

# Lithium Plating in Lithium-Ion Cells

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# Introduction

- **What is lithium plating?**
  - *Lithium metal that has been deposited on the surface of the anode, but has not moved into the carbon intercalation sites*
  - *Carbon sites could be filled (or nearly filled)*
  - *Lithium metal deposited more rapidly than intercalation can occur*
- **Why is lithium plating bad?**
  - *Lithium capacity is lost from the cell; can give rapid capacity loss*
  - *Lithium metal can become isolated from the anode surface, leaving conductive metal to accumulate in the separator*
  - *Eventually continued lithium plating can cause a metallic path to form through the separator to give a short circuit*
  - *Changes in cell compression (material volume expansion or end plate tightening) could allow the metal deposits in the separator to short circuit the cell.*
- **How can we reliably detect and avoid metallic lithium plating?**



# Types of Metallic Lithium Plating

- **Homogeneous lithium plating**
  - *Occurs over large areas of anode within cell*
  - *Can result from the carbon becoming completely “filled” with Li*
  - *Can result from high charge current (excessive deposition rate)*
  - *Can result from low temperature (slow intercalation rate)*
- **Heterogeneous or “localized” lithium plating**
  - *Can occur around any non-uniformity in the cell that redirects the current away from a direct path from the cathode to the anode during charge*
  - *Most often seen at edges, corners, around particles, or separator wrinkles*
  - *Typically linked to cell design or stack defects*
  - *Exacerbated by the conditions causing homogeneous plating*
- **Real cell lithium plating probably includes aspects of both homogeneous and heterogeneous plating**



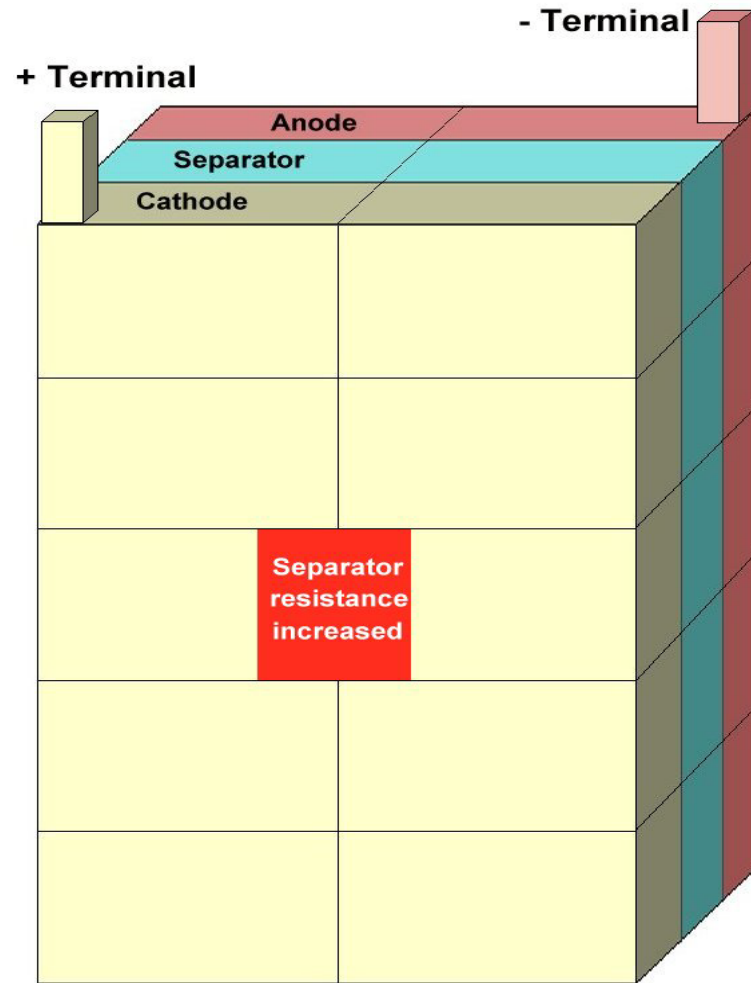
# What Can Cell Models Tell Us About Li Plating?

- **We use a 3-D finite element model of a prismatic cell**
  - *Includes all the processes known to occur in Li-ion cells*
  - **Described in:** A. H. Zimmerman and M. V. Quinzio, *Method for Predicting the Reliability of Lithium-Ion Batteries*, Presented at the 2008 Power Sources Conference, Philadelphia, PA, June 2008, paper 25-1.
- **Modeling tells us when Li plating can occur during charge, and where it is most likely to occur in the cell stack**
  - *Li plating occurs when local Li deposition rate exceeds intercalation rate*
  - *In the anode, plating depends on local current density, intercalation rate constant, temperature, SEI, intercalation path factor, and Li content in the carbon*
  - *In the cell stack, plating can be strongly influenced by local variations in current density*
- **Model allows us to easily analyze different cell designs and simulate various defects in cells**



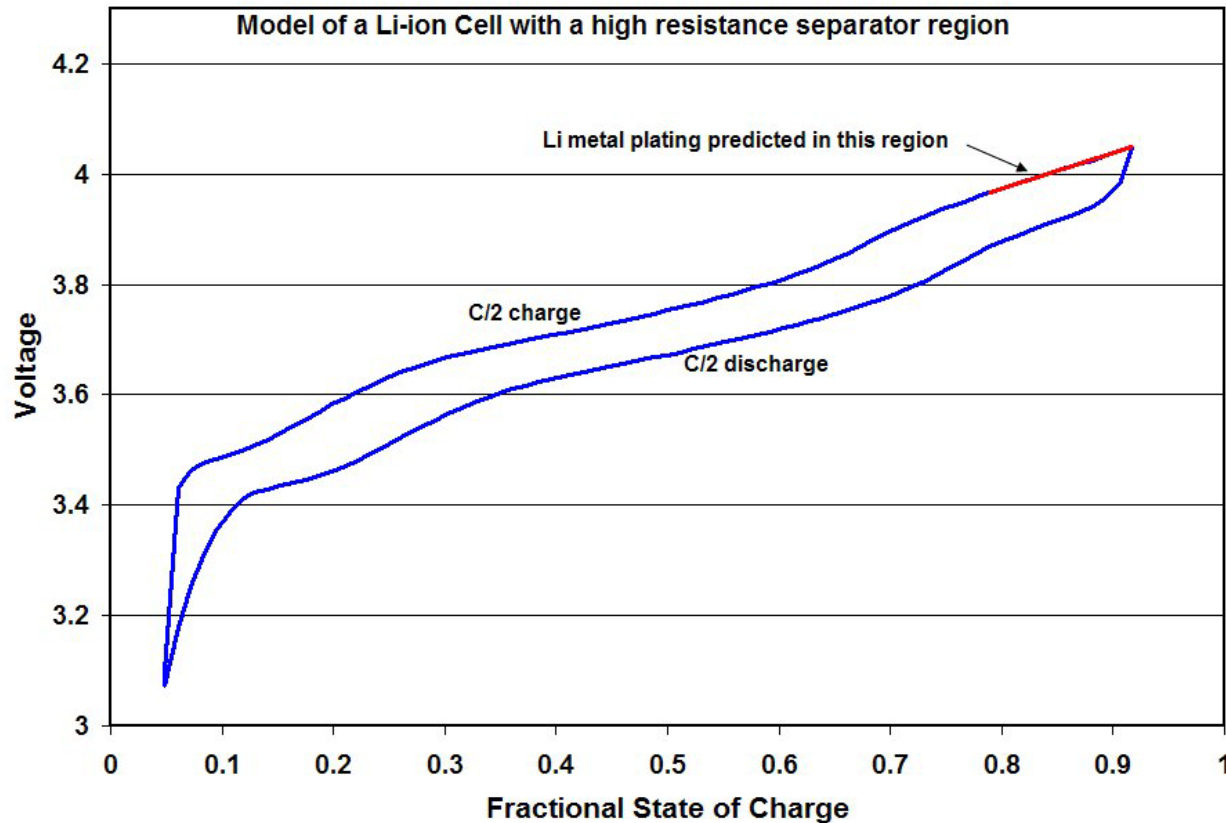
# Example of a Model Analysis

- High separator resistance region inserted in middle of stack
  - *Could simulate poor stack compression, or low separator porosity*



