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Supplementary Materials for

Stabilizing electrodeposition in elastic solid electrolytes containing immobilized anions

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Supplementary Materials

Perturbed equations at high current densities

The equations for the perturbed cation concentration in the diffusion region and electrical potential in the migration region are:

$$\frac{d^2C_c'}{dz^2} - k^2C_c' + \frac{\nu_c + \nu_{a,m}}{2RT}\frac{dC_c}{dz}\frac{dp^{s\prime}}{dz} = 0 \tag{S1}$$

$$\frac{d^2\phi'}{dz^2} - k^2\phi' + \frac{1}{K^s}\frac{d\phi}{dz}\frac{dp^{s\prime}}{dz} = 0 \tag{S2}$$

This gives the perturbation to current density in the diffusion and migration regions respectively as,

$$\mathbf{e}_z \cdot \mathbf{J}' = J' = -2RTF\mu_c\frac{dC_c'}{dz} - \mu_c F\left(\nu_c + \nu_{a,m}\right)C_c\frac{dp^{s\prime}}{dz} \quad \text{for } z > l \tag{S3}$$

$$\mathbf{e}_z \cdot \mathbf{J}' = J' = -\mu_c F C_0 C_{a,f0}\left[F\frac{d\phi'}{dz} + F\frac{1}{K^s}p^{s\prime}\frac{d\phi}{dz} + \frac{RT}{K^s}\left(1 + \frac{K^s\nu_c}{RT}\right)\frac{dp^{s\prime}}{dz}\right] \quad \text{for } z < l \tag{S4}$$

The perturbations to the governing deformation equations 8 – 11 (in the main paper) yield

$$\frac{d^2u_x^s}{dz^2} - k^2u_x^s + 2\alpha^s ik\left(iku_x^s + \frac{du_z^s}{dz}\right) = 0 \tag{S5}$$

$$\frac{d^2u_z^s}{dz^2} - k^2u_z^s + 2\alpha^s\frac{d}{dz}\left(iku_x^s + \frac{du_z^s}{dz}\right) = 0 \tag{S6}$$

$$\frac{d^2p^{s\prime}}{dz^2} - k^2p^{s\prime} = 0 \tag{S7}$$

$$\frac{d^2u_x^m}{dz^2} - k^2u_x^m + 2\alpha^m ik\left(iku_x^m + \frac{du_z^m}{dz}\right) = 0 \tag{S8}$$

$$\frac{d^2u_z^m}{dz^2} - k^2u_z^m + 2\alpha^m\frac{d}{dz}\left(iku_x^m + \frac{du_z^m}{dz}\right) = 0 \tag{S9}$$

$$\frac{d^2p^{m\prime}}{dz^2} - k^2p^{m\prime} = 0 \tag{S10}$$

where

$$\mathbf{u}^{s\prime} = u_x^s\mathbf{e}_x + u_z^s\mathbf{e}_z \tag{S11}$$

$$\mathbf{u}^{m\prime} = u_x^m \mathbf{e}_x + u_z^m \mathbf{e}_z \tag{S12}$$

with $\mathbf{e}_x$ and $\mathbf{e}_z$ being the unit vectors in the x and z directions respectively. The deformation equations can be solved analytically to obtain

$$u_x^s = \frac{1}{ik}\left[\left(Z_0^s\left(1+\alpha^s\right) - c_3^s k + \alpha^s Z_1^s kz\right)\sinh\left(kz\right) + \left(Z_1^s\left(1+\alpha^s\right) - c_1^s k + \alpha^s Z_0^s kz\right)\cosh\left(kz\right)\right] \tag{S13}$$

$$u_z^s = \left(c_1^s - \alpha^s Z_0^s z\right)\sinh\left(kz\right) + \left(c_3^s - \alpha^s Z_1^s z\right)\cosh\left(kz\right) \tag{S14}$$

$$p^{s\prime} = -K^s \nabla \cdot \mathbf{u}^{s\prime} = -K^s\left[Z_0^s \sinh\left(kz\right) + Z_1^s \cosh\left(kz\right)\right] \tag{S15}$$

$$u_x^m = \frac{1}{ik}\left(Z_1^m\left(1+\alpha^m\right) - c_3^m k + \alpha^s Z_1^m kz\right)\exp\left(kz\right) \tag{S16}$$

$$u_z^m = \left(c_3^m - \alpha^m Z_1^m z\right)\exp\left(kz\right) \tag{S17}$$

$$p^{m\prime} = -K^m \nabla \cdot \mathbf{u}^{m\prime} = -K^m Z_1^m \exp\left(kz\right) \tag{S18}$$

On solving the transport equations (24) and (25), we get

$$C_c' = \left[A_c - \frac{K^s\left(v_c + v_{a,m}\right)}{8RT} J Z_0^s z\right]\sinh\left(kz\right) + \left[B_c - \frac{K^s\left(v_c + v_{a,m}\right)}{8RT} J Z_1^s z\right]\cosh\left(kz\right) \tag{S19}$$

$$\phi' = \left[A_\phi - \frac{1}{2\mu_c F C_{a,f0} C_0} J Z_0^s z\right]\sinh\left(kz\right) + \left[B_\phi - \frac{1}{2\mu_c F C_{a,f0} C_0} J Z_1^s z\right]\cosh\left(kz\right) \tag{S20}$$

The above set of solutions covers the concentration in the diffusion region, electric potential in the migration region and deformations of the separator and metal, and hence encompasses the governing equations in both the small and large current densities cases. The unknown integration constants are given by the boundary conditions and can be easily obtained in the limit of large kL analytically.

The boundary conditions are given by continuity of concentration, potential and current density across the two region interface, and chemical equilibrium at the two electrodes. Continuity of concentration, potential and current density across the two region interface are written as

$$C_c'\Big|_l + \frac{dC_c}{dz}\Big|_l l' = 0 \tag{S21}$$

$$\phi'\Big|_l + \frac{d\phi}{dz}\Big|_l l' = 0 \tag{S22}$$

$$-2RTF\mu_c \left.\frac{dC_c'}{dz}\right|_l = -\mu_c F C_0 C_{a,f0}\left[F\left.\frac{d\phi'}{dz}\right|_l + \frac{F}{K^s}\left.p^{s\prime}\right|_l \left.\frac{d\phi}{dz}\right|_l + \frac{RT}{K^s}\left(1+\frac{K^s v_c}{RT}\right)\left.\frac{dp^{s\prime}}{dz}\right|_l\right] \tag{S23}$$

The equilibrium at the metal-separator interface gives

$$v_m \left.p^{m\prime}\right|_0 = F\left(\left.\phi'\right|_0 + \left.\frac{d\phi}{dz}\right|_0\right) + \frac{RT}{K^s}\left(1+\frac{K^s v_c}{RT}\right)\left.p^{s\prime}\right|_0 \tag{S24}$$

Similarly, the equilibrium at the counter-electrode-separator interface is obtained as

$$2RT\frac{\left.C_c'\right|_L}{\left.C_c\right|_L} + \left(v_c + v_{a,m}\right)\left.p^{s\prime}\right|_L = 0 \tag{S25}$$

The deformation boundary conditions based on force balance at the metal-separator interface and continuity of tangential and normal deformation in equations 12 – 16 at the metal-separator interface yield

$$G^s\left[\left(2\alpha^s-1\right)ik\left.u_x^s\right|_0 + \left(2\alpha^s+1\right)\left.\frac{du_z^s}{dz}\right|_0\right] = G^m\left[\left(2\alpha^m-1\right)ik\left.u_x^m\right|_0 + \left(2\alpha^m+1\right)\left.\frac{du_z^m}{dz}\right|_0\right] + \gamma k^2 \tag{S26}$$

