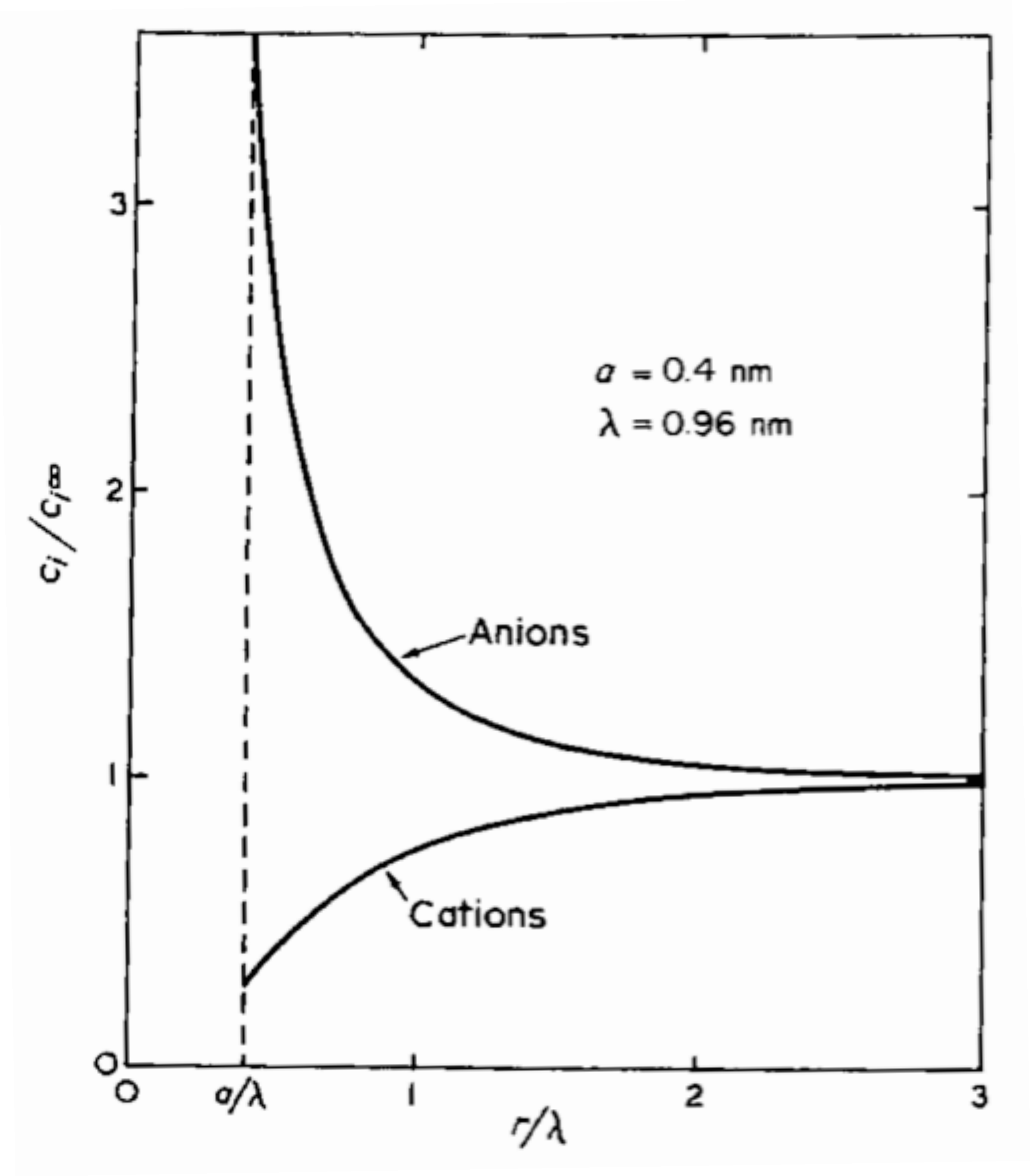
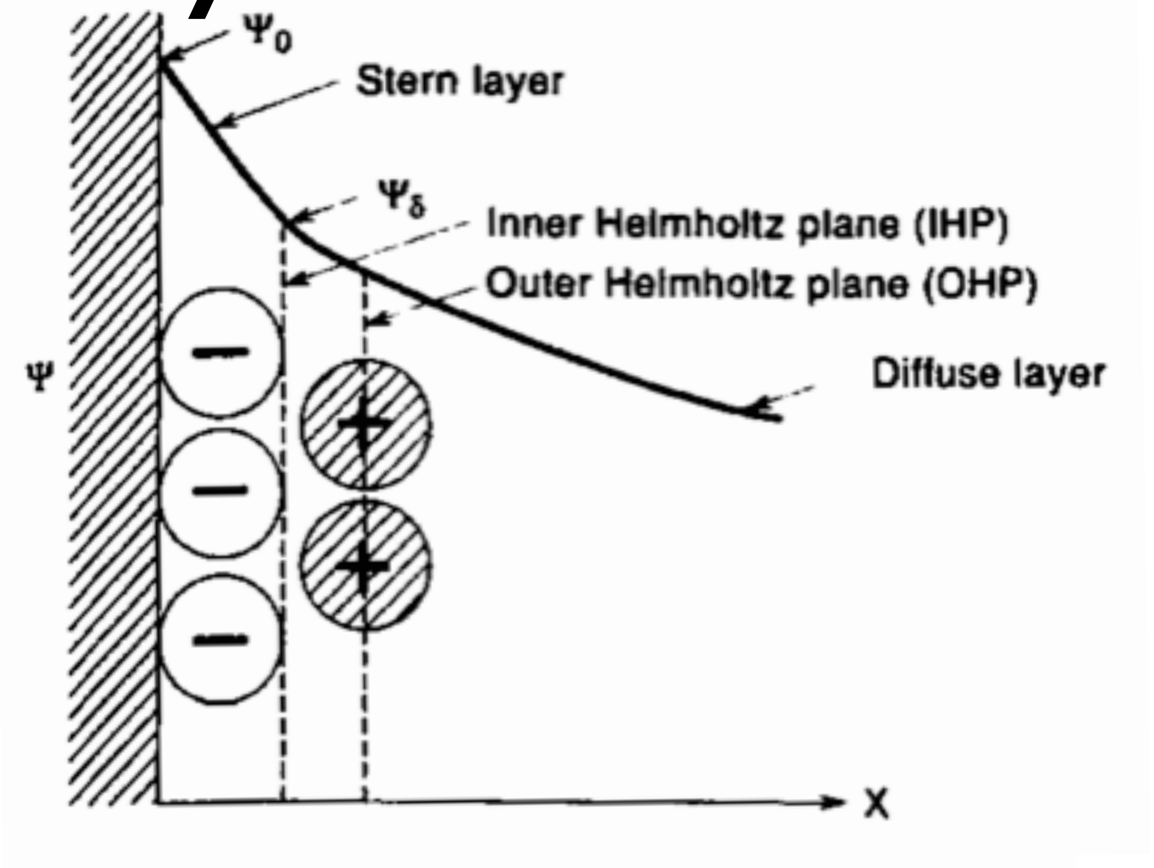
The Electrode Interface II

