Understanding Electrode Level Implications in the Lithium-ion Battery Thermal Behavior

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Lithium-ion batteries (LIBs) are poised to play a key role in vehicle electrification. Although significant progress has been made, safety remains a challenge in LIBs. In this regard, thermal implications due to the underlying electrochemical and transport interactions in the electrodes can be critical determinants in the LIB safety, performance and life. A typical cell operation encompasses three heat generation sources in the electrodes, namely entropic heat, reaction heat and Joule heat.

Entropic heat (also known as reversible heat) is the part of reaction enthalpy that materializes as heat (while the free energy part manifests as electrochemically available energy): $-nFE_{cell} = \Delta G^{rxn} = \Delta H^{rxn} - T\Delta S^{rxn}$, $Q_{entropic} = jT\dfrac{\partial E}{\partial T} = aiT\dfrac{\partial E}{\partial T}$; here $j = ai$ is volumetric current source terms, a is electrochemically active area and i is current density at the surface of active material particles. Reaction heat is due to the overpotential required for the electrochemical reaction at the active particle/electrolyte interface, $Q_{reaction} = j\eta$, where $\eta = \phi_s - \phi_e - E$ is overpotential at the surface of active material particles. On the other hand, the Joule heating is caused due to the transport resistances in electrolyte and solid phases as well as interfacial resistance:

$$Q_{Joule} = \left(\sigma^{eff}\nabla\phi_s \cdot \nabla\phi_s\right) + \left(\kappa\frac{\varepsilon}{\tau}\nabla\phi_e \cdot \nabla\phi_e\right) + \left(\kappa_D\frac{\varepsilon}{\tau}\nabla\phi_e \cdot \nabla\ln C_e\right)$$

Here σ^{eff} is effective electronic conductivity of the electrode structure, ε is electrode porosity and τ is tortuosity of the void phase. As is apparent, all the three terms depend on the microstructural properties of the electrodes, namely $a, \sigma^{eff}, \varepsilon$ and τ. The reaction heat and Joule heat are irreversible in nature.

Moreover, electrochemical operation demonstrates strong temperature dependence. For example, at low temperature operation, the transport resistance increases and may lead to higher Joule heating. Fundamental understanding of such thermo-electrochemical interactions in the Li-ion battery electrodes is imperative for assessing the thermal implications in the LIB safety. For example, even for the same electrode porosity, the electrochemical properties may strongly depend on the arrangement of the constituent phases, such as active material, binder and conductive additive in the porous electrode.

In this work, the electrode microstructure level interactions will be evaluated in terms of temperature excursion and thermal safety of Li-ion cells. Especially, the thermal effects will be evaluated for two different scenarios: (1) accelerated rate calorimetry (ARC), which is widely used to quantify reaction heats; and (2) external short circuit, which is representative of the tolerance to electrical abuse. Finally, the impact of electrode microstructural attributes, such as, active/inactive materials weight ratio, anode-to-cathode thermal imbalance and cross-talk will be elucidated and possible thermal management strategies will be discussed.