$$G^m\left[ik\left.u_z^m\right|_0 + \left.\frac{du_x^m}{dz}\right|_0\right] = G^s\left[ik\left.u_z^s\right|_0 + \left.\frac{du_x^s}{dz}\right|_0\right] \tag{S27}$$

$$\left.u_x^s\right|_0 = \left.u_x^m\right|_0 \tag{S28}$$

$$\left.u_z^m\right|_0 = 1 + v_m\frac{\left.J'\right|_0}{F\sigma} \tag{S29}$$

$$\left.u_z^s\right|_0 = 1 + v_c\frac{\left.J'\right|_0}{F\sigma} \tag{S30}$$

The corresponding boundary conditions at the counter-electrode-separator interface give

$$\left.u_x^s\right|_L = 0 \tag{S31}$$

$$\left.u_z^s\right|_L = v_c\frac{\left.J'\right|_L}{F\sigma} \tag{S32}$$

In the large kL limit, equations S25, S31 and S32 can be replaced with $\lim_{kz\to\infty} C_c' = 0$, $\lim_{kz\to\infty} u_x^s = 0$, and $\lim_{kz\to\infty} u_z^s = 0$ respectively.

Perturbed equations at low current densities

At low current densities, the governing transport equation is

$$\frac{d^2C_c'}{dz^2} - k^2C_c' + \frac{v_c + v_{a,m}}{2RT}\frac{dC_c}{dz}\frac{dp^{s\prime}}{dz} = 0 \tag{S33}$$

The boundary conditions are given by perturbations to the fast reaction kinetics at the two and can be written at the metal and the counter-electrode respectively as

$$v_m\, p^{m\prime}\Big|_0 = \frac{2RT}{C_c\big|_0}\left(C_c'\big|_0 + \frac{dC_c}{dz}\bigg|_0\right) + \left(v_c + v_{a,m}\right)p^{s\prime}\Big|_0 \tag{S34}$$

$$2RT\frac{C_c'\big|_L}{C_c\big|_L} + \left(v_c + v_{a,m}\right)p^{s\prime}\Big|_L = 0 \tag{S35}$$

The perturbed deformation governing equations and boundary conditions are the same as the high current density case, viz. equations S5 – S10 and equations S26 – S32 respectively. As before, equations S31, S32 and S35 can be replaced by $\lim_{kz\to\infty} u_x^s = 0$, $\lim_{kz\to\infty} u_z^s = 0$, and $\lim_{kz\to\infty} C_c' = 0$ respectively in the large kL limit.