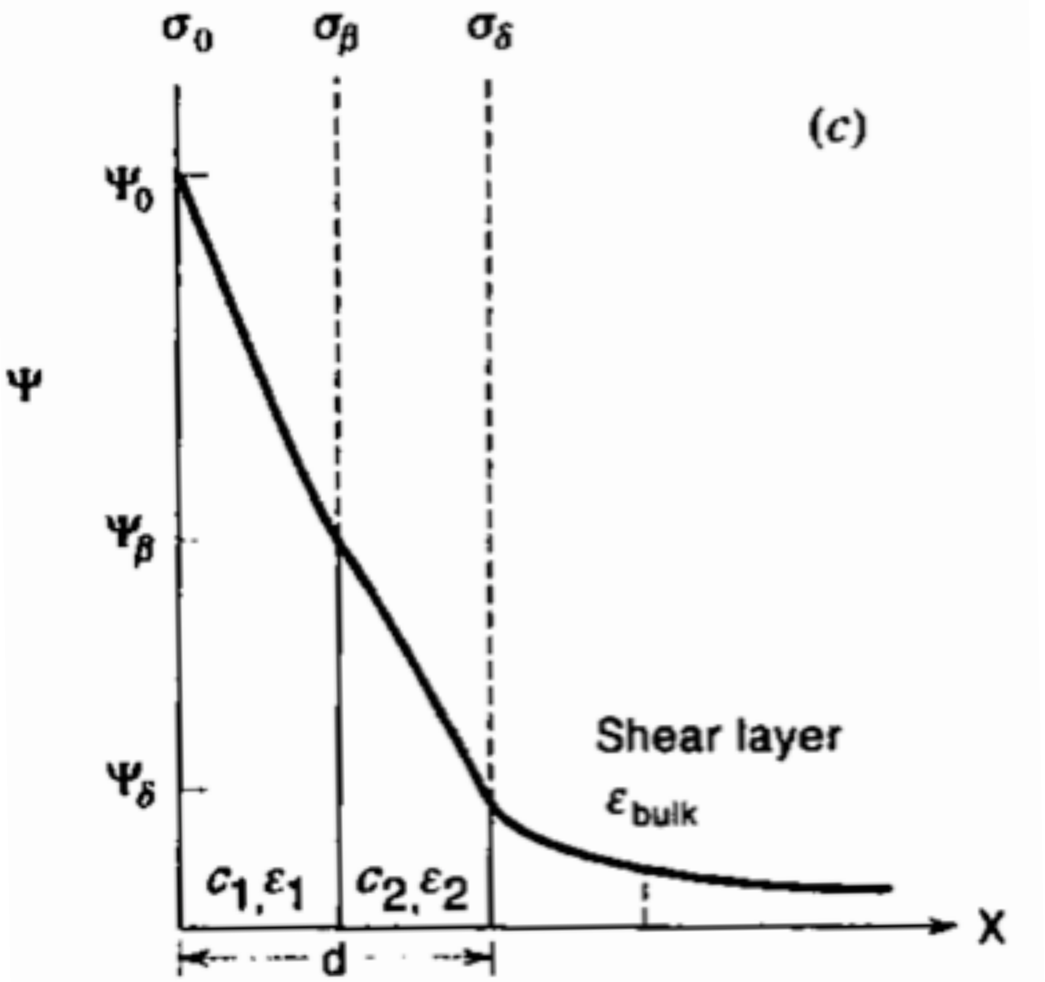
Lecture 17

R. Edwin García
redwing@purdue.edu

The Electrode-Electrolyte Interface







The Electrode-Electrolyte Interface

$$\nabla^2\phi = \frac{zec^*}{\varepsilon_r\varepsilon_o}\sinh\frac{ze\phi}{k_bT} - \frac{\rho_o(x,y,z)}{\varepsilon_r\varepsilon_o}$$

→ non-linear equation

$$\nabla^2\phi = \frac{z^2e^2c^*}{\varepsilon_r\varepsilon_o k_bT}\phi - \frac{\rho_o(x,y,z)}{\varepsilon_r\varepsilon_o}$$

→ linearized equation

$$\kappa^2 = \frac{z^2e^2c^*}{\varepsilon_r\varepsilon_o k_bT}$$

Debye constant

The Butler-Volmer Relation

$$Li \rightleftarrows Li^{+} + e^{-}$$

Detailing the rate at which Li intercalates

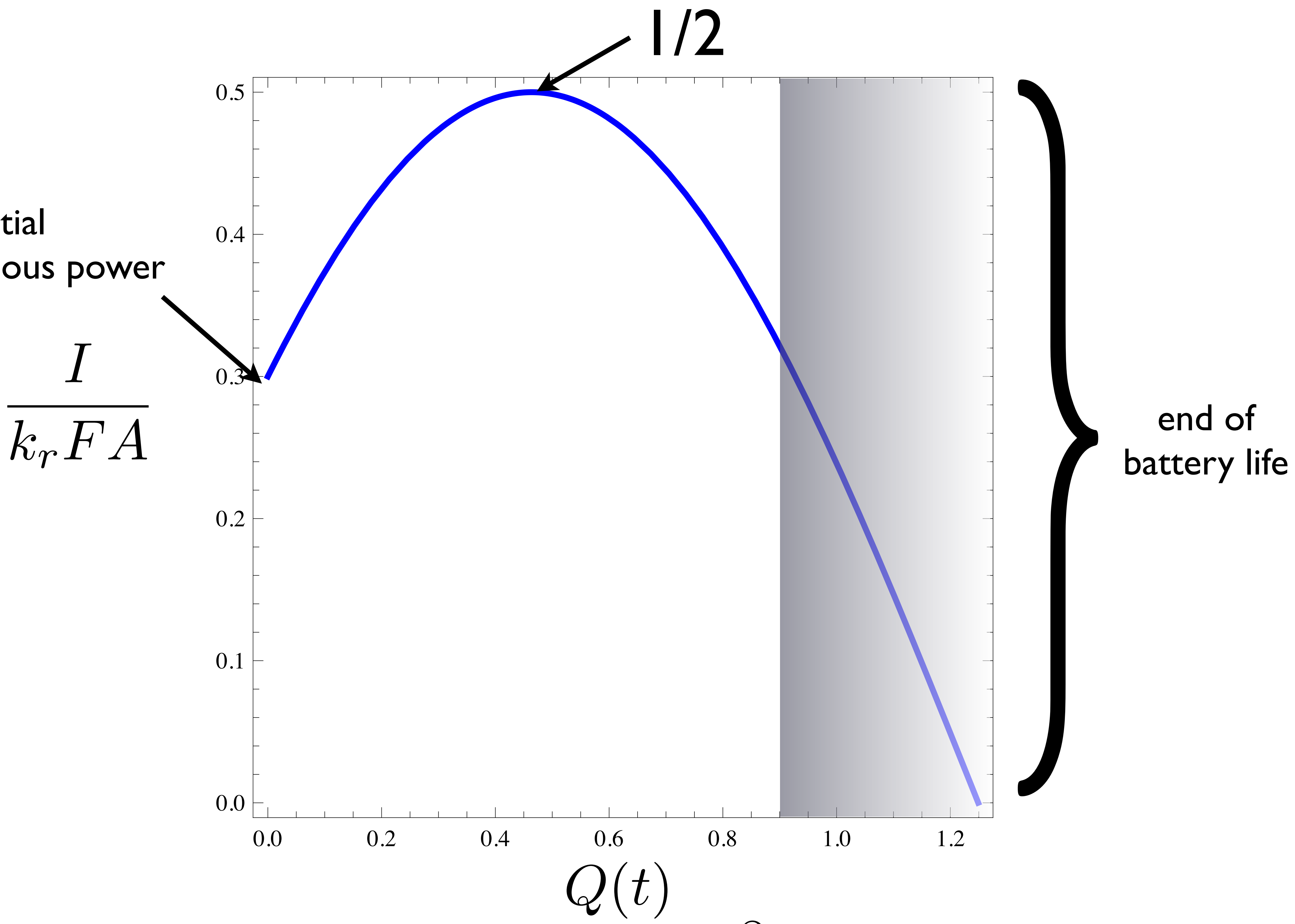
$$LiM \leftrightarrows e^{-} + Li^{+} + M$$