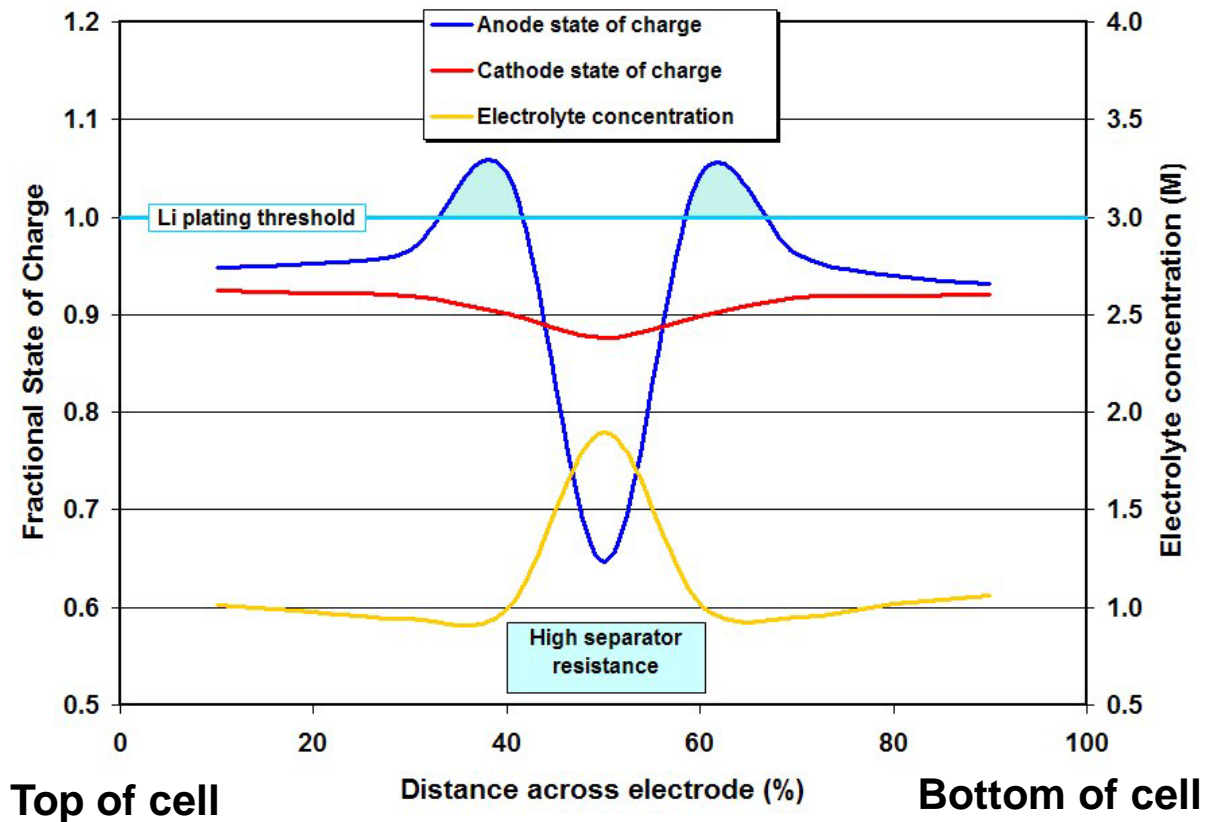
# Modeled Charge and Discharge Voltage

- Overall voltage not changed much by the high resistance region
- Metallic Li plating was predicted during the last 15% of the recharge



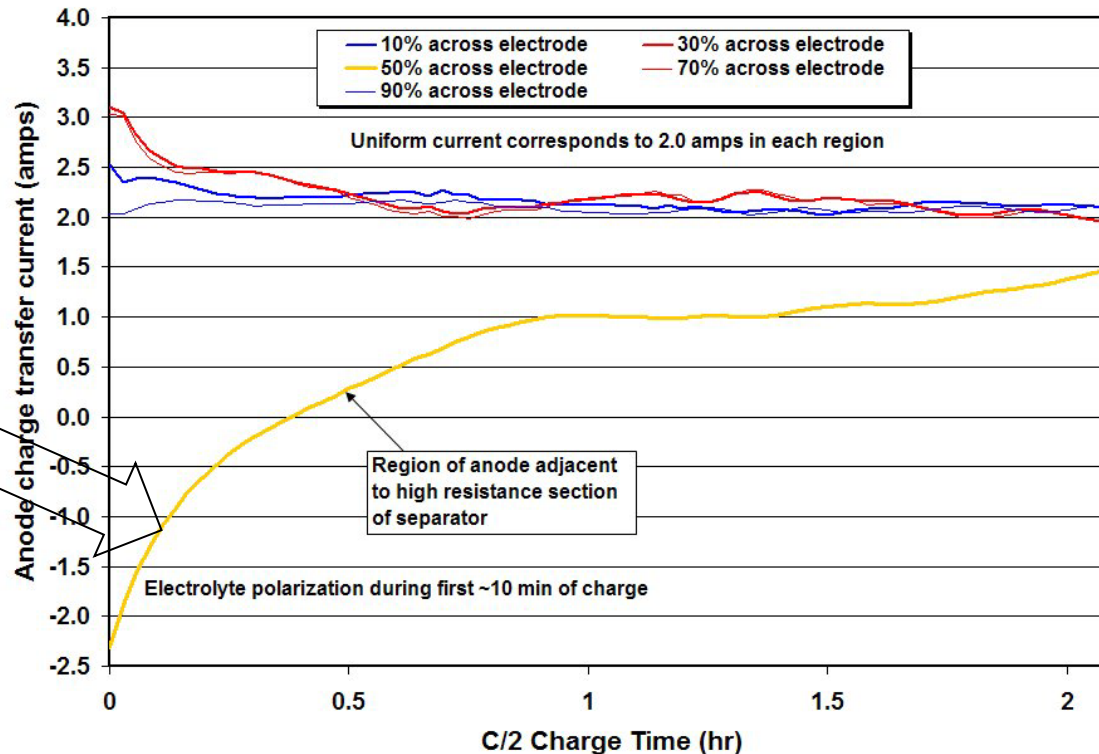
# Modeled End-of-Charge Cell State

- Plating predicted at edges of high resistance region
- High anode SOC and electrolyte gradients, little cathode SOC gradient



# Model Current Uniformity during Charge

- Anode in high resistance region continues to discharge during the first 24 minutes of recharge, due to higher SOC
- Eventually the rest of the anode gets charged higher and the high resistance region begins to increase its SOC



