Electrode Specific Degradation Tailored by the Directionality of Thermal Gradients in Li-ion Batteries

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UL Battery Safety Science Symposium
The Navy’s Corporate Laboratory located in Washington, DC
Employs ~2000 PhD’s spanning many topics (space, radar, optical science, chemistry, materials science, biological, and computing)

Thomas Edison,
New York Times, May 1915
"The Government," he proposed in a published interview, "should maintain a great research laboratory.... In this could be developed...all the technique of military and naval progression without any vast expense." -$1.5M allotted by congress and construction began 1920
Plating Conditions Commercial cells

Discharge Capacity (Ah)

Cycle Number

Ambient, 20°C
Low Temperature, 0°C

Equilibrium 20°C
Equilibrium 0°C
Transient

Thermal Transient Facilitates Plating in COTS 18650s

Only Distinction is the Temperature in the First Cycle

Over half the ions deposit as metal


EOL X-ray Radiographs
Safety Implications of Cell’s Thermal and Electrochemical History

- Revealed Importance of Temporal Variation in Temperature
- Transition to coin cells for Fundamental Understanding: spatial and temporal control over temperature

Thermal Gradients in metallurgy: an analog for electrochemistry

Must consider **Temporal and Spatial Thermal Variations**

**Metal Solidification**
Liquid Undercooling Induced Dendrite

**Electrochemical Deposition**
Thermal Gradient Induced Dendrite

- **Nucleation**
  - Mold
  - Molten Metal
  - Undercooling
  - Diffusion slowed
  - Li

- **Growth**
  - Mold
  - Molten Metal
  - Rapid Growth
  - Anode
  - Cathode

Proof of Concept in Optical Cell

Opportunity for in-situ observation lithiation under abusive conditions

Ambient (~22°C)

Thermal Gradient (surface 0°C, opposite electrode 40°C)

Love et al. ECS Electrochem. Lett. 2015, 4, A24-A27

Thermal Gradient Reliably Induces Plating at Graphite Anode

With this condition plating initiated on the 7th-9th cycle.


*Replicated 6X
Actual Interelectrode Gradient and Context for Pouch Cells
Areas with low temperature rise are altered the most by thermal gradient. Those areas of low temperature rise also have minimal to no plating tendency allowing us to isolate these behaviors to the application of the gradient.
Directionality of Thermal Gradient causes Diverging Modes

$\Delta T_{\text{int}} = +2^\circ C$  $\Delta T_{\text{int}} = -2^\circ C$

- Pos. $34^\circ C$
- Neg. $34^\circ C$
- Pos. $36^\circ C$
- Neg. $36^\circ C$

$T_{\text{avg}} = 35^\circ C$

Determining Degradation Modes

Incremental capacity analysis for SOH Grid and EV


Electrode Specific Degradation and Informed Sensitivities

- Tailored Accelerated Aging Technique
- Understand behavior for Thermal Management Sensitivity

Impact and Application of Thermal Gradient Findings

1. Understand its thermal-electrochemical coupling
   - Intercalation electrodes (graphite, NMC)
   - Reproduce realistic battery failure modes
   - Understand and improve battery safety

   Carter et al. Cell Reports Physical Science 2, 100351, March 24, 2021

2. Enable high-energy, next-generation batteries
   - Li metal anode
   - Promote reversible lithium plating and stripping
   - Enable high-rate charging

   Atkinson et al. Materials Today Energy 18, 100538, 2020
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