$$i_{\circ} = Fk_{r}(c_{T} - c_{s})^{\alpha_{a}} c_{s}^{\alpha_{c}}$$

The simplest interfacial kinetics

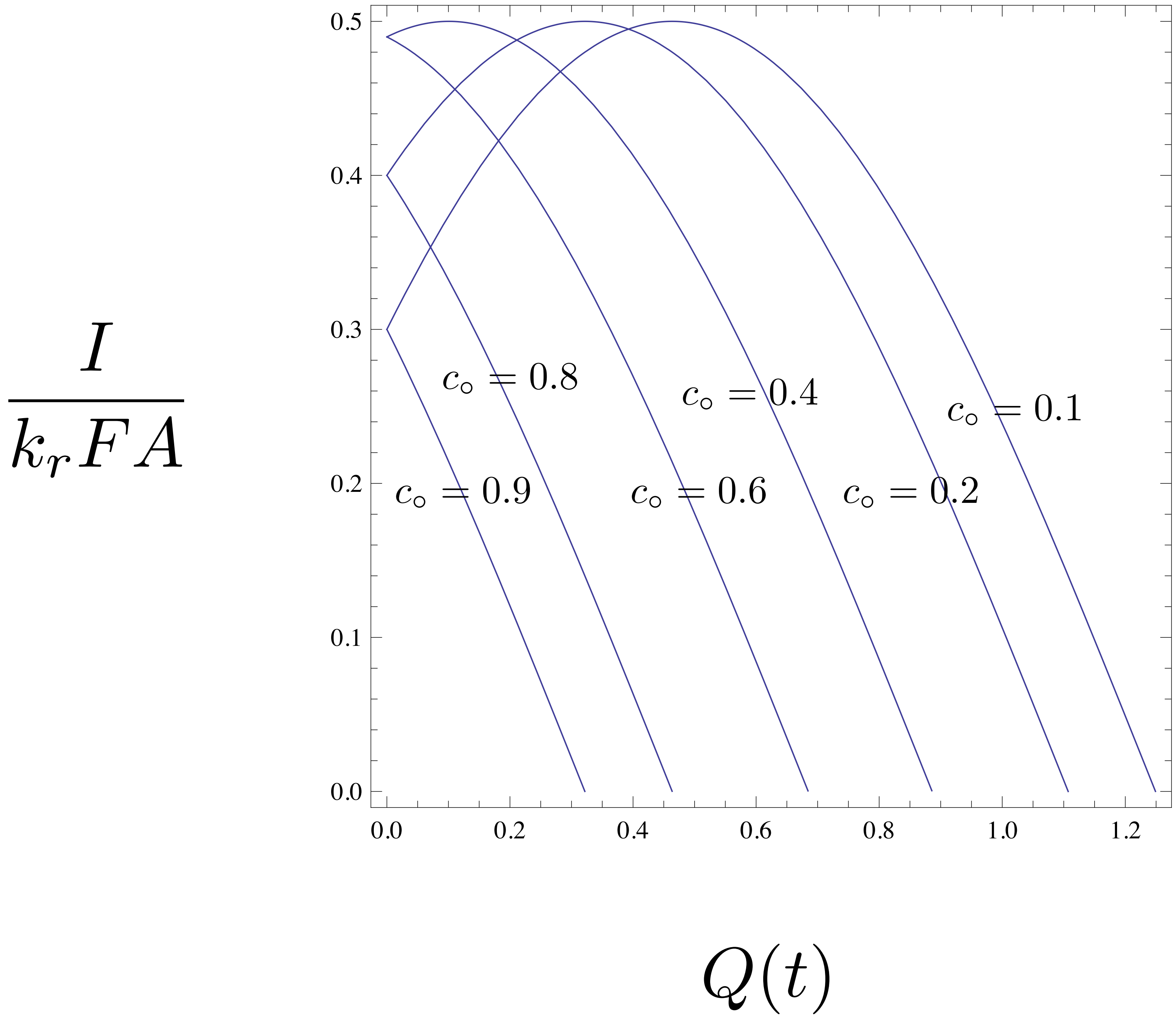
$$\vec{J} \cdot \hat{n} = i_{\circ} \left(\exp(\frac{\alpha_{a} F z \eta}{RT}) - \exp(-\frac{\alpha_{c} F z \eta}{RT}) \right)$$

Effect on Power Density



$$\frac{\partial c}{\partial t} = A(\eta, T) c^{1/2} (1 - c)^{1/2}$$

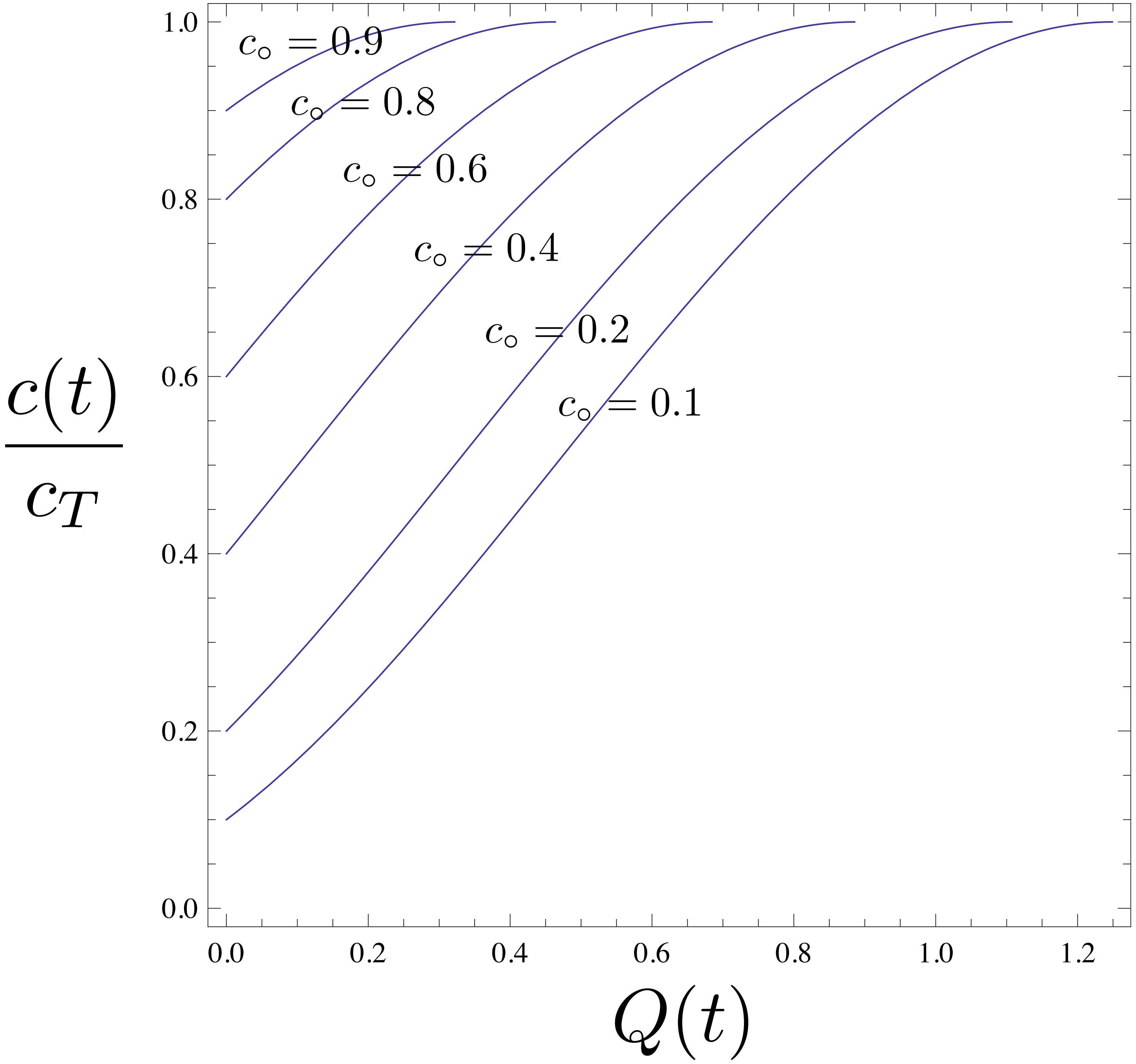
Effect on the Electrode Material



$$\frac{\partial c}{\partial t} = A(\eta, T)c^{1/2}(1 - c)^{1/2}$$

Effect on the Battery

$$\frac{\partial c}{\partial t} = A(\eta, T)c^{1/2}(1-c)^{1/2}$$



Tafel Kinetics

Butler-Volmer Kinetics:

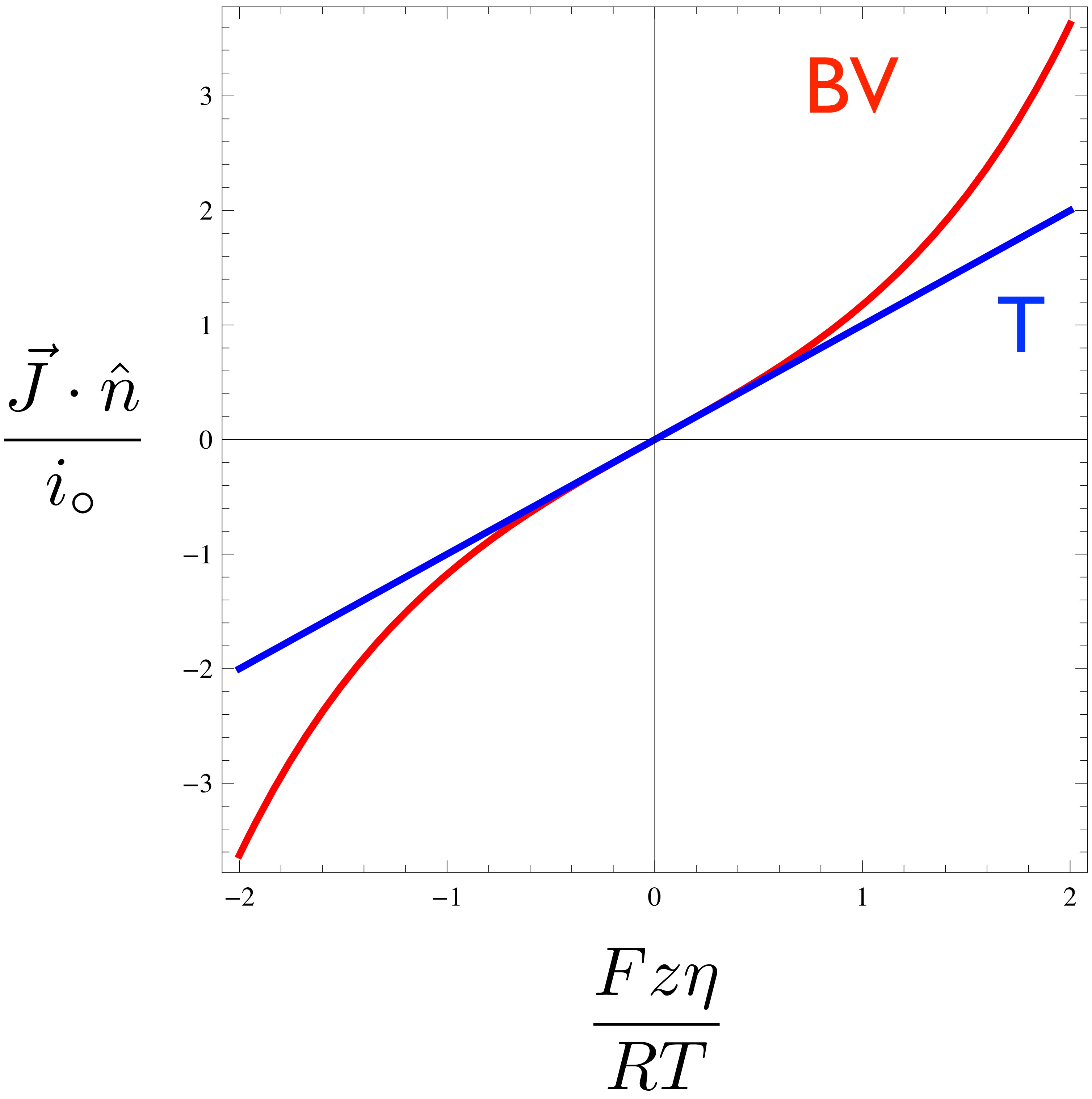
$$\vec{J}\cdot\hat{n} = i_\circ\left(\exp(\frac{\alpha_a F z\eta}{RT}) - \exp(-\frac{\alpha_c F z\eta}{RT})\right)$$

$$i_\circ = F k_r (c_T - c_s)^{\alpha_a} c_s^{\alpha_c} c_e^{\alpha_a}$$

if $\alpha_a = \alpha_c = 1/2$ and $\frac{Fz\eta}{RT} \ll 1$

$$\vec{J}\cdot\hat{n} = i_\circ \frac{Fz\eta}{RT}$$

Tafel Kinetics



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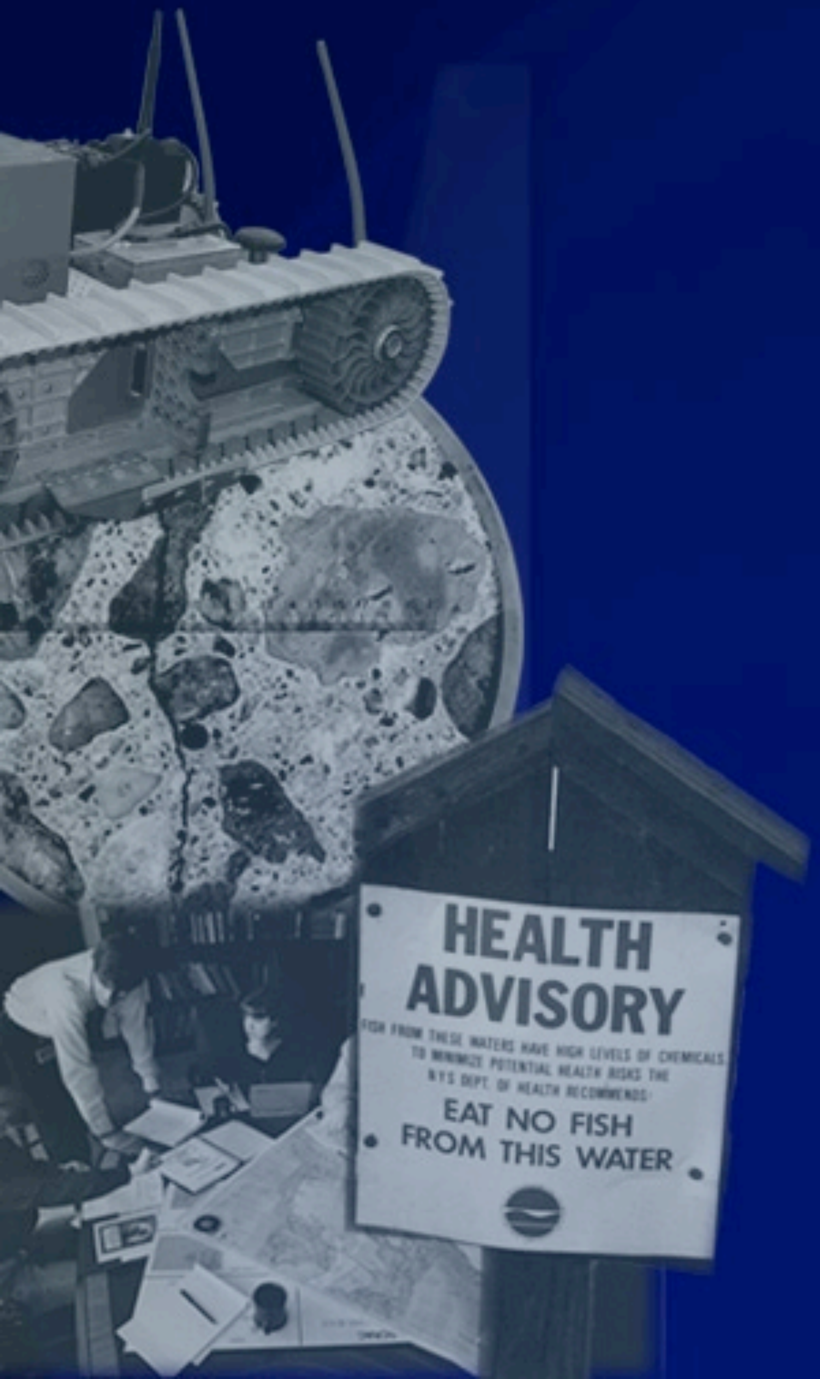


Understanding Lithium-Ion Degradation and Failure Mechanisms by Cross-Section Analysis

Quinn Horn

Kevin White

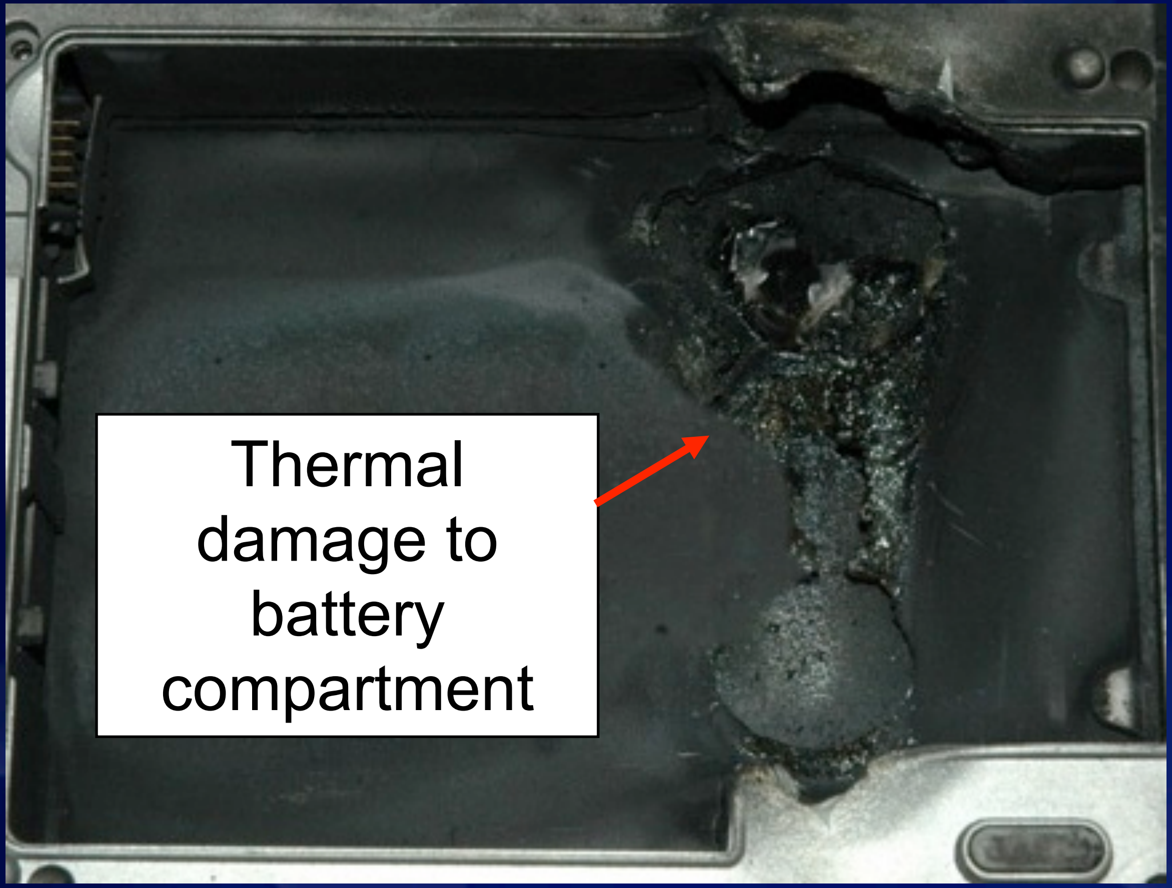
Exponent, Inc.

