Insight Into Lithium-Ion Battery Degradation By a Calorimetric Approach

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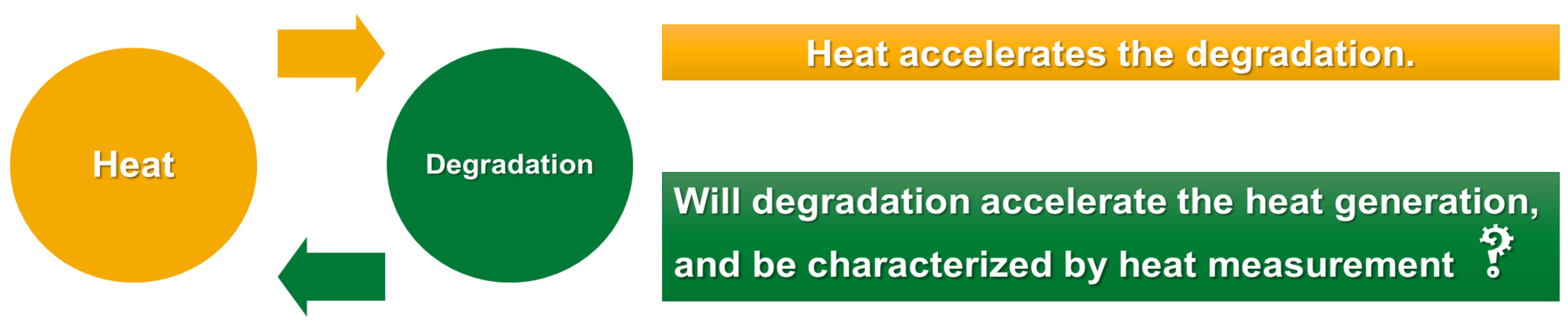
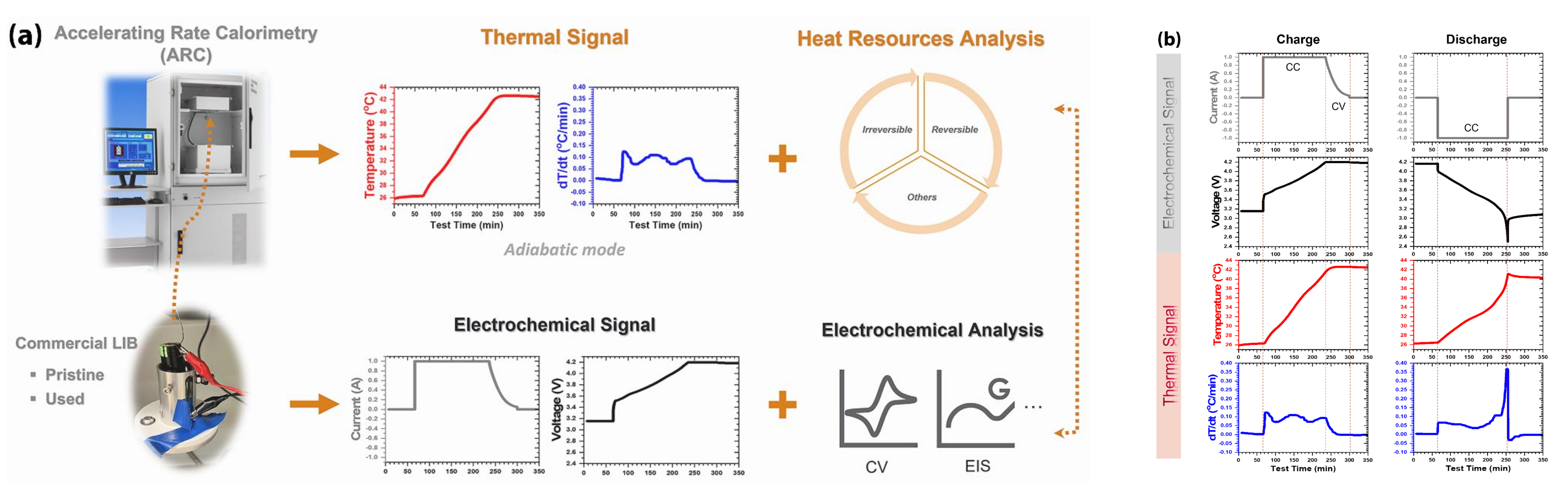
Introduction:

Battery degradation depends not only on component chemistry, but also on complex physical-chemical processes in diverse operating conditions (including dynamic cycles, temperature/thermal effects, the time between operations, and other environmental factors). Among factors, heat (or temperature) plays a crucial role in LIB degradation through anode (SEI), electrolyte and cathode. It is evident that there is a direct relationship between heat and degradation, wherein heat accelerates the process of degradation. Furthermore, it is worth considering the reverse scenario: can degradation also accelerate the generation of heat, and can this be identified/characterized through heat measurements? This represents a crucial focus of our investigation.