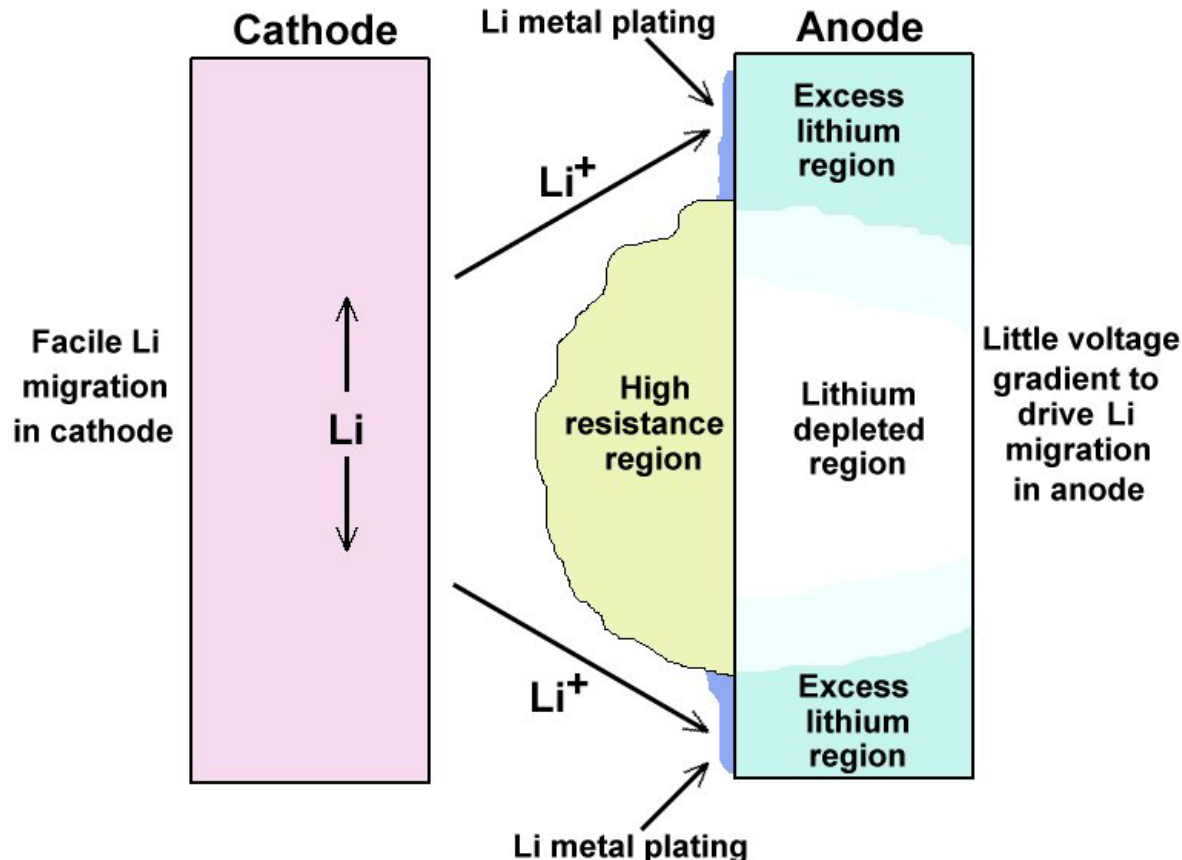
Unusual electrolyte polarization offers a target for detection





# Plating Mechanism Suggested by Model

- Li from cathode in high resistance region is deposited around edges of region
- Lithium capacity of carbon is exceeded in these regions, resulting in plating



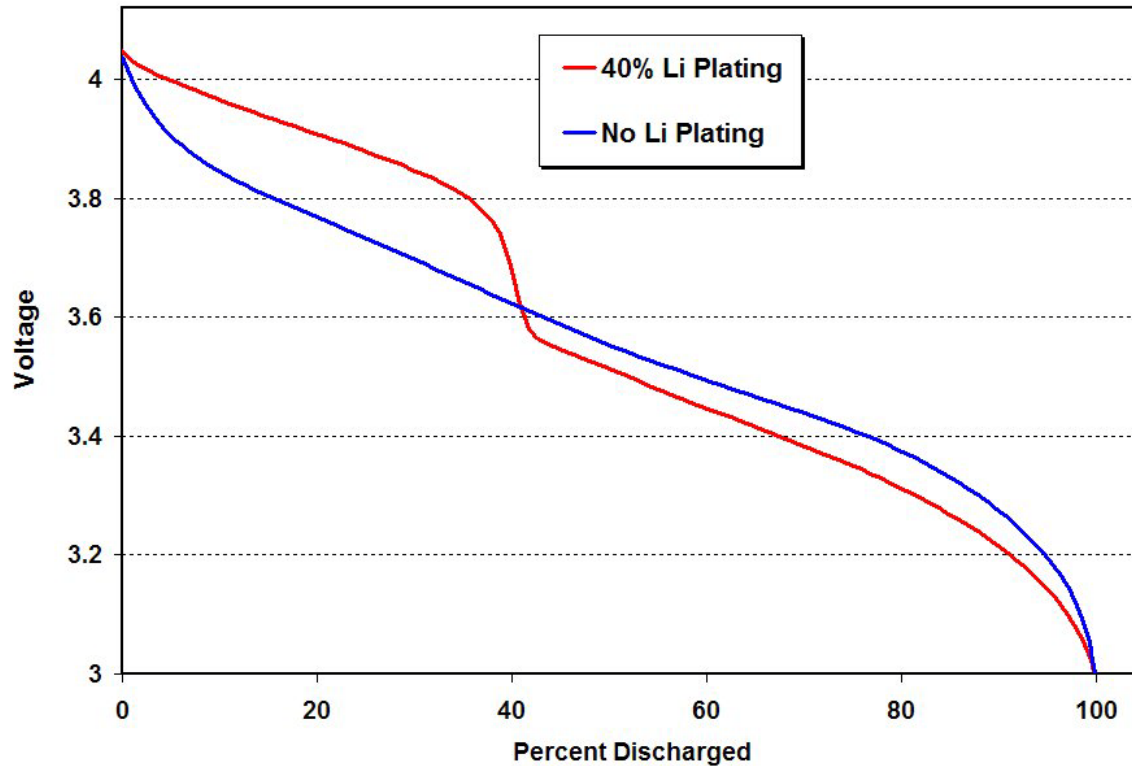
# How Can Li Plating be Detected?