Natick, Massachusetts

211th Meeting of the Electrochemical Society

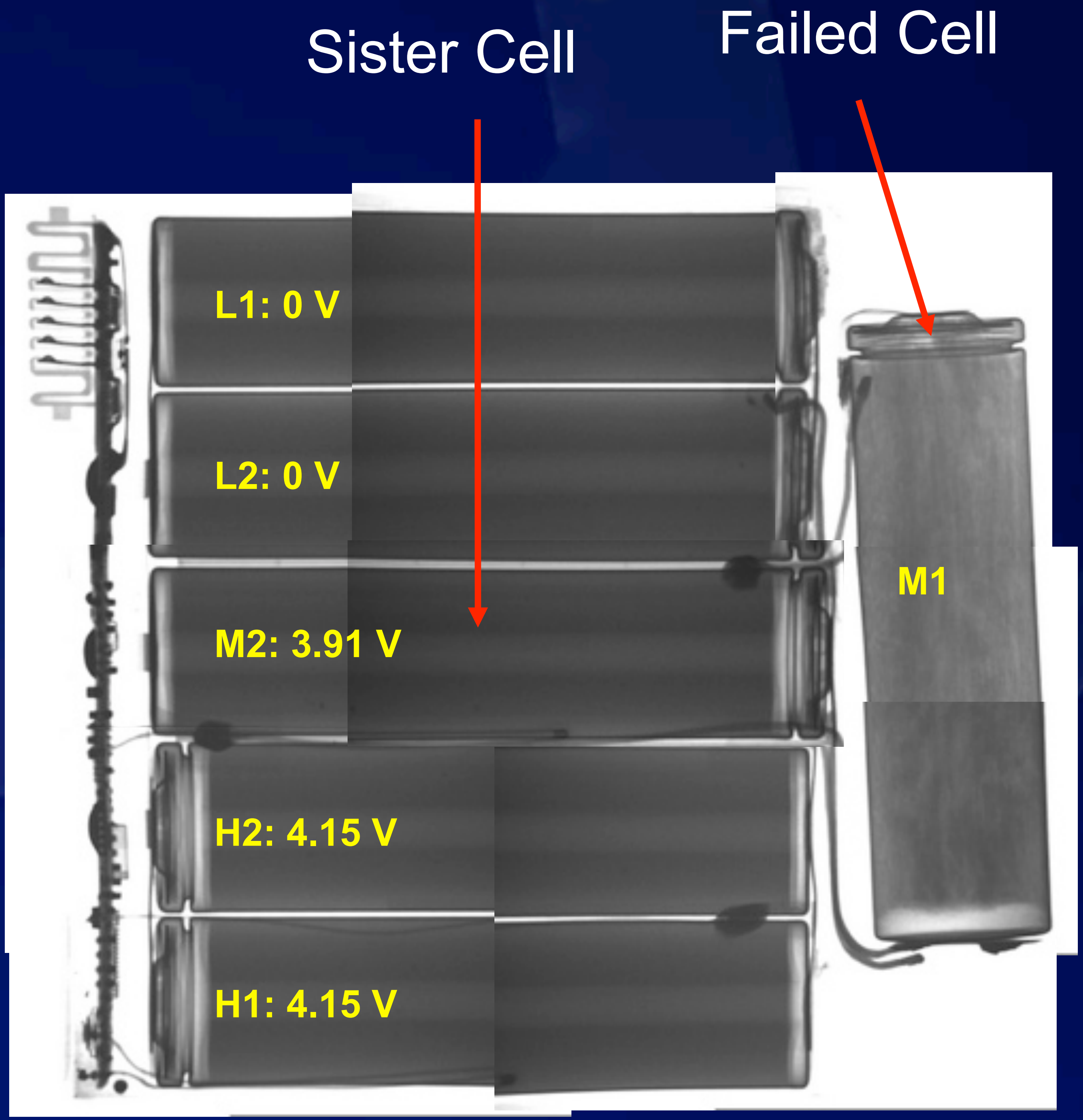
May 8, 2007

Field Failure of a Notebook Battery Pack

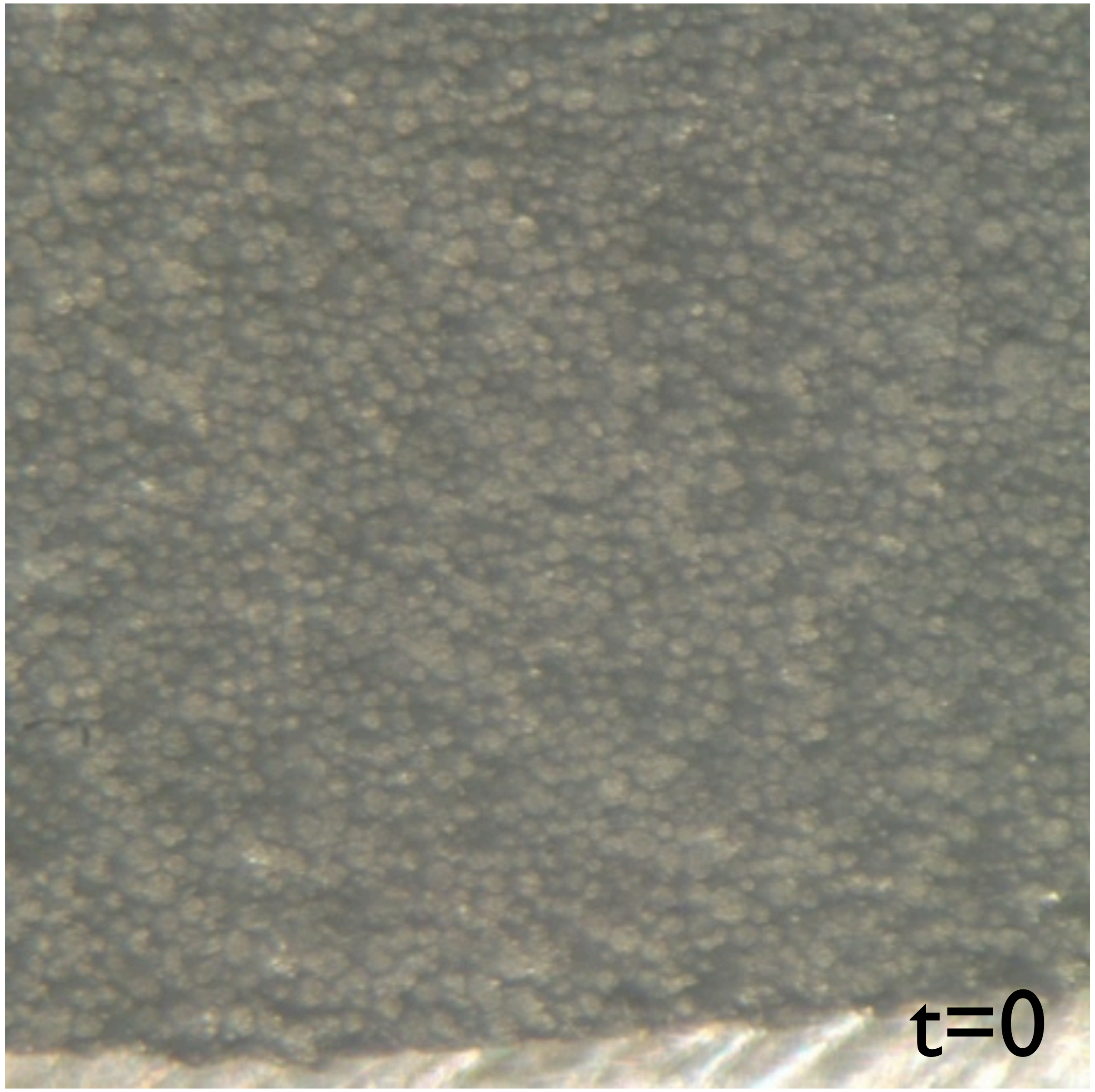


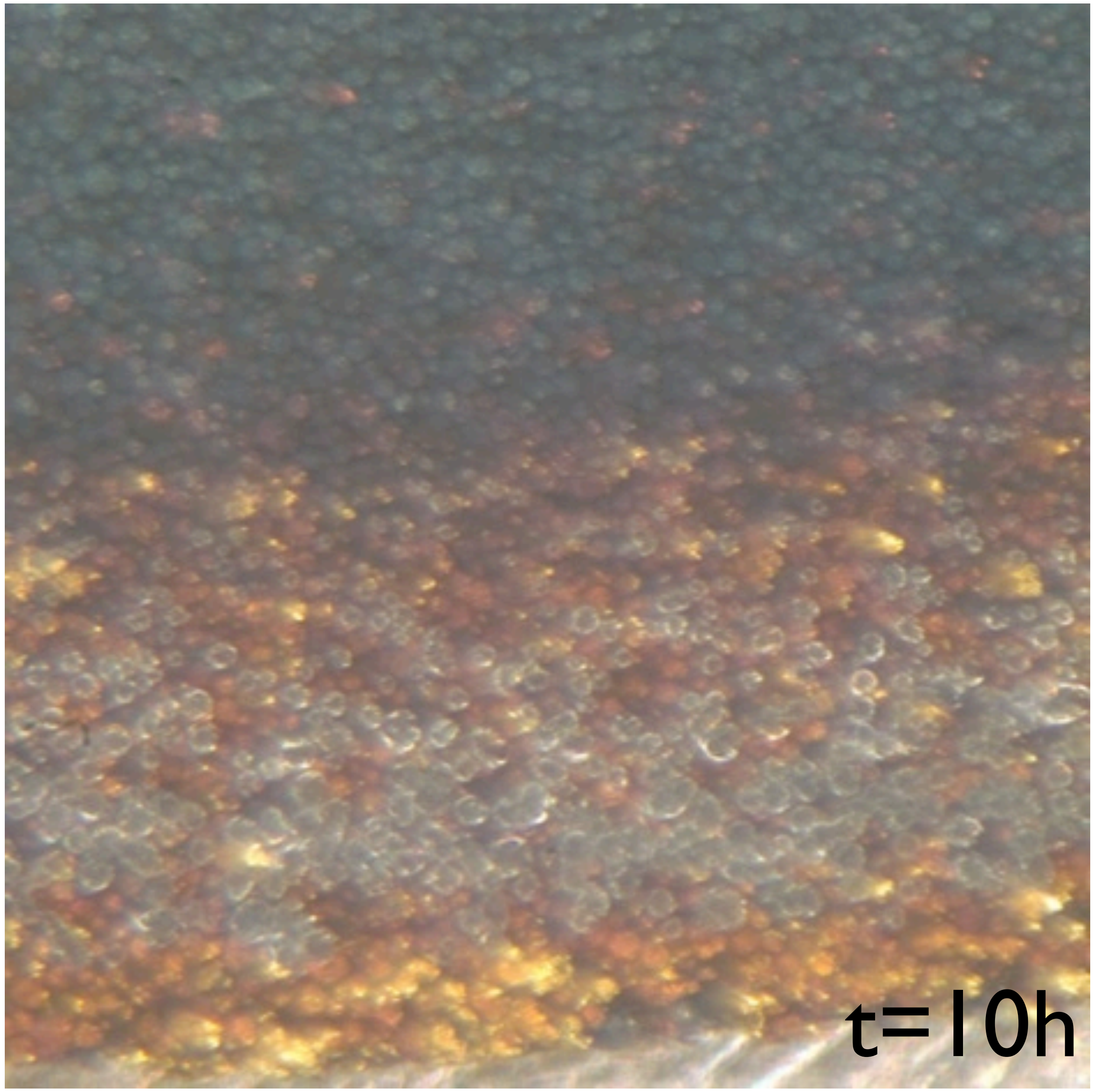
Thermal damage to battery compartment

Cell M2 is the "sister cell" to the failed cell (i.e. M1 and M2 were in parallel and therefore experienced the same voltage conditions)

