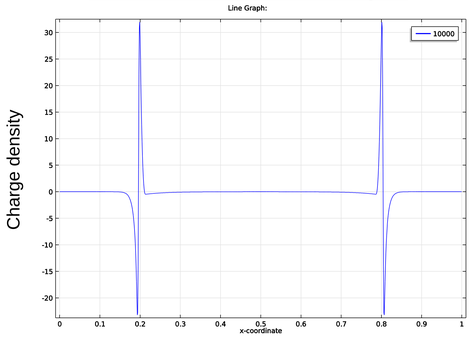


Blue: metal ions
Green: electrons
Red: cations
Cyan: anions

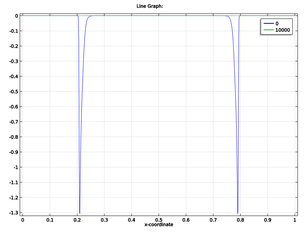
Equilibrium concentrations

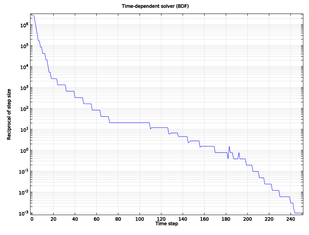


Formation of electric double layers



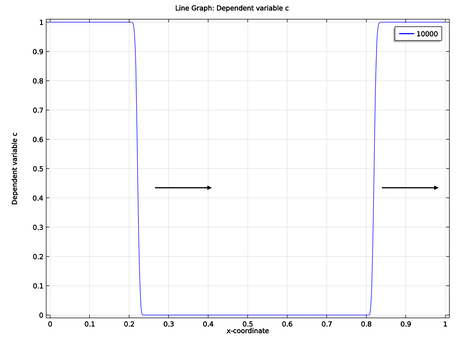
Reaction rate and rate of convergence



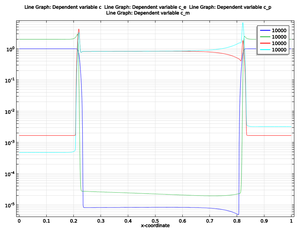


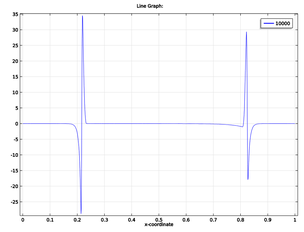
Numerical results for applied potential

Metal ion concentration



Concentrations and charge density





Future work

- Variable permittivity (includes Stern layer).
- Comparison with sharp interface models (e.g., Butler-Volmer kinetics with Frumkin correction).

References

1. Bazant, M. Z. Theory of Chemical Kinetics and Charge Transfer based on Nonequilibrium Thermodynamics. *Acc. Chem. Res.* **46,** 1144–1160 (2013).
2. Guyer, J. E., Boettinger, W. J., Warren, J. A. & McFadden, G. B. Phase field modeling of electrochemistry. I. Equilibrium. *Phys. Rev. E* **69,** 021603 (2004).
3. Guyer, J. E., Boettinger, W. J., Warren, J. A. & McFadden, G. B. Phase field modeling of electrochemistry. II. Kinetics. *Phys. Rev. E* **69,** 021604 (2004).

Acknowledgements

- Funding by Agency for Science, Technology and Research (A*STAR), Singapore.