- **Discharge voltage**
  - *Li metal discharges at a higher cell voltage*
- **Charge voltage over potential**
  - *An increase in anode over potential expected when Li plating starts*
- **Resistance changes during recharge**
  - *An increase or peak in anode resistance expected when Li plating starts*
- **Changes in electrolyte polarization in cell**
  - *An increase in electrolyte polarization voltage expected in response to Li plating*
- **Calorimetry**
  - *Extra heat dissipation expected immediately after Li plated out*



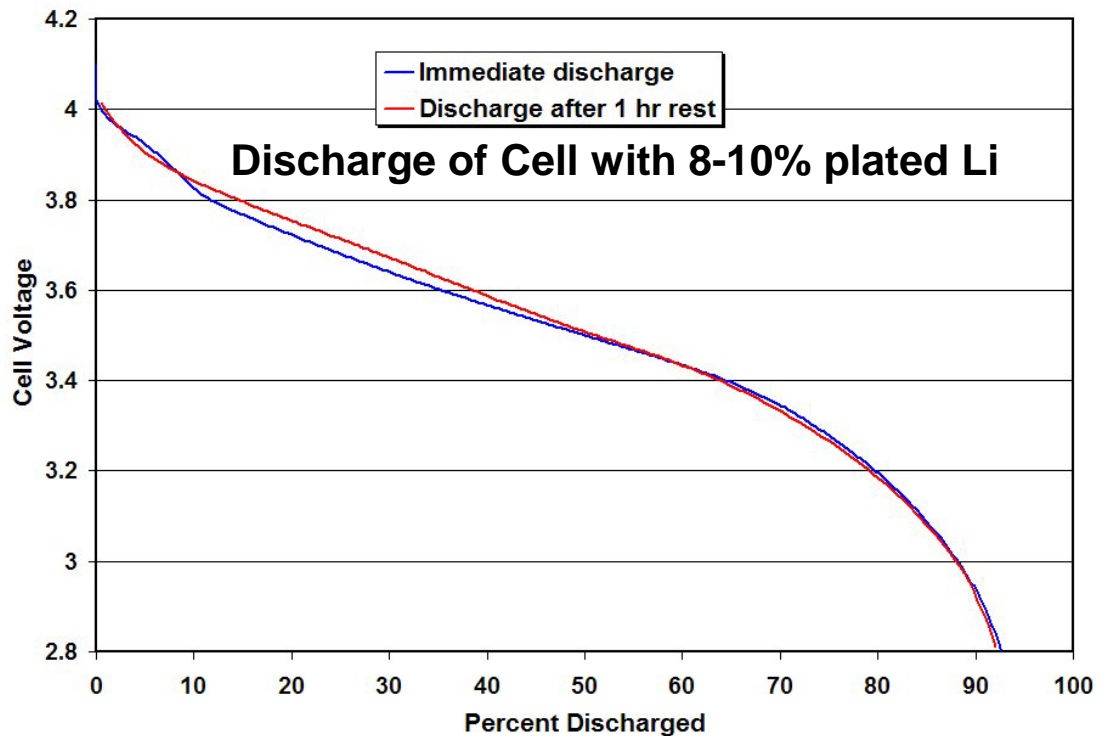
# Discharge Voltage and Li Plating

- Works well when large amounts of active Li are plated
- Difficult to see small amounts, cannot see isolated Li



# Plated Li Goes Away with Time

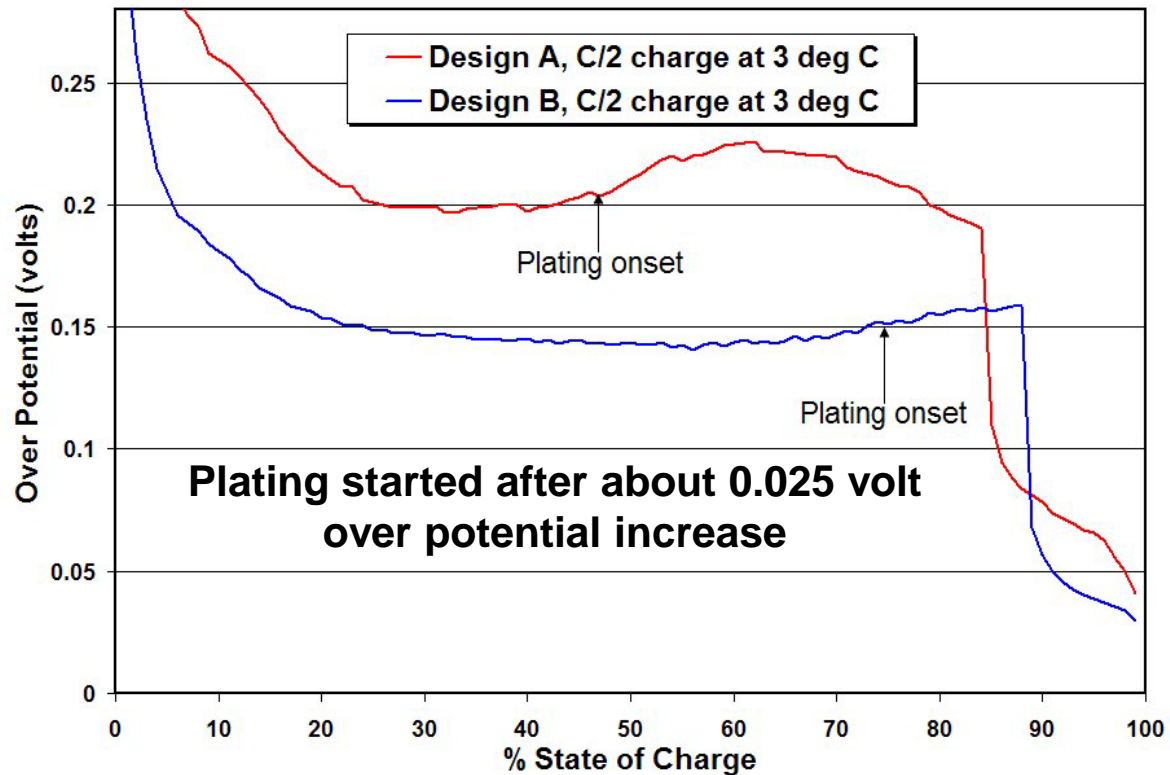
- Some is absorbed into the carbon anode
- Some becomes separated from the anode and waits in the separator



