Modelling Battery Overpotential with the Barton-Bockris Model for Li/Na Plating and Al-Li Two-Phase Reaction

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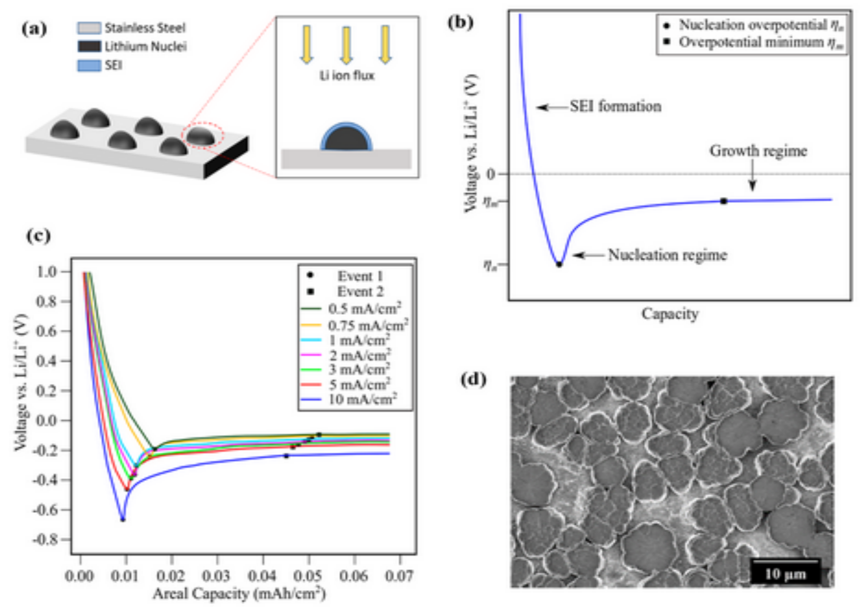
(1) Overpotential during Plating



Overpotential in Lithium batteries caused by dendritic growth [2]

(2) Barton-Bockris Model

$$E(t) = E_{OCV} \pm \eta(t)$$

$$\eta_{BB}(r) = \eta_a(I) + \eta_d(r, I) + \eta_i(r)$$

$$\eta(t) = \frac{RT}{zF}\ln\left(\frac{I}{I_0}\right) + \frac{RTI}{z^2F^2D_jC_jA}r(t) + \frac{2\gamma M}{zF\rho}\frac{1}{r(t)}$$

Overpotential model proposed by Barton and Bockris can be used to derive hard-to-measure material constants

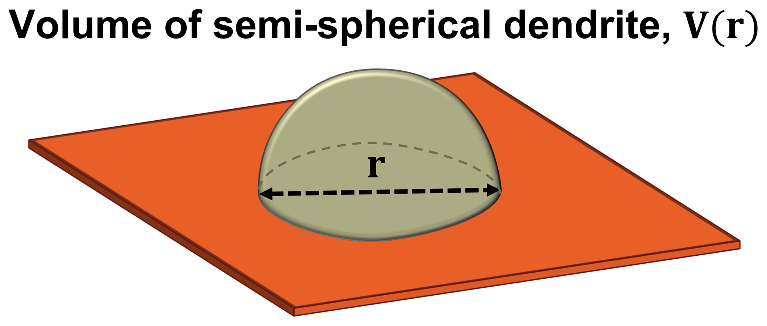
(3) Computational Methods

(A)	Derive Barton-Bockris model in terms of r	$E_{BB}(r)$
(B)	Select dataset to model	$E_{data}(t)$
(C)	Select growth model	$r_m(t)$
(D)	Substitute growth model into BB model	$E_{BB}(r_m(t))$
(E)	Generalize BB model for fitting	$E_{BB}(t, A, B, C)$
(F)	Use code to fit data/ extract fit parameters	(A, B, C)
(G)	From parameters, calculate material properties	(I_0, D, γ)