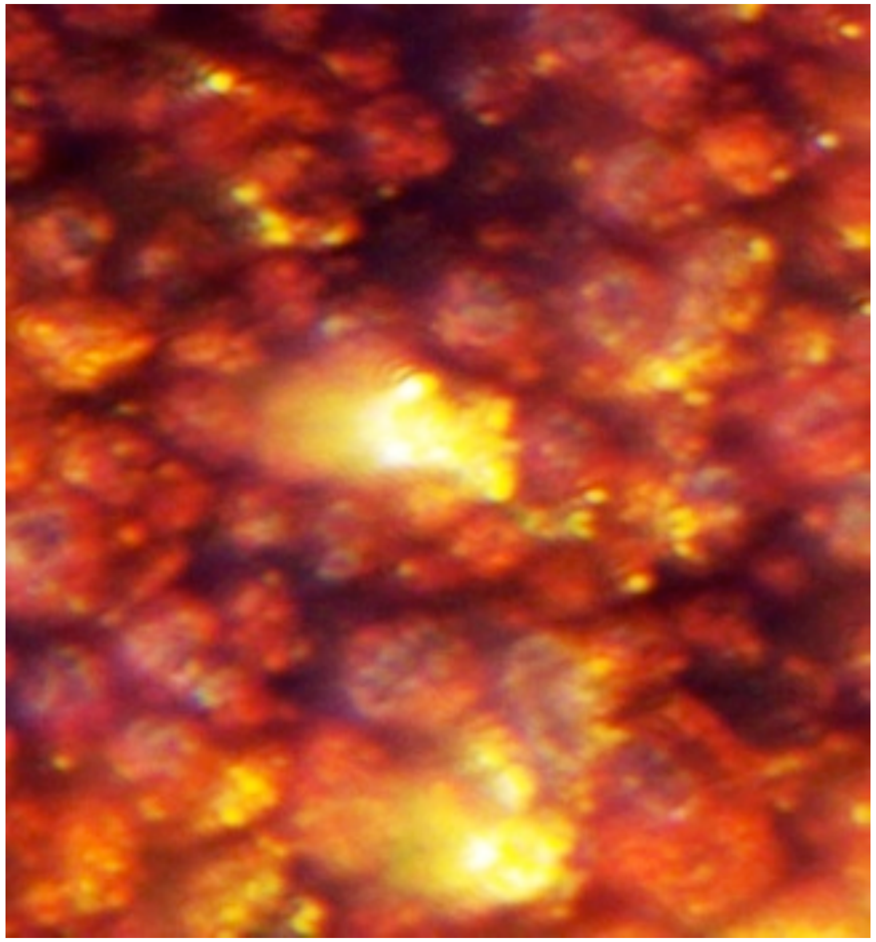


In Situ Experiments

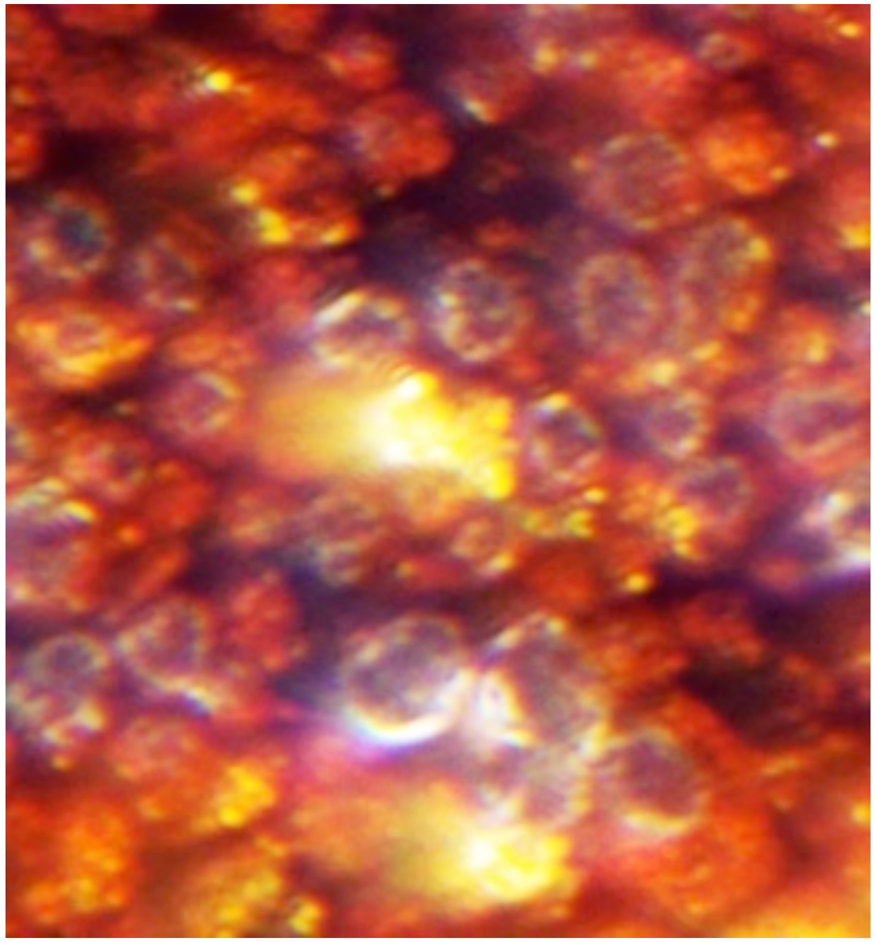




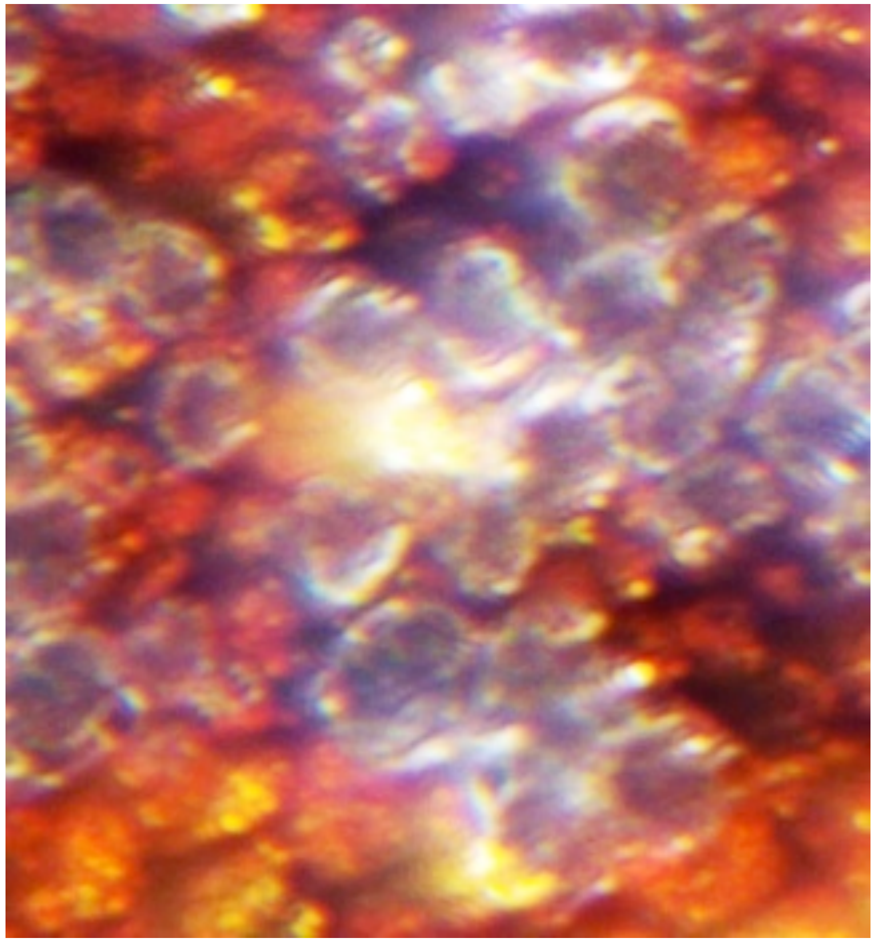
S. J. Harris, A. Timmons, D. R. Baker, and C. Monroe. Direct in situ measurements of Li transport in Li-ion battery negative electrodes. Chem. Phys. Lett., 485(4-6):265–274, January 2010.