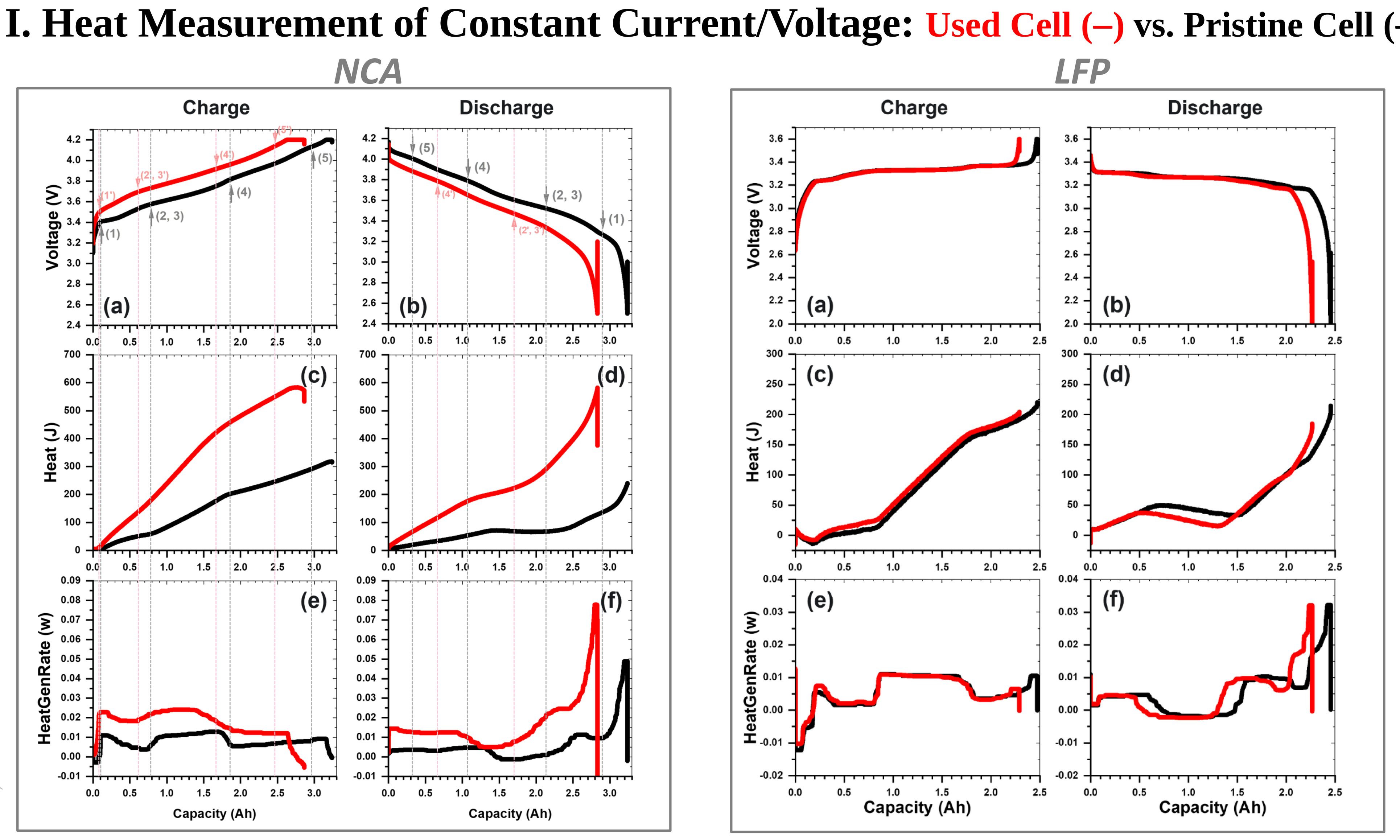
Objectives and Approaches:

- The relationship between thermal characteristics and degradation/reliability was investigated.
- An in-situ heat measurement methodology for LIBs under grid services was developed.
- The thermal behavior of two commercial cells with distinct cathode chemistries (Ni-rich layered oxide and olivine) before and after 2+ years' peak shaving (PS) operation was determined by using adiabatic mode-based calorimetry. The flowchart of developed methodology and an example of in-situ heat measurement are shown in (a) and (b).



