Modeling Competitive Reactions and Heat Transfer Effects Applicable to Thermal Runaway in Lithium-Ion Batteries

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I: Competitive Energy Release Pathways
• Charged electrode species and organic electrolyte are reactive materials
  • Thermodynamically unstable
• Short circuits and thermal decomposition (TD) compete for common reactants
• Total mixed heat release is not a summation (pure TD is upper limit)

Exothermic Reaction Paths

Energy Release

II: Effective Environment Temperature
• Thermal runaway (TR) occurs when heat sources exceed heat dissipation losses

\[ mc \frac{dT}{dt} = \dot{Q}_{\text{source}} - \dot{Q}_{\text{loss}}, \quad \text{where} \quad \dot{Q}_{\text{loss}} = hA(T - T_{\infty}) + \varepsilon\sigma A(T^4 - T_{\infty}^4) \]
• Energy sources driving thermal decomposition can be external or internal
• For internal source \( P \), linearize losses and assume thermal equilibrium

\[ \frac{dT}{dt} = 0, \quad \dot{Q}_{\text{loss}} = \dot{Q}_{\text{source}} \]

If \( \dot{Q}_{\text{source}} = P \) and \( \dot{Q}_{\text{loss}} \) is linearized as \( \dot{Q}_{\text{loss}} = h_{\text{eff}} A(T - T_{\infty}) \).

Effective Environment Temperature Derived

Effective environment temperature is basis to compare internal/external sources
Examples modeled as 0D for \( h_{\text{eff}} = 18 \text{ mW/m}^2\text{K} \) with \( P = \frac{V^2}{R} \)

III: Cooling Requirements for Short Circuits
• Models can be used to estimate cooling requirements to mitigate TR
  • Homogeneous (0D) heating of 1.5 Ah 18650 shown at lower far left
  • Inhomogeneous deviations from 0D case shown at lower center + right
• Define power of short in effective environment temperature to correlate minimum internal short resistance that can be mitigated with degree of cooling

\[ T_{\text{eff}} = T_{\infty} + P/h_{\text{eff}} A \text{ and } P = \frac{V^2}{R} \]

\[ R_{\text{min}} = \frac{V^2}{h_{\text{eff}} A(T_{\text{eff}} - T_{\infty})} \]

IV: Thermal and Chemical Inhomogeneities
• 2-D axisymmetric simulations of 18650, vary % of total resistance (heat) in nail
  • Nail is hot because heat release is concentrated in small volume
  • Thermal degradation reactions dominate near hot nail
  • Short circuit reactions are more common near cooler periphery

Heat Transfer Coefficient (W/m²K)

Heat of Reaction (kJ/mol Li)

Surface Temperature (°C)

Effective Environment Temperature Derived

Effective Environment Temperature is max from short w/o TR

With Temperature-Limited Short, Few Reactants Remain for TR → small TR

Nail penetration data (1.5 Ah 18650), courtesy of Loraine Torres-Castro at Sandia National Laboratories
For related work, see also: