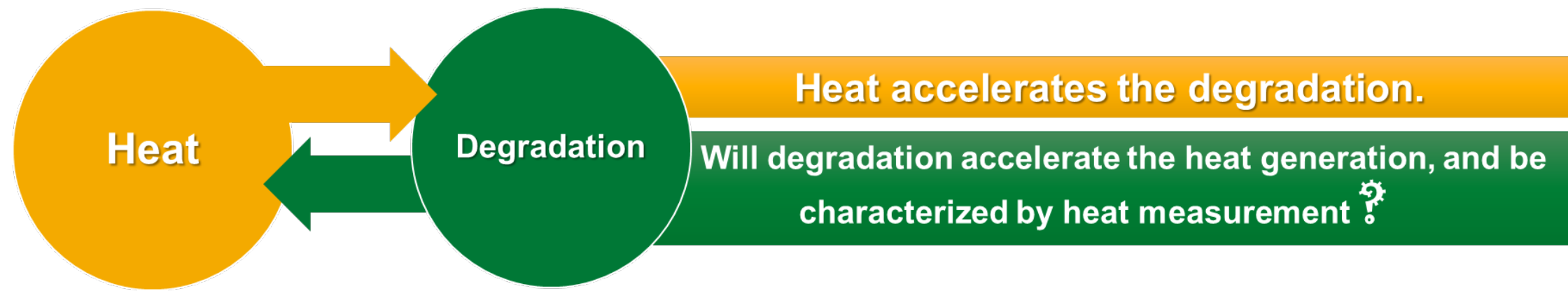


A Thermal Perspective on Battery Degradation Mechanisms

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Introduction: Battery degradation depends not only on component chemistry, but also on complex physicochemical processes under diverse operating conditions. Among these factors, heat (or temperature) plays a critical role in battery degradation through interface, 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 accelerate the generation of heat, and the degradation mechanism can be identified through heat measurements? This represents a crucial focus of our investigation.

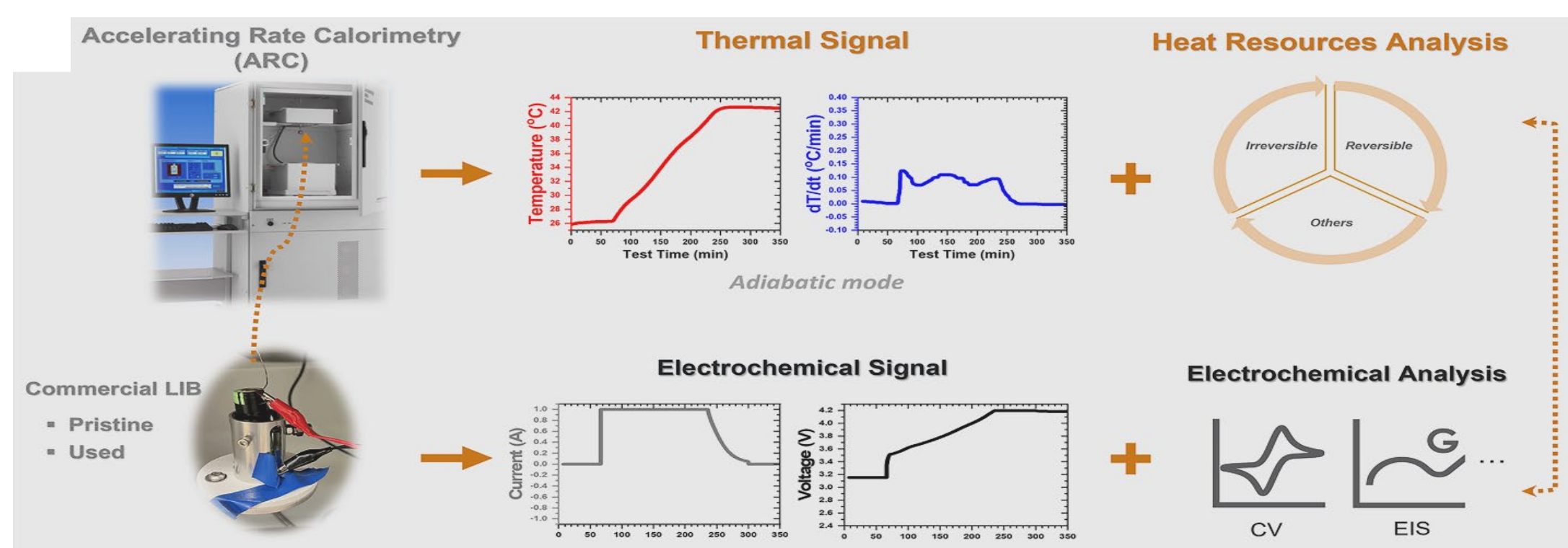


Objectives and Approaches:

- Investigate the relationship between heat generation (thermal characteristics) and degradation/reliability in rechargeable batteries.
- Quantify heat through diverse methodologies to capture heat sources.
- Develop and validate thermal diagnostics in lithium-ion batteries (LIBs) and extend them to sodium-ion batteries (SIBs) for future grid-scale applications.

