# The Electrode Interface III

Lecture 18

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# The Butler-Volmer Relation

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

Detailing the rate at which Li intercalates

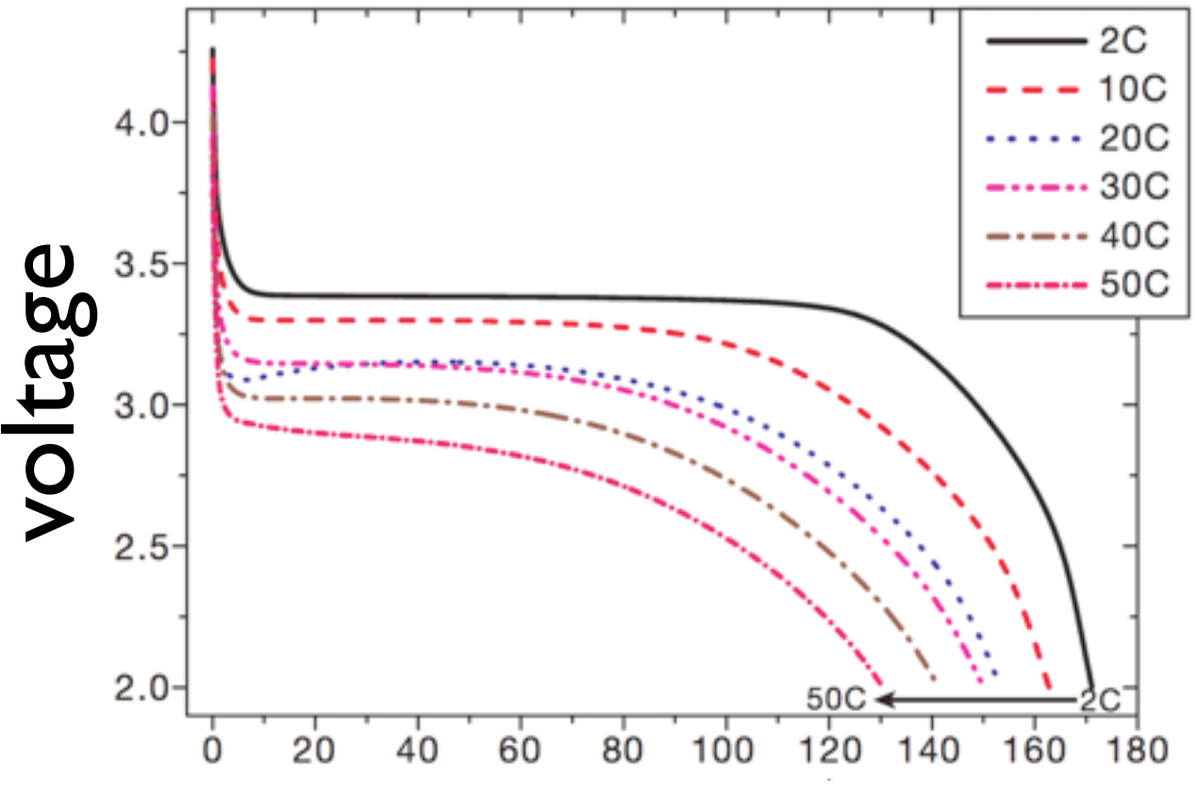
$$LiM \leftrightarrows e^- + Li^+ + M$$

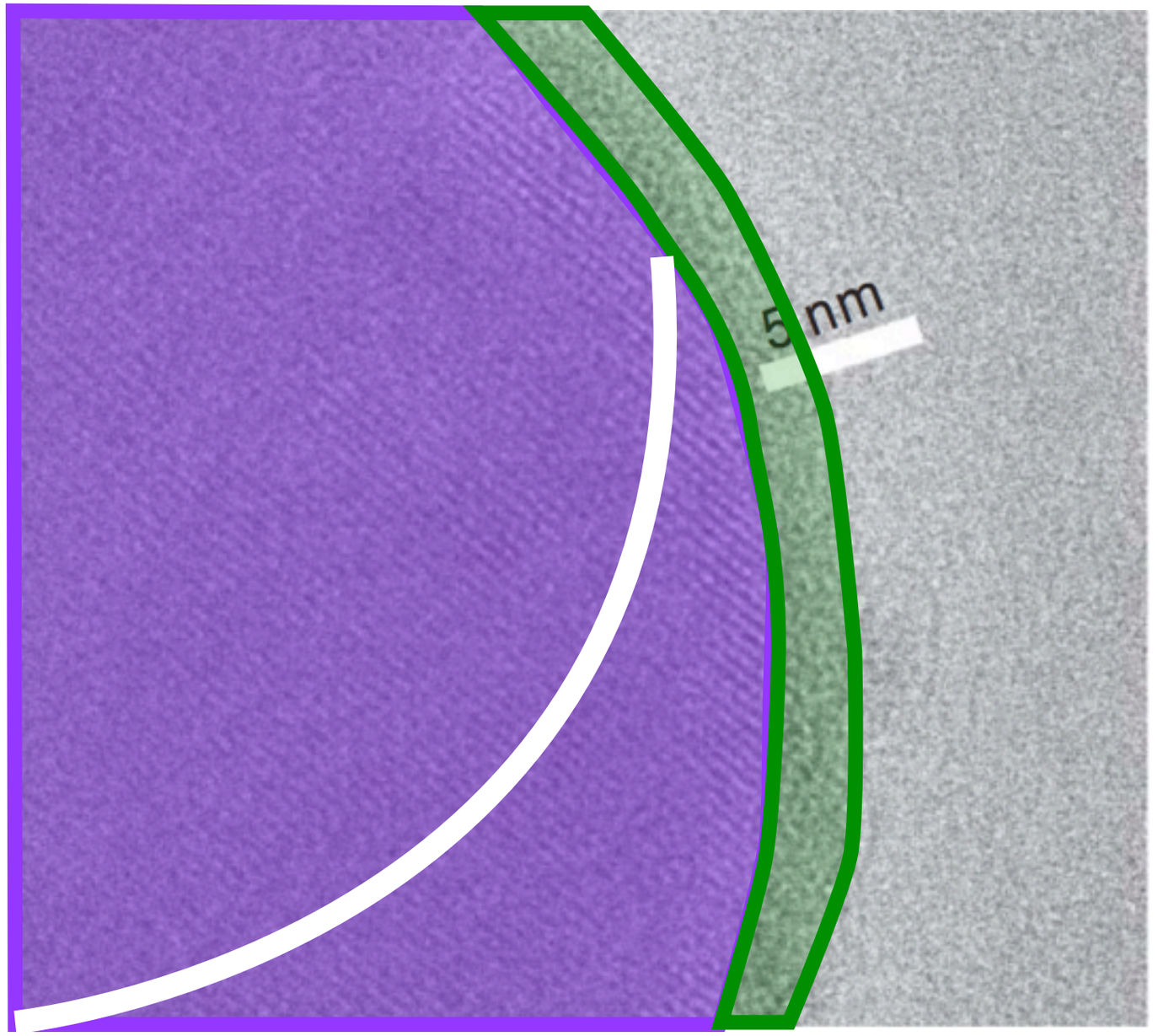
$$i_\circ = F k_r (c_T - c_s)^{\alpha_a} c_s^{\alpha_c}$$

