Linear stability analysis of time-dependent electrodeposition in charged porous media

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Motivation

- Electroplating of metals such as copper
- For batteries, want to use metal anode for high capacity and energy density, e.g. lithium metal batteries, and charging of metal anode = electrodeposition
- Want to perform at high currents but may cause formation and propagation of dendrites
- Dendrites can cause non-uniform layers, internal short circuits and thermal runaway

Lithium dendrites

Bai, P., Li, J., Brushett, F. R. & Bazant, M. Z. *Energy Environ. Sci.* 9, 3221–3229 (2016).

Copper dendrites in free solution (copper(II) sulfate electrolyte)

Elezgaray, J., Léger, C. & Argoul, F. J. *Electrochem. Soc.* 145, 2016–2024 (1998).

Electrodeposited copper films in charged cellulose nitrate (CN) membranes

Han, J.-H., Wang, M., Bai, P., Brushett, F. R. & Bazant, M. Z. *Scientific Reports* 6, 28054 (2016).

Aim

- Use linear stability analysis to determine if pore **surface charges** of a charged porous medium can suppress dendritic growth

Limiting current and Sand's time

- If applied current > limiting current, concentration at cathode reaches 0 at Sand's time (t_s)
- At $t = t_s$, electric potential and electric field diverge
- For electrodeposition, dendrites form near t_s

Overlimiting current (OLC) and its mechanisms

- Surface conduction (SC)
 - Electromigration of counterions in electric double layers next to **charged** pores or sidewalls
 - Ionization of surface functional groups
 - Layer-by-layer (LbL) deposition of polyelectrolytes
 - Expected to dominate in nanometer scale pores

Leaky membrane model for surface conduction (SC)

SEM images of CN membranes

Han, J.-H., Wang, M., Bai, P., Brushett, F. R. & Bazant, M. Z. Scientific Reports 6, 28054 (2016).

SEM images of AAO membranes

Hulteen, J. C. & Martin, C. R. J. Mater. Chem. 7, 1075–1087 (1997).

- Nernst-Planck (species conservation) equations for cations and anions coupled with macroscopic electroneutrality: $-e(z_+c_+ + z_-c_-) = \rho_s$

$$\rho_s = \frac{a_p \sigma_s}{\epsilon_p}$$
- Butler-Volmer (BV) reaction kinetics at anode and cathode, e.g. copper electrodeposition and electrodisolution

ρ_s = volume-averaged background charge density
 a_p = internal pore surface area/volume ratio
 σ_s = pore surface charge/area ratio
 ϵ_p = porosity

Scales and dimensionless variables and parameters

- Concentration: c_0 = bulk electrolyte concentration
- Charge density $\rho_s: z_+ e c_0$
- Time: diffusion time (L^2/D_{amb})
- **Current density: limiting current density (J_{lim})**
- **Damkohler number (Da):** $\text{Da} = \frac{e\epsilon_p k_0}{J_{\text{lim}}}$
 - $\text{Da} \gg 1$: diffusion-limited
 - $\text{Da} \ll 1$: reaction-limited

$$D_{\text{amb}} = \frac{(z_+ - z_-) D_+ D_-}{z_+ D_+ - z_- D_-}$$

$$J_{\text{lim}} = \frac{2(z_+ - z_-) e\epsilon_p D_+ \nu_- c_0}{L}$$

$J > 1$: overlimiting

$J = 1$: limiting

$J < 1$: underlimiting

Linear stability analysis

- Electrode surface: $x = h(\xi, t)$ where $\xi = [y, z]^T$
- Sinusoidal spatial perturbation with wavevector $k = [k_y, k_z]^T$ around **transient** base state

Transient
base state

Amplitude

Growth rate

$$h(\xi, t) = \underbrace{h_0(t)}_{\text{Transient base state}} + \underbrace{\epsilon \Re[h_1 \exp(ik \cdot \xi + \omega t)]}_{\text{Amplitude}} + \mathcal{O}(\epsilon^2)$$

$$c(x, \xi, t) = c_0(x, t) + \epsilon \Re[c_1(x) \exp(ik \cdot \xi + \omega t)] + \mathcal{O}(\epsilon^2),$$

$$\phi(x, \xi, t) = \phi_0(x, t) + \epsilon \Re[\phi_1(x) \exp(ik \cdot \xi + \omega t)] + \mathcal{O}(\epsilon^2).$$