Heat measurement methodologies:

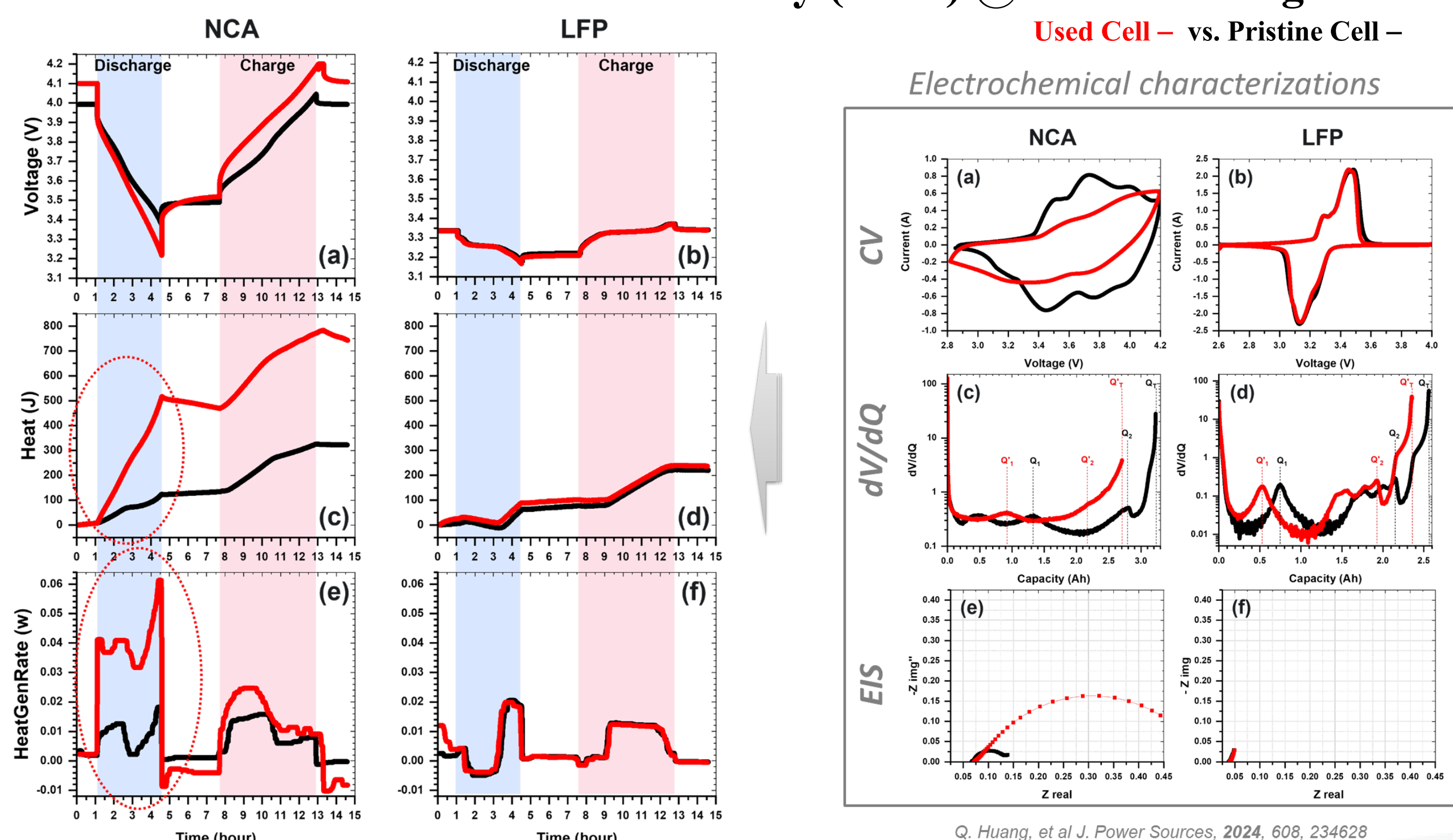
- Direct Calorimetry:** *in situ* heat measurement using Accelerating Rate Calorimetry (ARC) in adiabatic mode under grid service conditions.
- Electrochemical Entropy:** quantify reversible heat via entropy change (ΔS) from temperature-dependent open-circuit voltage (OCV-T) profiles.
- Thermal behavior and degradation analysis:** compare cell thermal behavior before and after extended cycling/service life to assess degradation effects.
- Validation and translation:** apply both thermal methods to state-of-the-art LIBs with varying cathode chemistries (Ni-rich layered oxide and olivine), which guide thermal diagnostics for emerging SIB technologies.