Results and Discussion:

I. Heat Measurement of Constant Current/Voltage: Used Cell (–) vs. Pristine Cell (–)



More Degradation → More Heat Generated (NCA vs. LFP)

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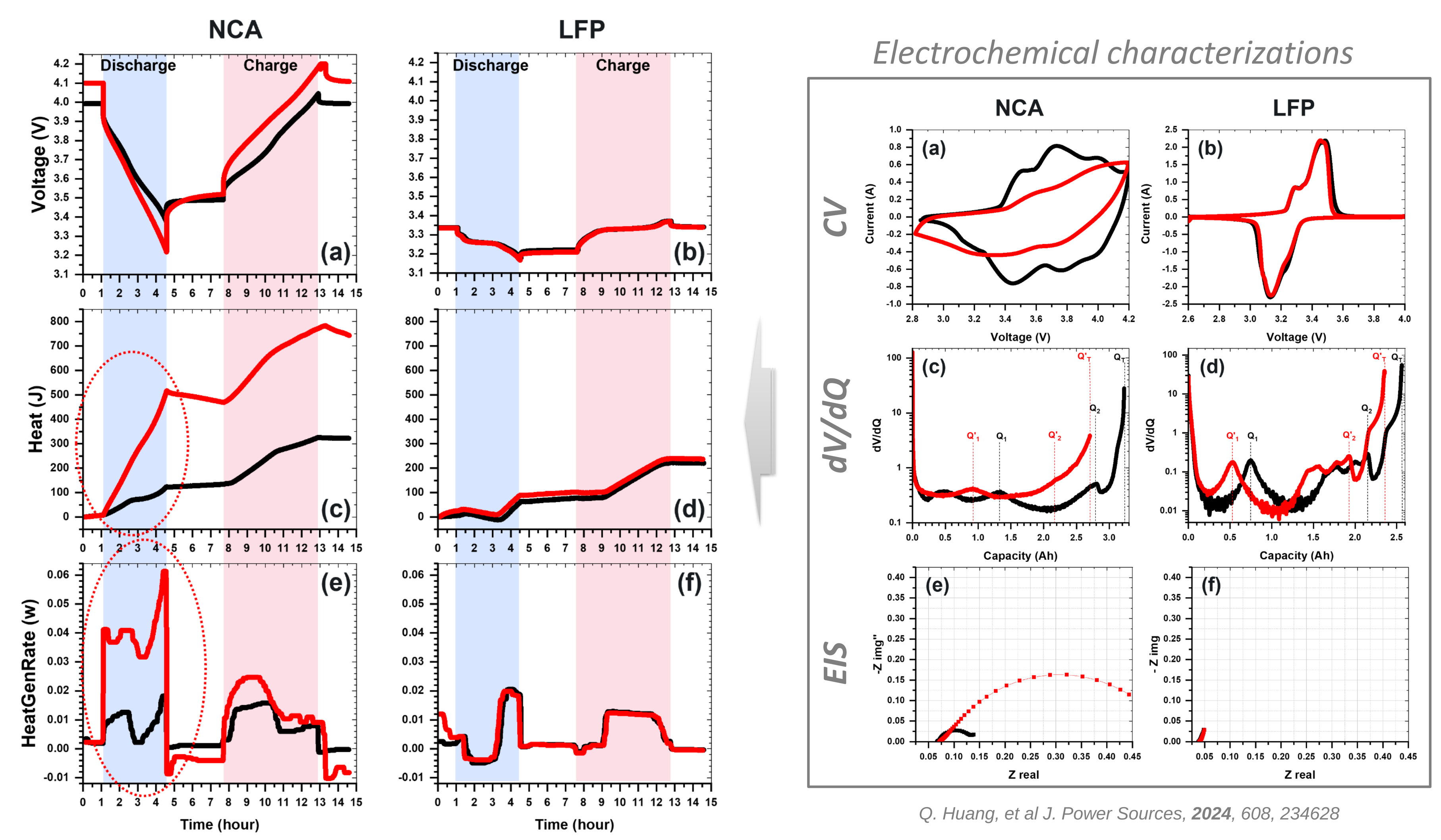
II. Heat Measurement of Peak Shaving Service: Used Cell (–) vs. Pristine Cell (–)