(3) Hemispherical Growth Model

Deriving Hemispherical Growth Model, $r_{hs}(t)$

Volume of semi-spherical dendrite, $V(r)$



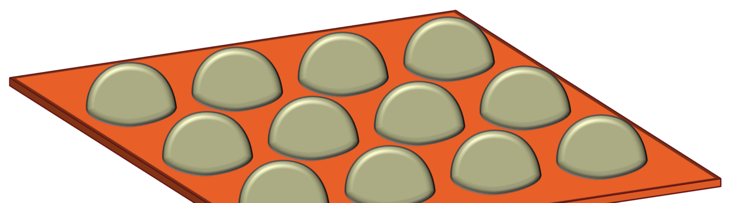
$$m(r,t) = \frac{It}{q} = \rho n V_{hs}(r)$$

$$\frac{MIt}{zF} = \rho n\left(\frac{2}{3}\pi r^3\right)$$

$$r_{hs}(t) = \left(\frac{3MIt}{2\pi zF\rho n}\right)^{\frac{1}{3}}$$

$$r_{hs}(t) = 0.782\left(\frac{MI}{zF\rho n}\right)^{\frac{1}{3}} t^{\frac{1}{3}}$$

Volume of n semi-spherical dendrites, $nV(r)$



Plugging $r_{hs}(t)$ into Barton-Bockris Model

$$\eta_{BB}(t) = \frac{RT}{zF}\ln\left(\frac{I}{I_0}\right) + 0.782\frac{RT}{D_jC_jA}\left(\frac{MI^4}{z^7F^7\rho n}\right)^{\frac{1}{3}} t^{\frac{1}{3}} + 2.559\gamma\left(\frac{M^2 n}{z^2F^2\rho^2 I}\right)^{\frac{1}{3}} t^{-\frac{1}{3}}$$

Plugging $r_{hs}(t)$ into Barton-Bockris Model

$$\eta_{BB}(t) = A + Bt^{\frac{1}{3}} + Ct^{-\frac{1}{3}}$$

$$I_0 = I\exp\left(-A\frac{zF}{RT}\right) \qquad D_jn^{\frac{1}{3}} = 0.782\frac{RT}{BC_jA}\left(\frac{MI^4}{z^7F^7\rho}\right)^{\frac{1}{3}} \qquad \gamma n^{\frac{1}{3}} = \frac{C}{2.559}\left(\frac{z^2F^2\rho^2 I}{M^2}\right)^{\frac{1}{3}}$$

(4) Diffusion Growth Model

General Diffusion Growth Model, $r_{gd}(t)$

$$r_{gd}(t) = \sqrt{Dt}$$

Plugging $r_{gd}(t)$ into Barton-Bockris Model

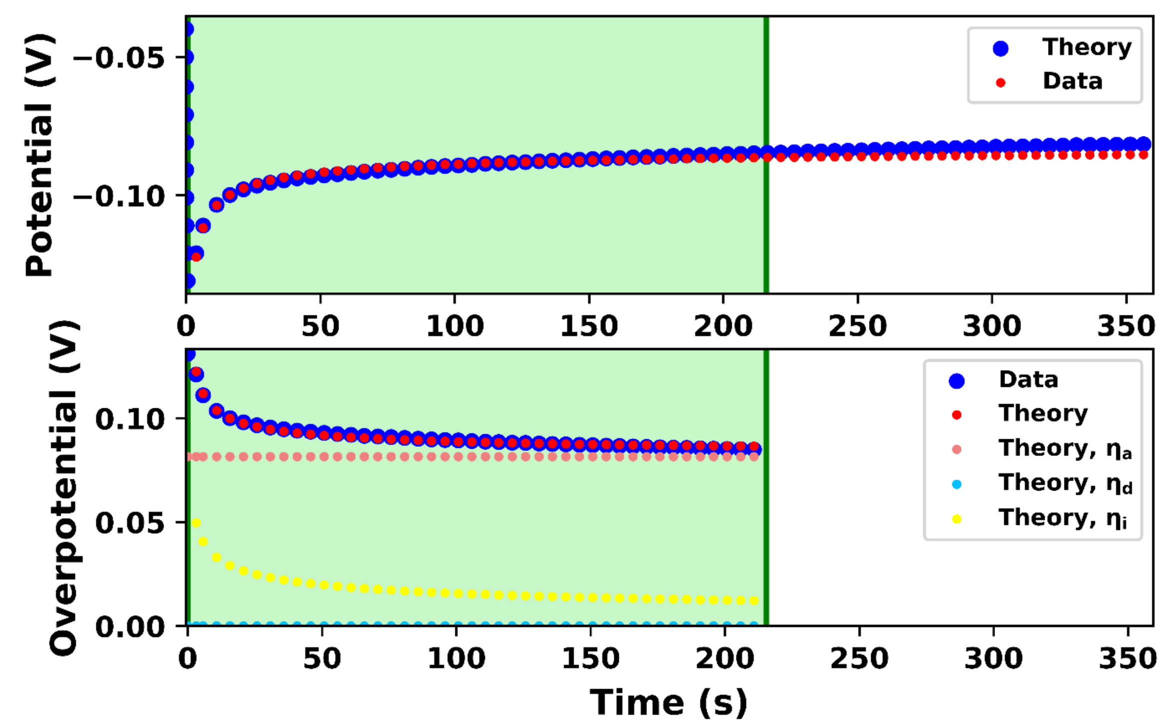
$$\eta_{BB}(t) = \frac{RT}{zF}\ln\left(\frac{I}{I_0}\right) + \frac{RTI}{z^2F^2D^{\frac{1}{2}}C_jA}t^{\frac{1}{2}} + \frac{2\gamma M}{zF\rho D^{\frac{1}{2}}}t^{-\frac{1}{2}}$$