# Over Potential vs. SOC and Temperature

- Look for added anode over potential at low temperature and high charge rate

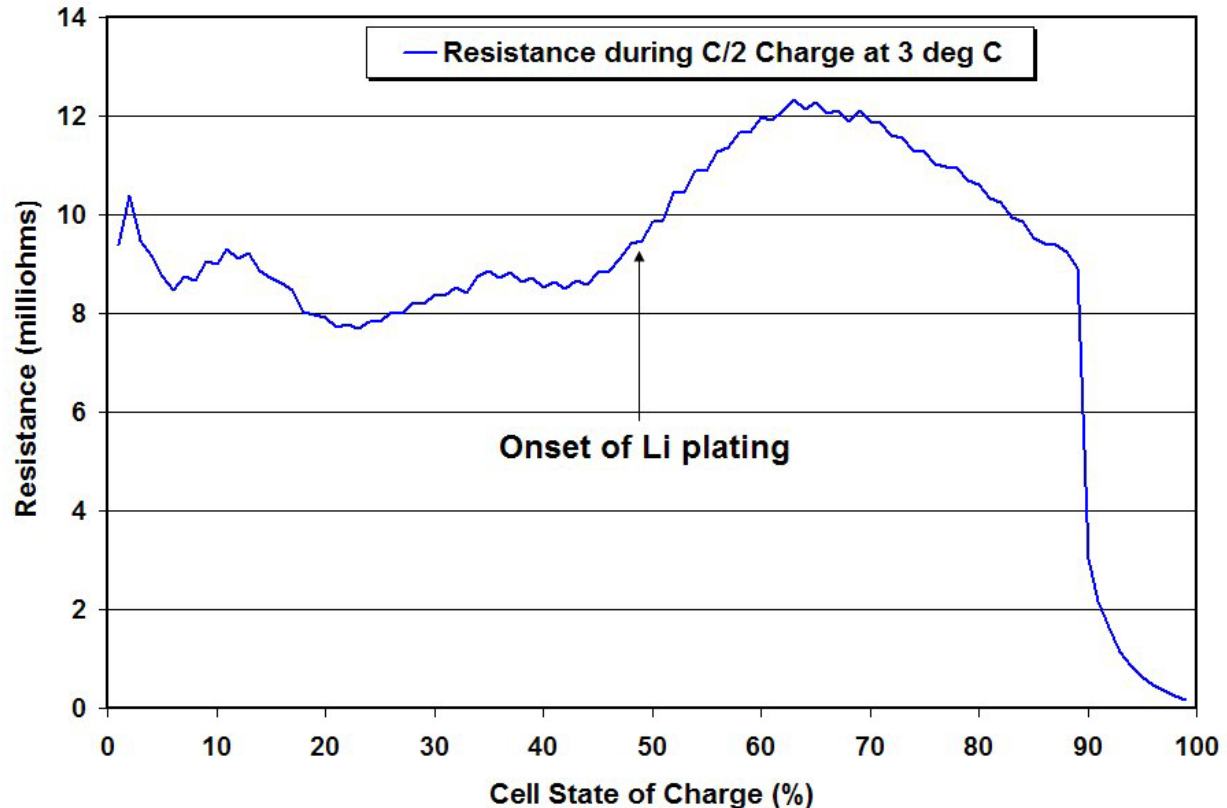
Over potential is  
charge voltage  
minus reversible  
potential