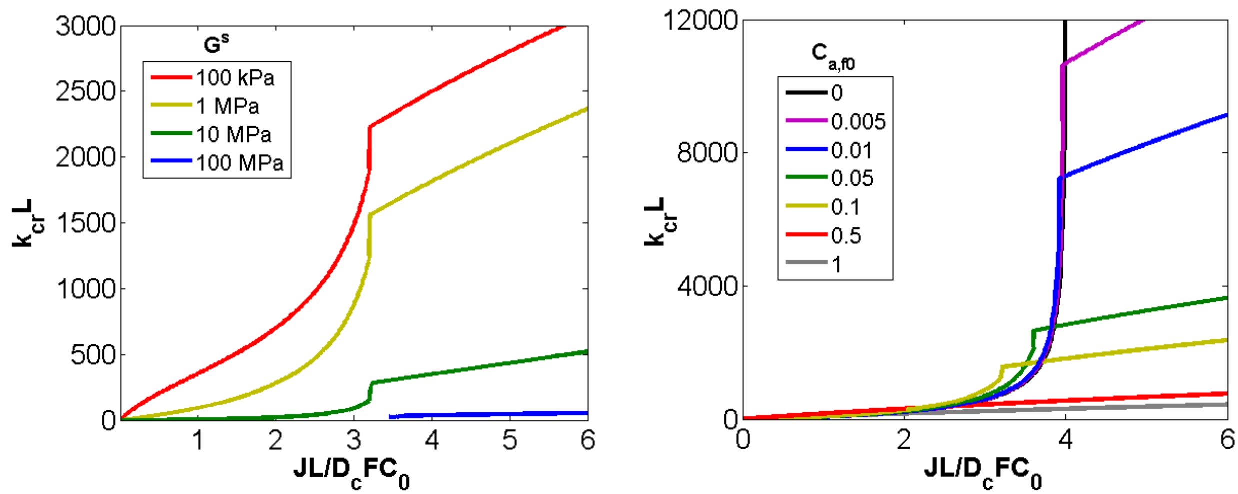

fig S1. Critical wave number versus current density for (**A**) $C_{a,f0}$ = 0.1 with varying G^s, and (**B**) G^s = 1MPa with varying $C_{a,f0}$

table S1. List of symbols, subscripts, and superscripts.

Symbol	Representation
A_r, B_r	Integration constants appearing in eqs. (42) and (43) ($r = c, \phi$)
C_i	Concentration of species i (i = c, a,m, a,f)
C_0	Initial salt concentration
$C_{a,f0}$	Base state fixed anion fraction
c_1^s, c_3^s, c_3^m	Integration constants appearing in eqs. (36) – (41)
D_i	Diffusivity of species i (i = c, a,m)
Eb	Electrical-Bond number
Ec	Elastocapillary number
Ee	Electrical-elastic number
Eo	Elasto-osmotic number
$\mathbf{e}_r$	Unit vector in r-direction ($r = n, x, z$)
e	Base of natural logarithm (Euler's constant) = 2.71828…
F	Faraday's constant = 96,485 C/mol
G^j	Shear modulus of material j (j = s, m)
G	Ratio of shear moduli of metal and separator G^m/G^s
H_c	Position of the metal-separator interface
H_{sf}^j	Position of the surface of material j in the stress-free state
$\mathbf{I}$	Identity tensor
i	Imaginary unit $\sqrt{-1}$
$\mathbf{J}$	Current density vector
J	Component of current density normal to the electrode-separator surface
K^j	Bulk modulus of material j (j = s, m)
k	Wavenumber of perturbation
k_{cr}	Wavenumber of the critical mode, whose growth rate is zero
k_f	Final mode to be stabilized
k_{mu}	Most unstable mode, whose growth rate is the highest
L	Inter-electrode distance
l	Migration region thickness
$\mathbf{N}_i$	Flux vector of species i (i = c, a,m)
N_i	Component of flux of i normal to the electrode-separator surface
$\mathbf{n}$	Direction normal to the electrode-separator surface
p^j	Pressure in material j (j = s, m)
R	Ideal gas constant = 8.314 J/(mol-K)
Se	Surface tension-elasticity number
T	Temperature = 300 K
t	Time

$\mathbf{u}^j$	Deformation field in material j (j = s, m)
u_r^j	Deformation field in material j in direction r ($r = x, z$)
V	Ratio of partial molar volumes of cation in the separator to metal v_c/v_m
v_i	Partial molar volume of species i (i = c, a,m)
x	Direction parallel to the surface
Z_0^s, Z_1^s, Z_1^m	Integration constants appearing in eqs. (36) – (41)
z	Direction normal to the surface
α^j	Parameter related to Poisson's ratio of material j as $1/\left[2\left(1-2\nu^j\right)\right]$
γ	Surface tension
ε	(Small parameter) Amplitude of the perturbation
K	Electrode-separator surface curvature
μ_i	Mobility of species i (i = c, a,m)
ν^j	Poisson's ratio of material j
$\boldsymbol{\sigma}^j$	Stress tensor in material j
σ	Perturbation growth rate
ϕ	Electrostatic potential in the separator
ψ_i	Chemical potential of species i (i = c, a,m, m)

Superscripts and subscripts

Super-/sub-script	**Refers to**
a,f	fixed anion
a,m	mobile anion
c	cation
s	separator
m	metal
′	perturbation
~	perturbed state
*	dimensionless