incubation



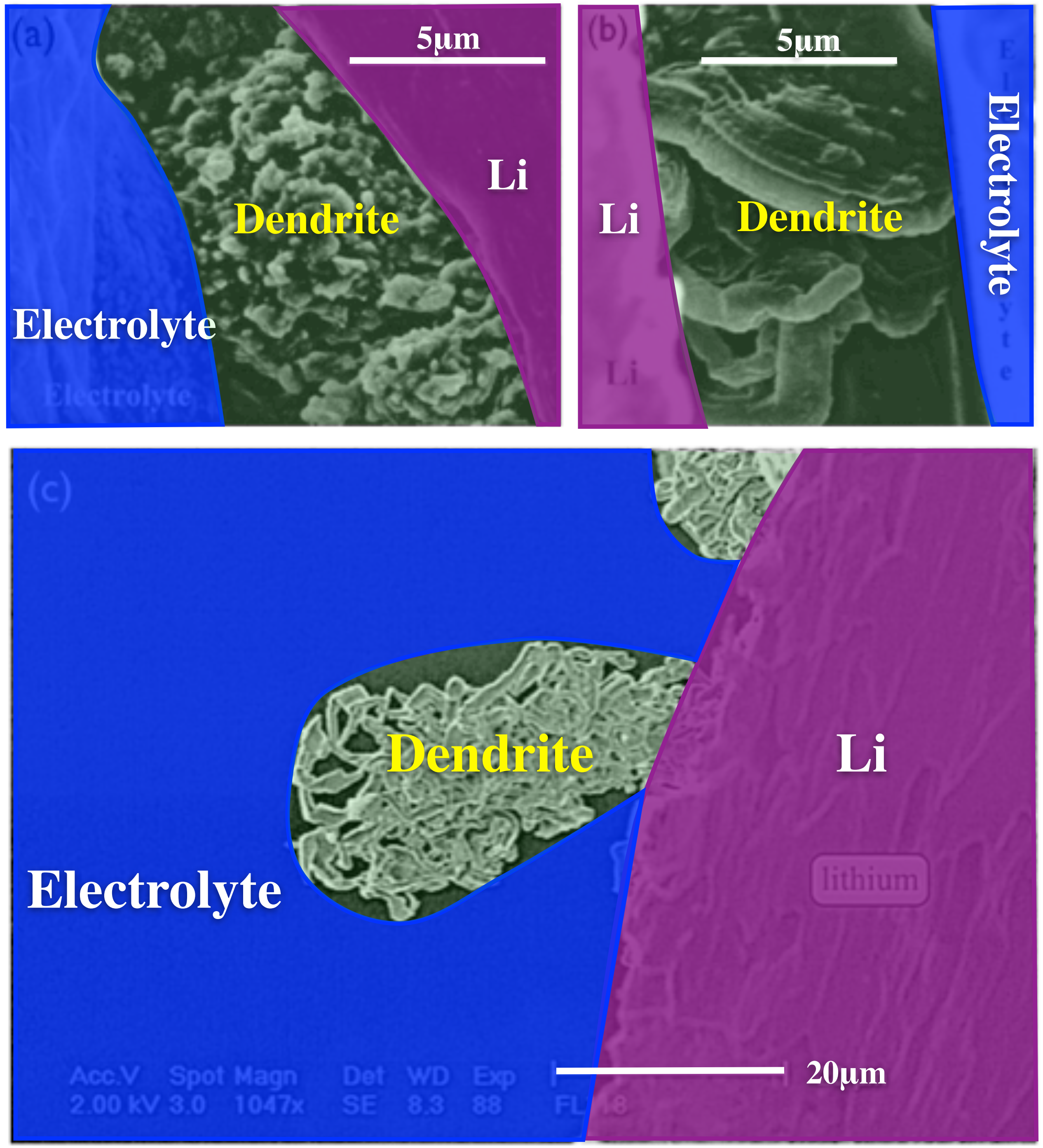
nucleation



growth

S. J. Harris, A. Timmons, D. R. Baker, and C. Monroe. Direct in situ measurements of Li transport in Li-ion battery negative electrodes. Chem. Phys. Lett., 485(4-6):265–274, January 2010.