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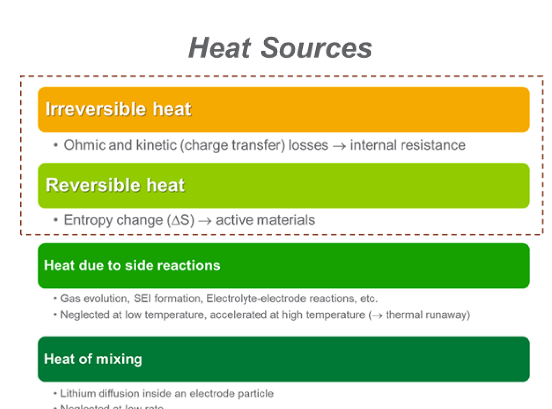
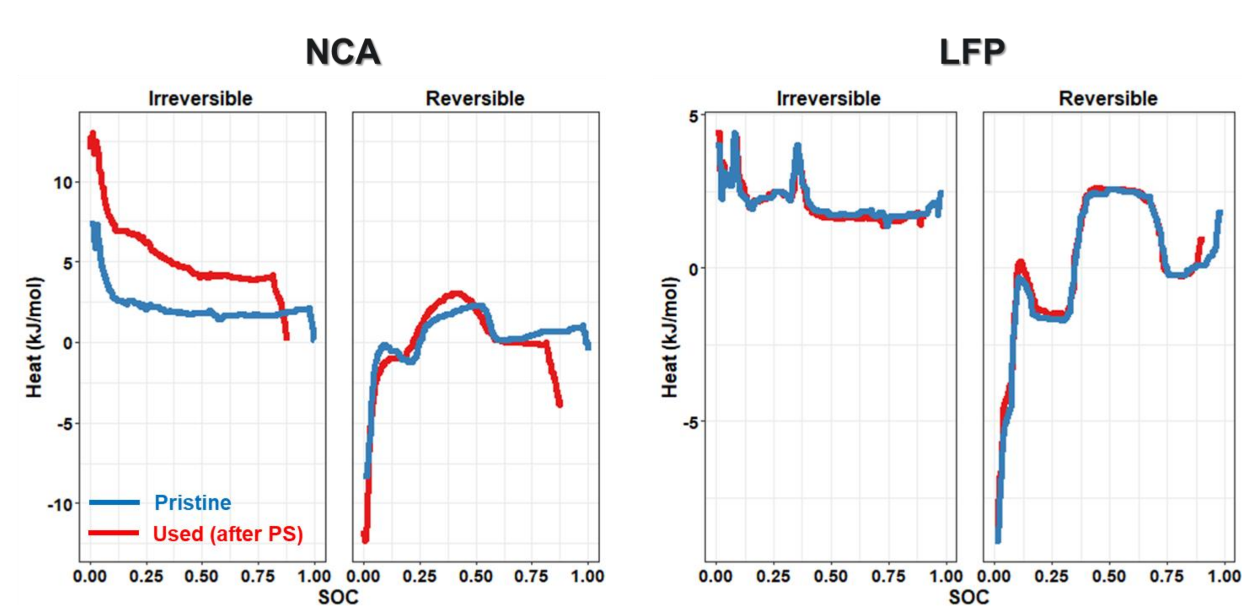
After 2+ years' PS, the NCA cell showed 16% capacity loss, with much more heat release (especially during discharge), associated with more degradation of NCA (cathode, anode and interface, as indicated in electrochemical characterizations – CV, dV/dQ, EIS). The LFP cell showed 6% capacity loss, with almost identical thermal behavior (aligned with electrochemical performances).

III. Heat Sources Separation



Cell	Irreversible ($I^2R t$)	Reversible ($T\Delta S$)
NCA	Increase	Shifting
LFP	No change	No change



Thermal behavior can interpret the degradation level /mechanism !

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NCA cell
- Irreversible: internal resistance increase (interface growth).
- Reversible: ΔS shift → active material degraded potentially.

LFP cell
- Irreversible (internal resistance) or reversible (active materials) heat did not change.

Summary and Future Work:

- A methodology for in-situ heat measurement of commercial LIBs was developed under grid services, disclosing the relationship between thermal characteristics and degradation/reliability.
- Through long-term grid service (2+ years of peak shaving), the two cathode chemistries (NCA and LFP) based commercial cells revealed quite distinct thermal behavior that corresponds to their respective degradation levels.
- By separation of the heat sources, the degradation mechanism in an NCA cell is associated with an increase in internal resistance (irreversible heat source) and degradation of active materials (entropy change shift, reversible heat source).
- Future work will focus on i) comprehensive heat database with diverse chemistry and size of cell/pack; ii) entropy change measurement to accurately identify reversible heat of full and half cells; and iii) thermal study on Na-ion battery (vs. LIB): heat and entropy change measurement.
- The heat data will aid in the development and calibration of our LIB state-of-health modeling in grid applications.

U.S. DEPARTMENT OF ENERGY

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