# Resistance vs. SOC and Temperature

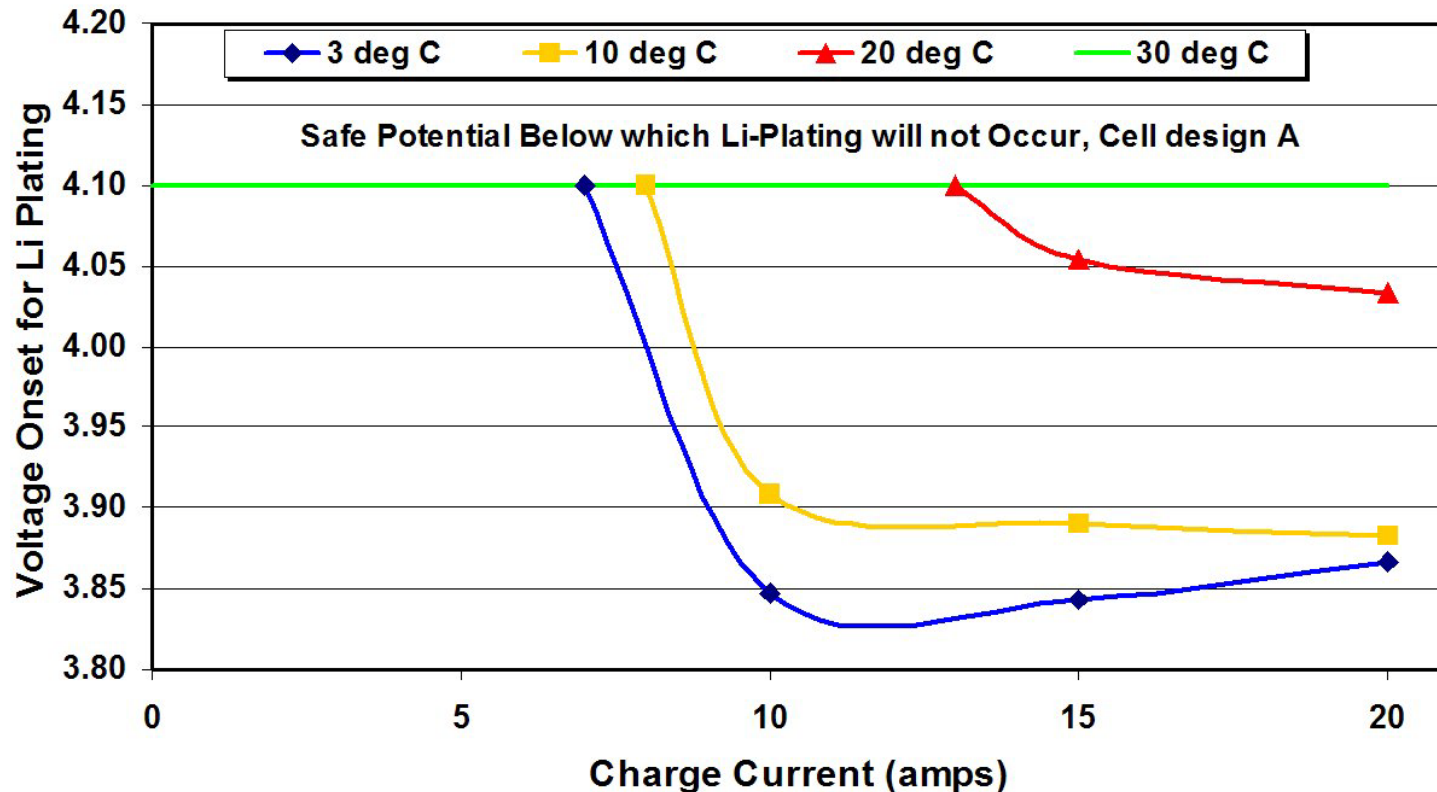
- Look for added anode resistance at low temperature and high charge rate

Resistance is the slope of the I/V curve for the cell during recharge



# Mapping the Safe Charging Region for a Cell

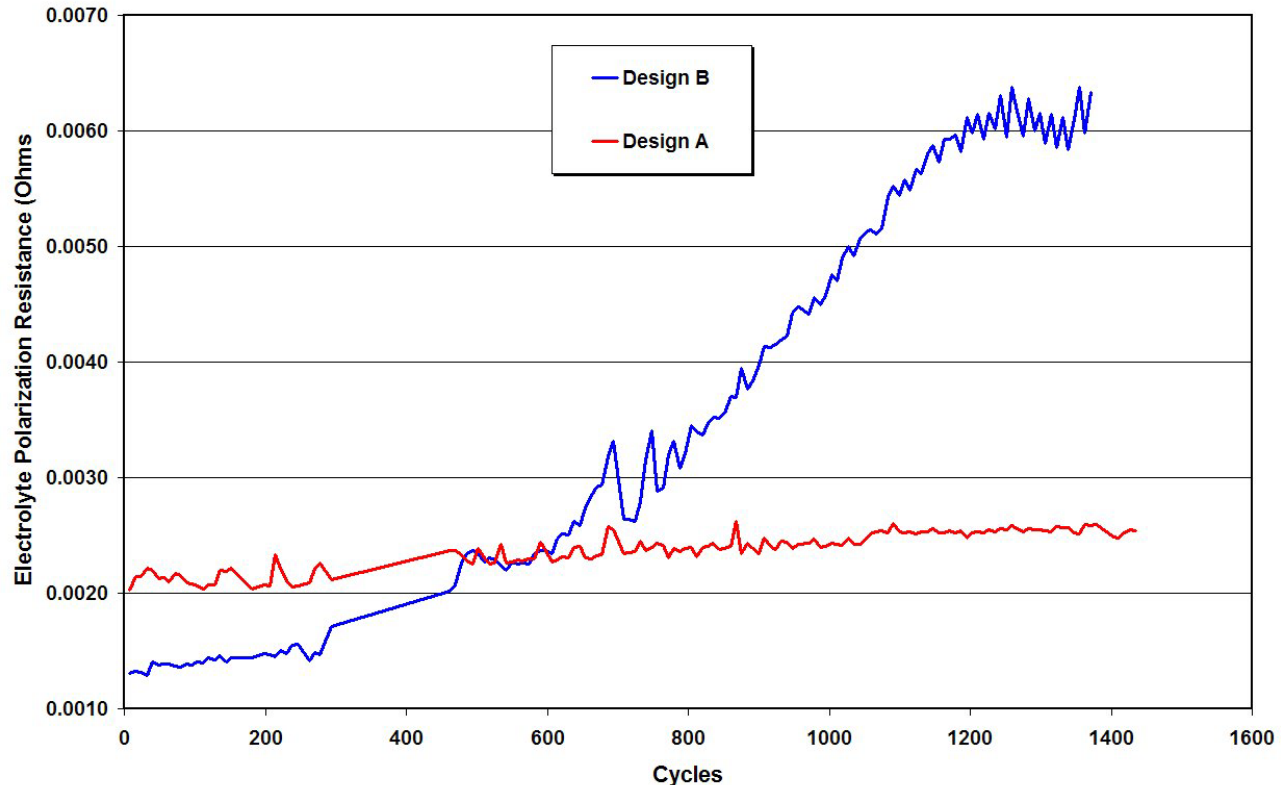
- Each cell design has a critical voltage threshold at each charge current and temperature, such that charging above that threshold will cause Li plating