The flowchart of developed in-situ heat measurement via direct calorimetry (ARC)

Results and Discussion:

Heat Measurement I. Direct Calorimetry (ARC) @ Peak Shaving Service

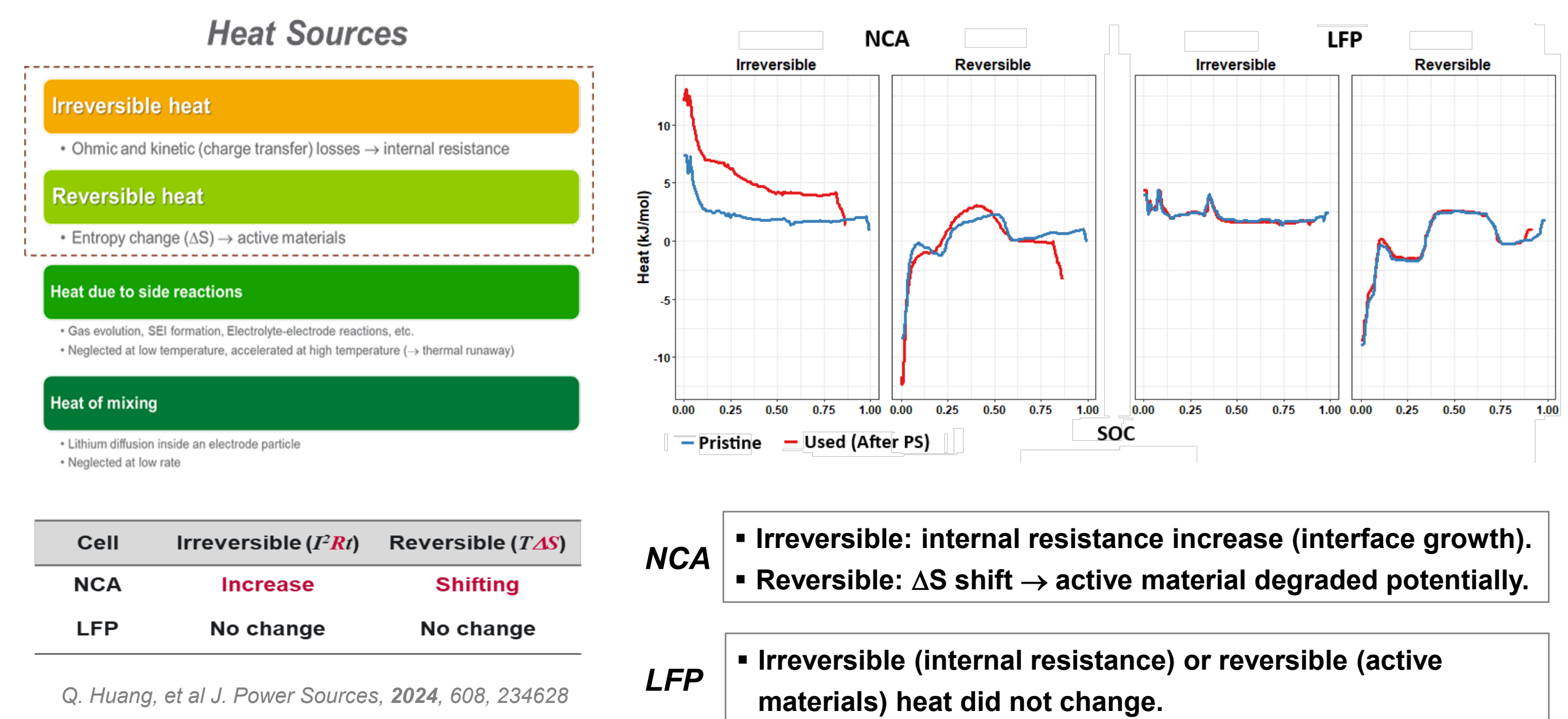


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After 2+ years' PS, the NCA cell showed 16% capacity loss, with much more heat release (discharge), associated with more degradation of NCA (cathode, anode and interface, as indicated in electrochemical characterizations). The LFP cell showed 6% capacity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

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

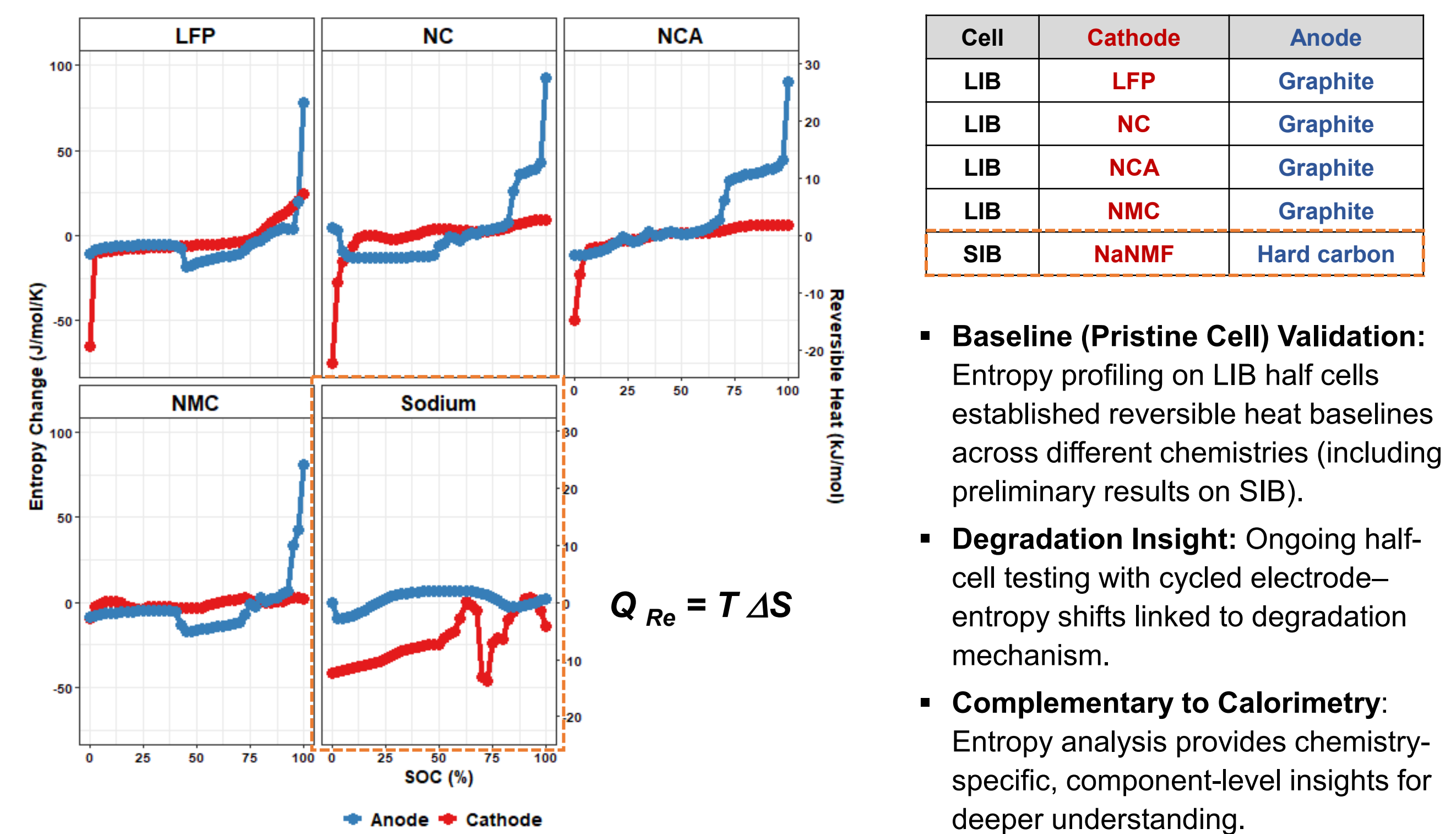
Heat Sources Separation: Irreversible Heat vs. Reversible Heat



Thermal behavior can interpret the degradation level /mechanism!