Lithium Dendrites

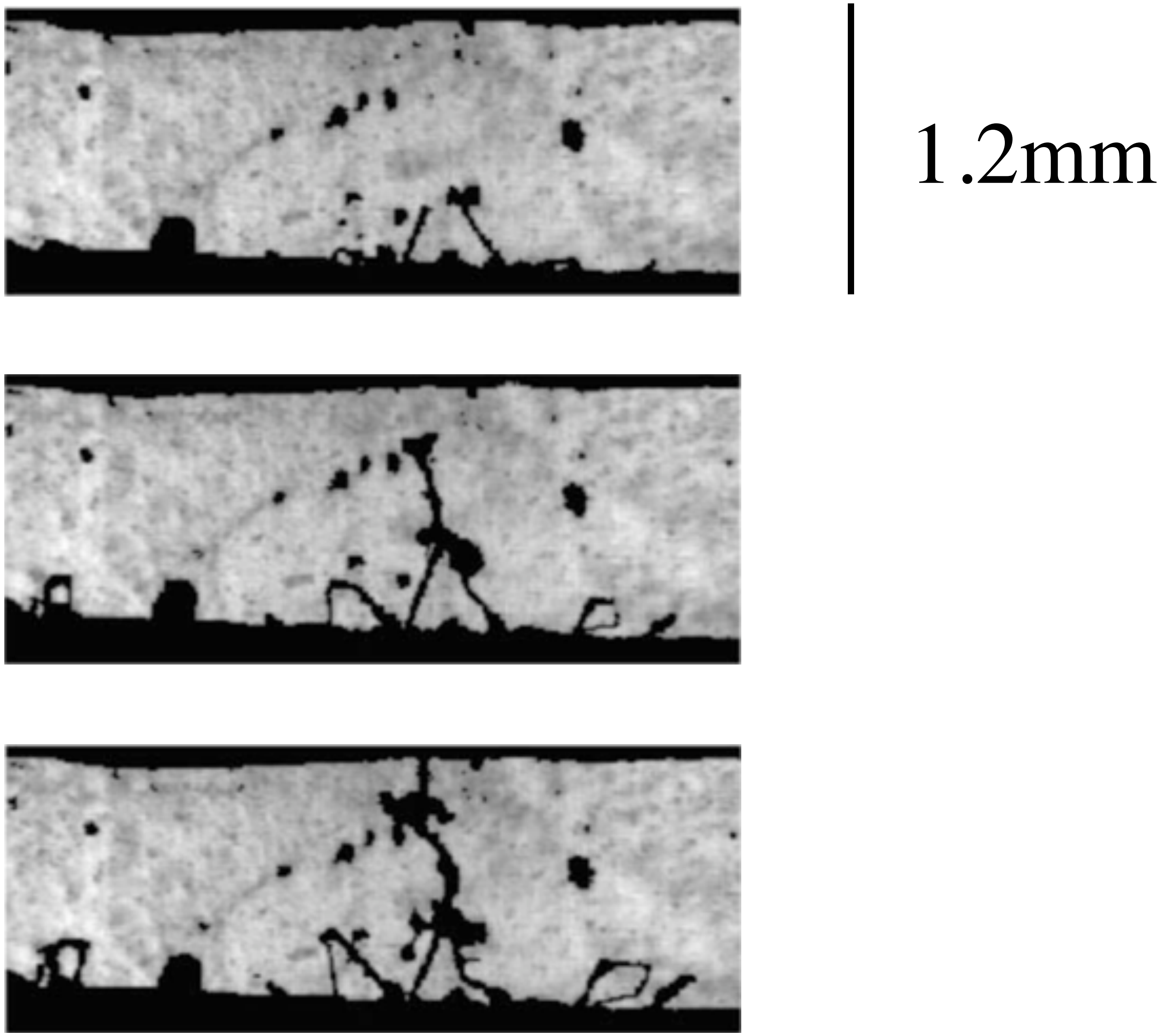


Slide courtesy of Zhiwen Liang

M. Dolle, L. Sannier. B. Beaudoin, M. Trentin, and J. M. Tarascon. Live Scanning Electron Microscope Observations of Dendritic Growth in Lithium/Polymer Cells. Electrochemical and Solid-State Letters, 5:A286-A289, 2002

F. Orsini, A. Du Pasquier, B. Beaudoin, J. M. Tarascon, M. Trentin, N. Langenhuizen, E. De Beer, and P. Notten. In Situ Scanning Electron Microscopy (SEM) Observation of Interfaces within Plastic Lithium Batteries. Journal of Power Sources, 76:19-29,1998

Tip-Controlled Dendritic Growth



t=56 hours

t=83 hours

t=100 hours

M. Rosso, C. Brissot, A. Teyssot, M. Dolle, L. Sannier, J. M. Tarascon, R. Bouchet, and S. Lascaud.
Dendrite Short-circuit and Fuse Effect on Li/Polymer/Li Cells. Electrochimica Acta, 51:5334-5340, 2006

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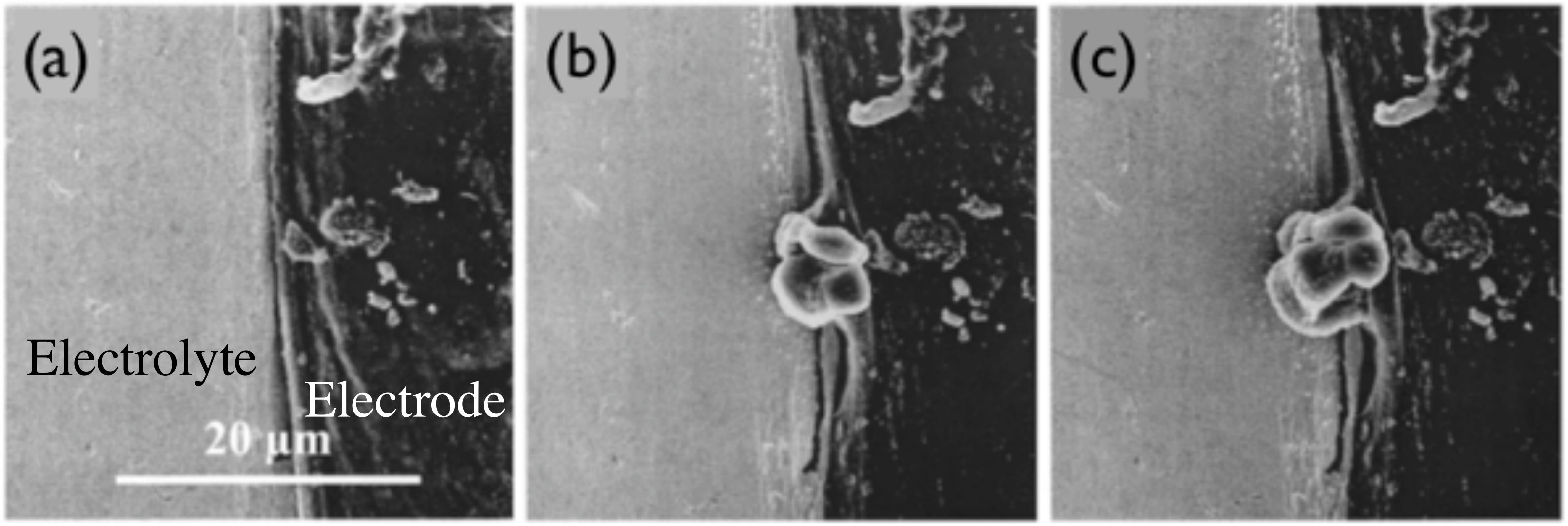
Base-Controlled Dendritic Growth

t=600s t=720s t=840s t=1140s t=1320s



t=0min t=160min t=200min

O. Crowther and A. C. West. Effect of Electrolyte Composition on Lithium Dendrite Growth. Journal of The Electrochemical Society, 155(11):A806-A811, 2008

M. Dolle, L. Sannier, B. Beaudoin, M. Trentin, and J. M. Tarascon. Live Scanning Electron Microscope Observations of Dendritic Growth in Lithium/Polymer Cells. Electrochemical and Solie-State Letters, 5:A286-A289, 2002

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Dendrite Growth Mechanisms

- Tip-Controlled:
    - Dendrite grows at the tip.
    - Base remains the same.
- Base-Controlled:
    - Dendrite is extruded at the base.
    - Tip remains the same.

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