# Electrolyte Polarization to Detect Localized Plating

- Measure slow (over ~10-15 minutes) relaxation component of cell voltage

Resistance is the slow voltage relaxation divided by a small current change that caused the relaxation



50% DOD life test at 10°C, 8 cycles per day\*

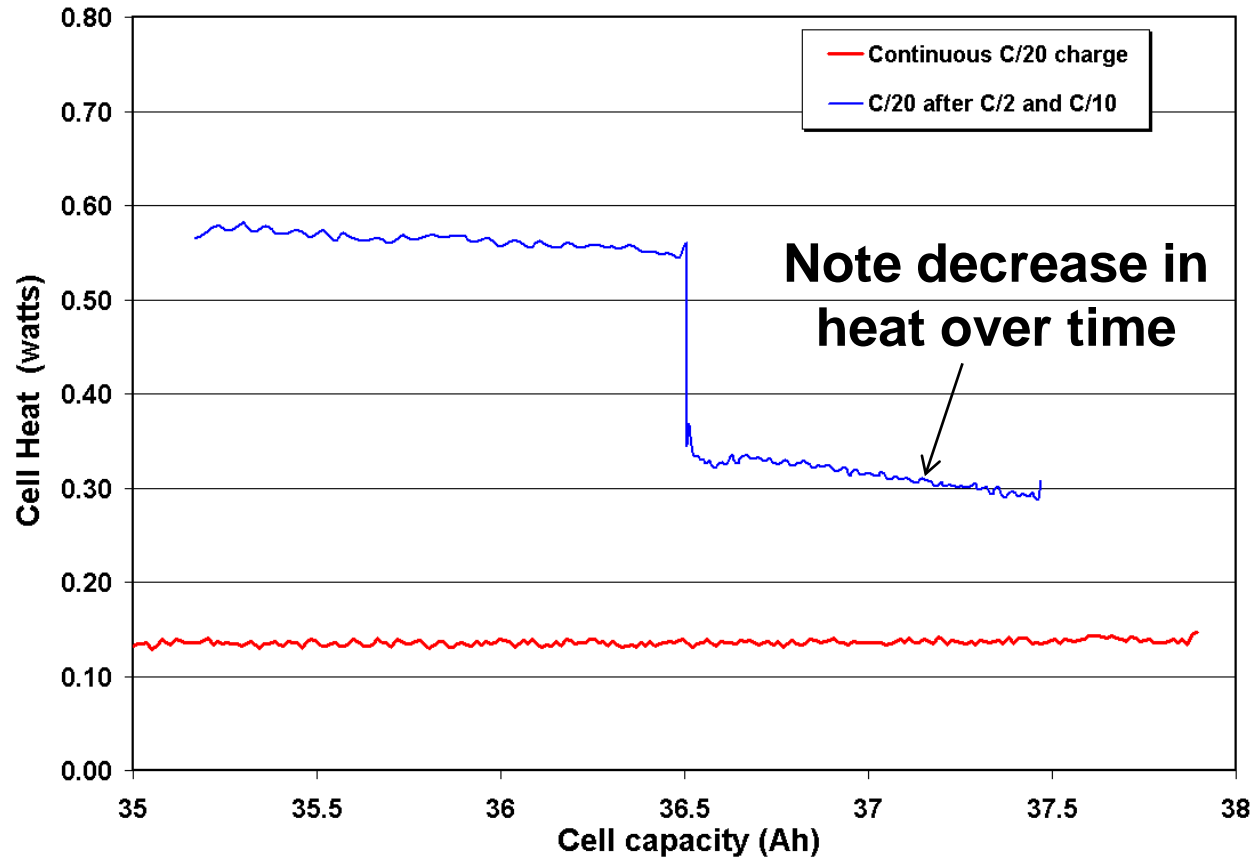
\*Cell B failed after 1400 cycles due to capacity loss, Cell A had little capacity loss





# Calorimetry\*

- Extra heat generation seen after high rate recharge to deposit Li metal



\* A. H. Zimmerman and M. V. Quinzio, *Thermal Behavior of Large Lithium-Ion Cells*, 2004 NASA Battery Workshop, November 2004.



# Conclusions

- **Many reasons for Li plating**
  - *Cell design factors*
  - *Cell operating environment (low temperature)*
  - *Charge rate*
  - *Non-uniformities within stack*
- **No single method can detect Li plating from all mechanisms**
- **Five methods identified as capable of detecting Li plating**
  - *Discharge voltage behavior*
  - *Charge voltage over potential*
  - *Cell resistance changes during recharge*
  - *Unusual changes in cell electrolyte polarization*
  - *Calorimetric detection of anomalous heat that decreases with time*



# Acknowledgement

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