- Substitute into the PDEs, BCs, ICs and match $\mathcal{O}(1)$ and $\mathcal{O}(\epsilon)$ terms
- **Determine dispersion relation $\omega(k)$**
 - **$\text{Re}(\omega) < 0$: linearly stable**
 - **$\text{Re}(\omega) > 0$: linearly unstable**
- **Analyze dependence of ω on key system parameters such as ϱ_s , Da and J_a (applied current density)**

Recall: wavelength $\lambda = 2\pi/k$

Capillary number =
dimensionless surface energy

$$\text{Ca} = \tilde{\gamma} = \frac{\Omega\gamma}{L_x k_B T} = 8.74 \times 10^{-5}$$

Sand's time

$$t_s = \frac{\pi}{16J_a^2}$$

Base state plots

- Fix $Da = 1$ and $J_a = 1.5$ (> 1 , overlimiting) for all six plots
- φ_s values are indicated in titles
- t/t_s values are indicated in legends

Can go beyond t_s
and reach steady state

Classical case

Similar to classical case

Anion
concentration

Electric field

Increasing φ_s

Negative charge

Zero charge

Positive charge

Physical intuition behind linear stability analysis

Dispersion relation

$$\rho_S = 0, \text{Da} = 1, J_a = 1.5$$

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- Instability from protruding surface receiving more flux/current vs. stability arising from surface energy penalty incurred in creating additional surface area
- Electrodiffusion destabilizing effect $\sim k$
- Surface energy stabilizing effect $\sim -\gamma k^2$

$\omega_{\max}$: maximum growth rate

$k_{\max}$: wavenumber corresponding to $\omega_{\max}$

k_c : critical wavenumber ($\omega = 0$)

Growth rate and wavenumbers: $\{k_{\max}, \omega_{\max}\}$ and k_c

- Not shown here: numerical and approximate solutions agree very well

Comparison with experimental data

- Copper electrodeposition in cellulose nitrate (CN) membranes: previously fitted ϱ_s , τ , Da , α_1 , ε_p using steady state current-voltage curves
- $\gamma = 1.85 \text{ J/m}^2$
- Assume steady state as time of EDS snapshots $\gg$ diffusion time scale
- Maximum wavelength $\lambda_{\text{max}} = 2\pi/k_{\text{max}}$
- Critical wavelength $\lambda_c = 2\pi/k_c$
- Characteristic pore size $h_c = 2d_p$
- Overall stabilization if $h_c < \lambda_c$
- If overall destabilization ($h_c > \lambda_c$), instability length scale = λ_{max}

Summary

- Linear stability analysis suggests negative surface charges can effectively suppress dendritic growth by reducing electric field at cathode
 - Good agreement between simple theory and experiment
- Surface charge is another knob for dendrite suppression

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Preprint: Khoo, E., Zhao, H. & Bazant, M. Z. Linear stability analysis of transient electrodeposition in charged porous media. arXiv:1901.05033 [physics] (2019).

Questions?

Backup slides

Overlimiting current (OLC) and its mechanisms

- Physical
 - **Surface conduction (SC)**
 - **Electromigration of counterions in electric double layers next to **charged** pores or sidewalls**
 - Ionization of surface functional groups
 - Layer-by-layer (LbL) deposition of polyelectrolytes
 - **Expected to dominate in nanometer scale pores**
 - Electroosmotic flow (EOF)
 - Electroosmotic instability (EOI)
- Chemical
 - Water splitting reaction
 - Current-induced membrane discharge caused by membrane deprotonation and water self-ionization

Leaky membrane model for surface conduction (SC)

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SEM images of AAO membranes

Hulteen, J. C. & Martin, C. R. J. Mater. Chem. 7, 1075–1087 (1997).