The simplest interfacial kinetics

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

# Engineering the Kinetics at the Interface




$k_r$

B. Kang and G. Ceder "Battery Materials for Ultra Fast Charging and Discharging." Nature (458) p.190-193,2009.

# 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.

Slide courtesy of Zhiwen Liang

# Lithium Dendrite Inhibition

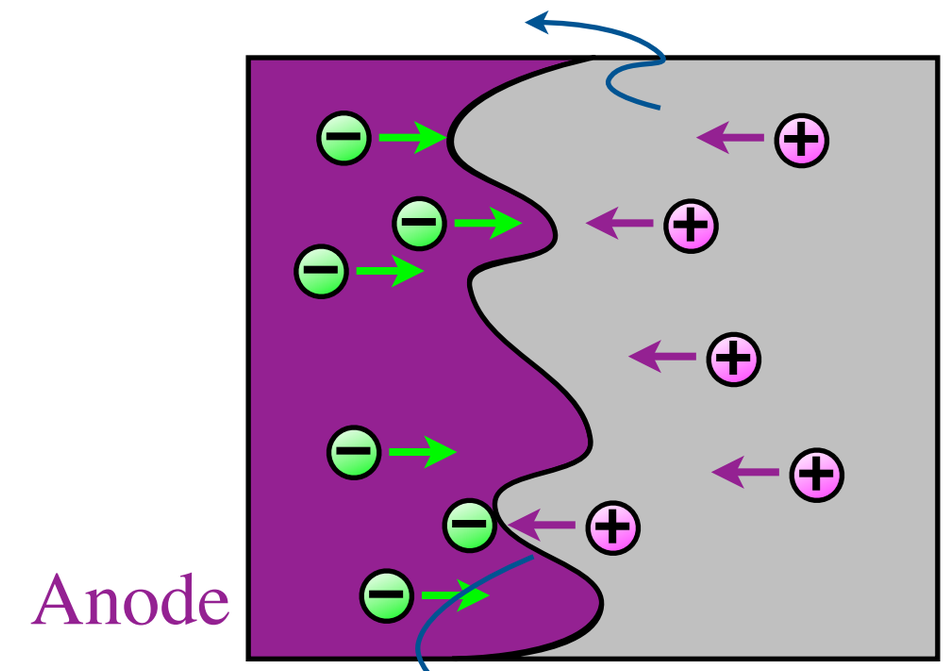
- Low Current Density Charging
- Intercalation Compound Anode
- Polymeric Solid Electrolyte
- Lithium Alloy Anode
- Additives in Electrolyte
- Pressure Application to the Cell
- Electrolyte Stirring

Slide courtesy of Zhiwen Liang

# Theoretical Description of Dendrite Formation during Charge

Bulk Diffusion of Active Species under Composition and Electric Potential Gradients

**Chazalviel's Model**




**Monroe-Newman's Model**

(Deposition at the Interface) Interaction of Deposition Rate, Ion Concentration, Current Density, Overpotential and Surface Tension

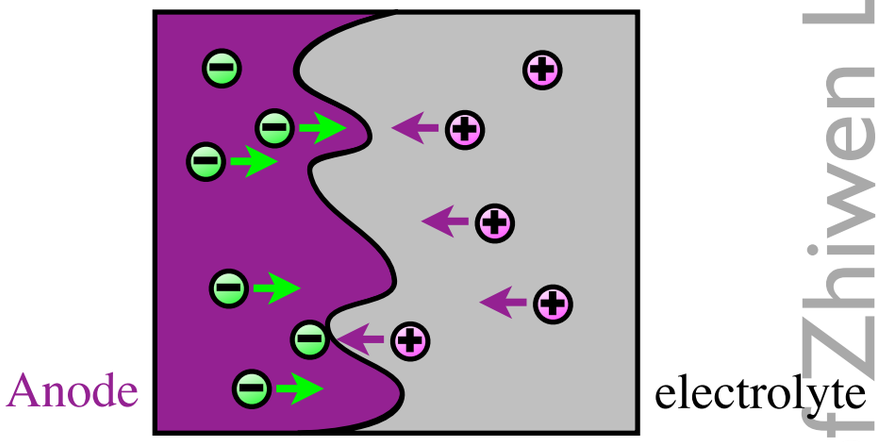
Slide courtesy of Zhiwen Liang

J. N. Chazalviel. Electrochemical Aspects of the Generation of Ramified Metallic Electrodeposits. Physical Review A, 42(12):7355–7367, 1990.

C. Monroe and J. Newman. Dendrite Growth in Lithium/Polymer Systems-A Propagation Model for Liquid Electrolytes under Galvanostatic Conditions. Journal of The Electrochemical Society, 150(10):A1377–A1384, 2003.

# Important Results of The Models

- Chazalviel's Model
  - Critical Current Density: $i^*$
  - Dendrite Incubation Time: $\tau_s$
  - Deposition Rate: constant $v \sim \mu_a E$




- Monroe-Newman's Model
  - Critical Current Density: $0.75i^*$
  - Dendrite Incubation Time: $\tau_s = 0$
  - Deposition Rate: accelerate

J. N. Chazalviel. Electrochemical Aspects of the Generation of Ramified Metallic Electrodeposits. Physical Review A, 42(12):7355–7367, 1990.

C. Monroe and J. Newman. Dendrite Growth in Lithium/Polymer Systems-A Propagation Model for Liquid Electrolytes under Galvanostatic Conditions. Journal of The Electrochemical Society, 150(10):A1377–A1384, 2003.



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# Irreversible Reactions

Butler-Volmer Kinetics:

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

$$+ \sum_{i=1}^{N} J_i$$

other reactions

For a single side reaction:

$$\frac{\partial \delta}{\partial t} = \frac{\Omega}{zF} j_{ir}$$