Heat Measurement II. Reversible Heat via Entropy Change (ΔS)

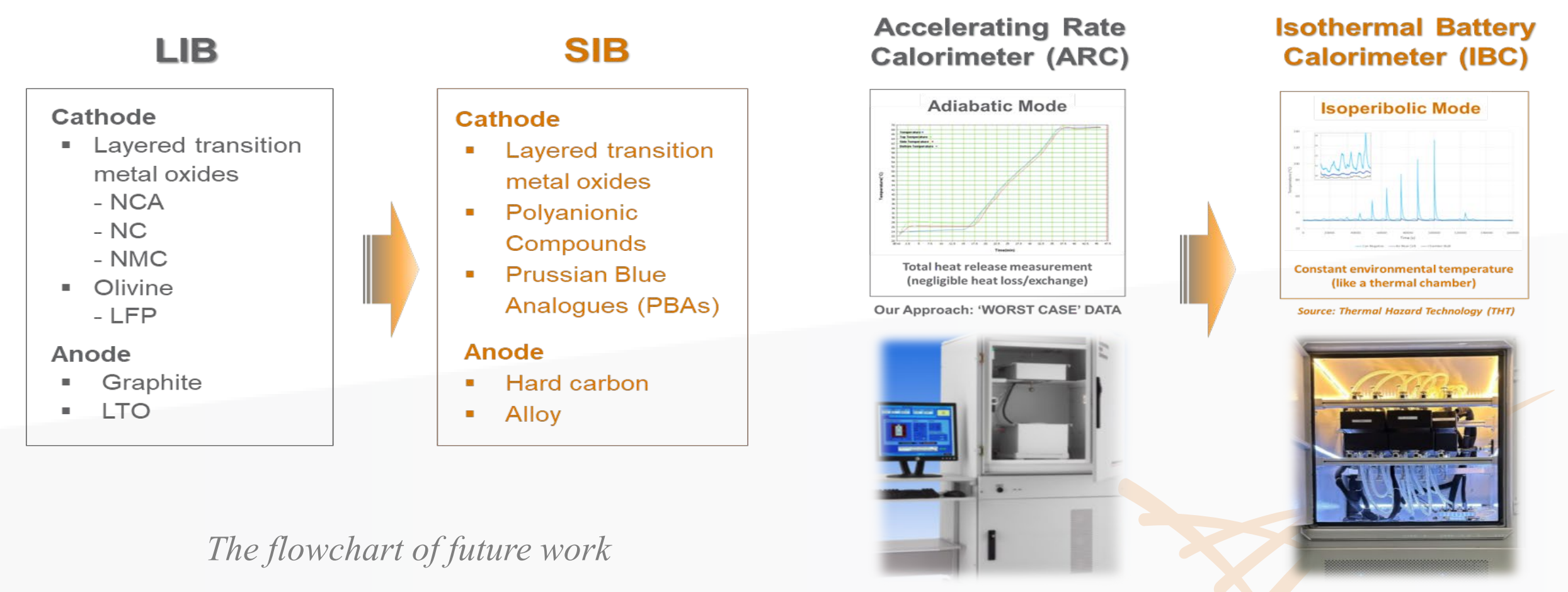
Entropy Change & Reversible Heat: Cathode & Anode Half Cells (Pristine)



- Baseline (Pristine Cell) Validation:** Entropy profiling on LIB half cells established reversible heat baselines across different chemistries (including preliminary results on SIB).
- Degradation Insight:** Ongoing half-cell testing with cycled electrode-entropy shifts linked to degradation mechanism.
- Complementary to Calorimetry:** Entropy analysis provides chemistry-specific, component-level insights for deeper understanding.

Summary and Future Work:

- We demonstrated a clear correlation between battery degradation and thermal behavior - greater degradation results in increased heat generation during operation.
- Two complementary thermal diagnostic methods were developed and validated in LIBs across multiple chemistries: *in situ* adiabatic calorimetry and entropy-based electrochemical measurements.
- These approaches revealed degradation-dependent heat release patterns, offering valuable insight into the evolving thermal and electrochemical states of the cell.
- Future work** includes: 1) Applying and refining these diagnostics for SIBs to support emerging grid-scale applications, 2) Commissioning a new **isothermal battery calorimeter (IBC)** to complement adiabatic ARC measurements and better simulate real-world service conditions, 3) Extending entropy analysis to aged/used cells to investigate component-level degradation and correlate thermal signatures with structural and interfacial changes.
- Thermal data generated through this work will also support the development and calibration of state-of-health models for LIBs (future SIBs) in grid applications.



The flowchart of future work