- Binary and asymmetric electrolyte, e.g. copper (II) sulfate (CuSO_4)
- Charged nanoporous membrane, e.g. cellulose nitrate (CN), anodic aluminum oxide (AAO)
- Nernst-Planck (species conservation) equations for cations and anions coupled with macroscopic electroneutrality:

$$-e(z_+c_+ + z_-c_-) = \rho_s$$

$$\rho_s = \frac{a_p \sigma_s}{\epsilon_p}$$

ρ_s = volume-averaged background charge density
 a_p = internal pore surface area/volume ratio
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 ϵ_p = porosity

- Butler-Volmer (BV) reaction kinetics at anode and cathode, e.g. copper electrodeposition and electrodisolution

Butler-Volmer (BV) reaction kinetics

- n -electron transfer reaction
- Charge conservation: $z_{\text{O}} - n = z_{\text{R}}$

$$\Delta\phi = \phi_{\text{e}} - \phi$$

$$\Delta\phi^{\text{eq}} = \frac{k_{\text{B}}T}{ne} \ln \frac{\hat{c}_{\text{O}}}{\hat{c}_{\text{R}}} + E^{\ominus}$$

$$\eta = \Delta\phi - \Delta\phi^{\text{eq}}$$

$$J_{\text{F}} = j_0 \left\{ \exp \left(-\frac{\alpha n e \eta}{k_{\text{B}}T} \right) - \exp \left[\frac{(1 - \alpha) n e \eta}{k_{\text{B}}T} \right] \right\}$$

$$j_0 = k_0 n e \hat{c}_{\text{O}}^{1-\alpha} \hat{c}_{\text{R}}^{\alpha}$$

$\Delta\phi$ = interfacial electric potential difference

$\Delta\phi^{\text{eq}}$ = Nernst potential

η = overpotential

j_0 = exchange current density

α = charge transfer coefficient

k_0 = rate constant

- Assume 1st step is rate-determining step (RDS) and 2nd step is at equilibrium
- Apply BV reaction kinetics to both steps

$$J_{\text{F}} = j_0 \left\{ \exp \left(-\frac{\alpha_1 e \eta}{k_{\text{B}}T} \right) - \exp \left[\frac{(2 - \alpha_1) e \eta}{k_{\text{B}}T} \right] \right\}$$

$$j_0 = 2ek_0 \hat{c}_{+}^{1-\frac{\alpha_1}{2}}$$

α_1 = charge transfer coefficient for 1st step (RDS)

Linear stability analysis

- Perturbation in **space** with wavenumber k around base state
- Base state = transient state, ϱ_s of any sign, galvanostatic
- Study effects of key system parameters on linear (in)stability of planar cathode/anode surface in charged nanoporous medium, which is quantified by its growth rate ω
 - ϱ_s (volume-averaged background charge density)
 - Da (Damkohler number)
 - Applied current density (galvanostatic) J_a
 - Sand's time t_s when concentration at cathode becomes zero: $t_s = \frac{\pi}{16J_a^2}$
- **Determine dispersion relation, i.e., relate growth rate ω to wavenumber k and key system parameters**

Capillary number =
dimensionless surface energy

$$\text{Ca} = \tilde{\gamma} = \frac{\Omega\gamma}{L_x k_B T} = 8.74 \times 10^{-5}$$

History

- Mullins and Sekerka (1963 and 1964)
 - Stability of shape of spherical particle undergoing diffusion-controlled or thermal-controlled growth
 - Stability of planar interface during solidification of dilute binary alloy
- Electrodeposition:

Authors (year)	Base state	q_s	Type of constraint
Pritzker and Fahidy (1992)	Steady state	0	N.A.
Sundström and Bark (1995)	Steady state	0	N.A.
Elezgaray, Léger and Argoul (1998)	Transient state	0	Galvanostatic
Tikekar, Archer and Koch (2014)	Steady state	< 0	N.A.
This work	Transient state	Any sign	Galvanostatic

Snowflake

Langer, J. S. Rev. Mod. Phys. 52, 1–28 (1980).

Copper dendrites in free solution (copper(II) sulfate electrolyte)

Elezgaray, J., Léger, C. & Argoul, F. J. Electrochem. Soc. 145, 2016–2024 (1998).

Analytical approximations

- For large k , possible to do a boundary layer analysis
 - k^{-2} (surface energy effect) = small parameter
 - Boundary layer thickness $\sim k^{-1}$
- Impose boundary conditions to determine arbitrary constants
- Very accurate for computing $\{k_{\max}, \omega_{\max}\}$ and k_c

$$\xi_1(k) = \frac{c_{0,t}}{zc_0 Dk},$$

$$\xi_2(k) = -\frac{z\phi_{0,x} + k}{zc_0 k},$$

$$B(k) = -\xi_1 h_1 + \xi_2 A,$$

$$A(k) = -\frac{\beta_v j_{0,0}(\hat{G}_1 - \xi_1 \hat{G}_3) - \beta_m \alpha_5 \xi_1 k}{\beta_v j_{0,0}(\hat{G}_2 + \xi_2 \hat{G}_3) - \beta_m [(\alpha_1 - \alpha_5 \xi_2)k - \alpha_2 \phi_{0,x}]} h_1,$$