Plugging $r_{gd}(t)$ into Barton-Bockris Model

$$\eta_{BB}(t) = A + Bt^{\frac{1}{2}} + Ct^{-\frac{1}{2}}$$

$$I_0 = I\exp\left(-A\frac{zF}{RT}\right) \qquad D = \left(\frac{RTI}{z^2F^2BC_jA}\right)^2 \qquad \gamma = \frac{CzF\rho D^{\frac{1}{2}}}{2M}$$

(5) Fitting Li Plating on Cu Data



Diffusion Model Fitting Parameters:

$A = 8.11 \cdot 10^{-2}$

$B = 3.15 \cdot 10^{-4}$

$C = 7.01 \cdot 10^{-2}$

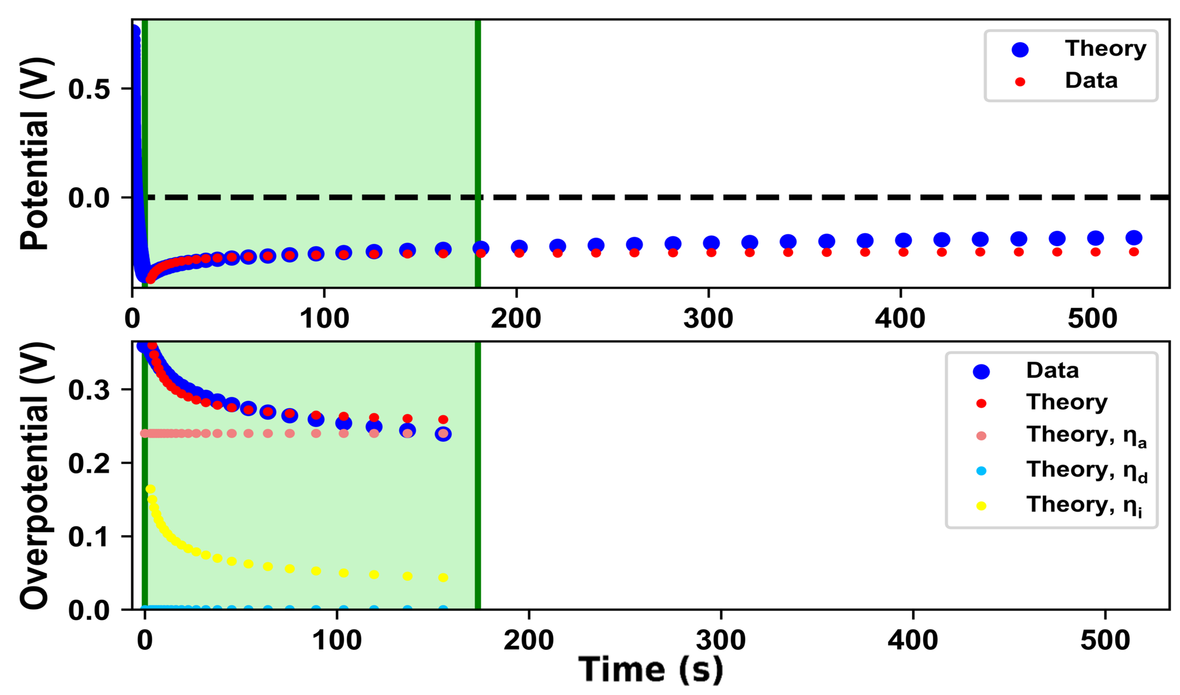
Diffusion Model Derived Properties:

$i_0 = 4.26 \cdot 10^{-2}\ \frac{mA}{cm^2}$

$D = 7.15 \cdot 10^{-3}\ \frac{dm^2}{s}$

$\gamma = 2.20 \cdot 10^{4}\ \frac{J}{dm^2}$

(6) Fitting Na Plating on Cu Data



Hemispherical Model Fitting Parameters:

$A = 2.11 \cdot 10^{-1}$

$B = 1.30 \cdot 10^{-7}$

$C = 2.31 \cdot 10^{-1}$

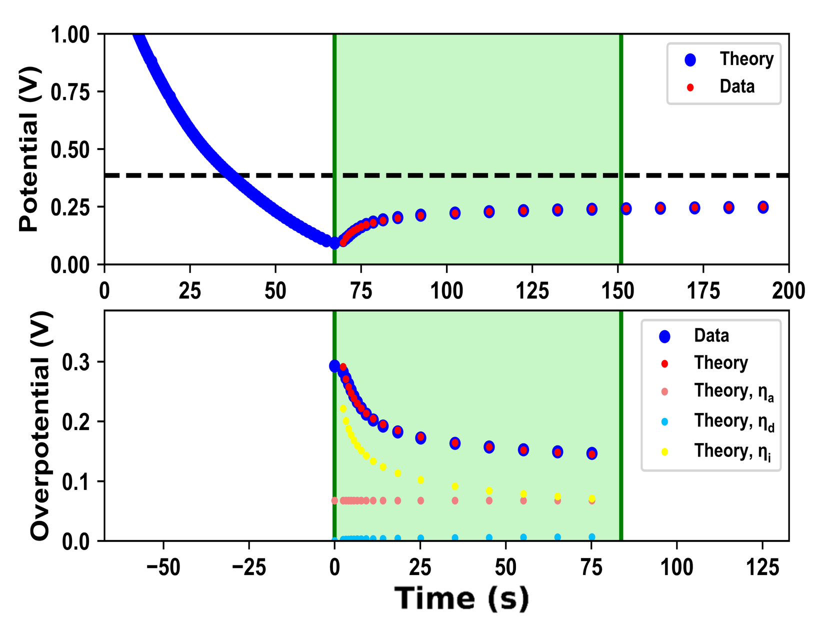
Hemispherical Model Derived Properties:

$i_0 = 8.59 \cdot 10^{-5}\ \frac{mA}{cm^2}$

$D_jn^{\frac{1}{3}} = 1.83 \cdot 10^{-1}\ \frac{dm^2}{s}$

$\gamma n^{\frac{1}{3}} = 1.34 \cdot 10^{3}\ \frac{J}{dm^2}$

(7) Fitting Al-Li Two-Phase Data



Hemispherical Model Fitting Parameters:

$A = 6.785 \cdot 10^{-2}$

$B = 1.535 \cdot 10^{-3}$

$C = 2.996 \cdot 10^{-1}$

Hemispherical Model Derived Properties:

$i_0 = 2.32 \cdot 10^{-2}\ \frac{mA}{cm^2}$

$D_jn^{\frac{1}{3}} = 3.04 \cdot 10^{-5}\ \frac{dm^2}{s}$

$\gamma n^{\frac{1}{3}} = 2.63 \cdot 10^{-5}\ \frac{J}{dm^2}$

References/ Acknowledgments

[1] A. Pei, et al., Nano Letters 2017 17(2), 1132-1139.
[2] P. Biswal, et al., Nano Letters 2019 19(11) 4009-8200.
[3] J.L. Barton, et al., Proc. R. Soc. Lond. A268485–505.
[4] D.R. Hamilton, Electrochimica Acta 1963 Volume 8, Issue 9
[5] J.W. Diggle, et al., J. Electrochem. Soc. 1969 116 1503.

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