$$\omega(k) = \beta_m \left\{ \frac{[(\alpha_1 - \alpha_5 \xi_2)k - \alpha_2 \phi_{0,x}] [\beta_v j_{0,0}(\hat{G}_1 - \xi_1 \hat{G}_3) - \beta_m \alpha_5 \xi_1 k]}{\beta_v j_{0,0}(\hat{G}_2 + \xi_2 \hat{G}_3) - \beta_m [(\alpha_1 - \alpha_5 \xi_2)k - \alpha_2 \phi_{0,x}]} - \alpha_5 \xi_1 k \right\}.$$

Numerical computation of dispersion relation

- 2nd-order accurate finite difference spatial discretization of the $\mathcal{O}(\varepsilon)$ equations
- Get a generalized eigenvalue problem $A\mathbf{v} = \omega B\mathbf{v}$ where A is non-singular and B is singular (because of time-independent terms in model), so the problem cannot be reduced to a standard eigenvalue problem
- Recall that eigenvalue algorithm scales as $\mathcal{O}(N^3)$ where N = number of unknowns, therefore very computationally expensive for $N \sim 10^3$ and above
- For accuracy, need large N , hence use “sparse” solver, which scales as $\mathcal{O}(kN^2)$ where k = number of eigenvalues requested
- Use MATLAB’s eigs solver, and Rostami and Xue’s more robust eigenvalue solver based on matrix exponential (Rostami, M. & Xue, F. SIAM J. Sci. Comput. A3344–A3370 (2018).)

Convergence analysis

- Fix $Da = 1$ and $J_a = 1.5$ (> 1 , overlimiting) for all three plots
- t/t_s and ρ_s values are indicated in titles
- N values are indicated in legends

Increasing ϱ_s →

Numerical computation of dispersion relation:

- 2nd-order accurate finite differences
- Generalized eigenvalue problem $A\mathbf{v} = \omega B\mathbf{v}$
- Solve using MATLAB's eigs solver

$\{k_{\max}, \omega_{\max}\}$ for convergence plots

Increasing ϱ_s →

- Numerical convergence is observed as N is increased from 251 to 4001
- $N = 1001$ is sufficiently fast and accurate; all simulations shown from now on use $N = 1001$

k_c for convergence plots

- Numerical convergence is observed as N is increased from 251 to 4001
- $N = 1001$ is sufficiently fast and accurate; all simulations shown from now on use $N = 1001$

Dispersion relations

- Fix $Da = 1$ and $J_a = 1.5$ (> 1 , overlimiting) for all three plots
- ϱ_s values are indicated in titles
- t/t_s values are indicated in legends

- Not shown here: increasing Da from 0.1 to 1 to 10 increases ω but this effect is very insignificant because the system is diffusion-limited when an overlimiting current is applied

Variation of ϱ_s for negative ϱ_s

- In terms of stabilizing effect, we observe diminishing returns of making ϱ_s increasingly negative

Comparison with experimental data

Depletable bulk concentration

- Regardless of sign of ρ_s , coions (same sign as ρ_s) can be depleted but counterions cannot be depleted as they need to reside in electric double layer to shield ρ_s
- Define “depletable bulk concentration” c :

$$c \equiv \begin{cases} \frac{c_-}{\nu_-}, & \rho_s \leq 0 \\ \frac{c_+}{\nu_+}, & \rho_s \geq 0 \end{cases}$$

$$\text{CuSO}_4: \nu_+ = 1, \nu_- = 1, z_+ = 2, z_- = -2$$

- Substitute in macroscopic electroneutrality equation and rearrange:

Initial condition or integral constraint:
set c to electrolyte concentration (c_0)
and compute c_-

$$\begin{aligned} c_- &= \begin{cases} \nu_- c, & \rho_s \leq 0 \\ \nu_- c - \frac{\rho_s}{z_- e}, & \rho_s \geq 0 \end{cases} \\ &= \nu_- \textcircled{c} - \frac{\rho_s + |\rho_s|}{2z_- e} \end{aligned}$$