Thermodynamic Diagnostics of Lithium-Ion and Sodium-Ion Battery Degradation

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PROJECT PROFILE

Topic: Safety & Reliability | Vertical: Safety & Reliability

Strategic Pathway: Stabilize

Project start and finish: FY25-FY27

PROBLEM

Lithium-ion batteries (LIBs) are widely used, while **sodium-ion batteries (SIBs)** are emerging as low-cost, abundant-material alternatives for grid-scale storage. However, both systems suffer from degradation that is difficult to diagnose early and mechanistically.

- Conventional diagnostics track capacity fade and impedance growth but provide limited mechanistic insight.
- Key degradation pathways—including active-material changes, interface/ solid-electrolyte interphase (SEI) instability, and electrolyte degradation—can remain hidden before obvious performance loss.
- LIBs and SIBs share related cell architectures and degradation physics, but a broadly validated thermodynamic diagnostic framework is still lacking.
- There is a need for non-destructive diagnostics that can reveal degradation signatures and connect them to material-level failure pathways.

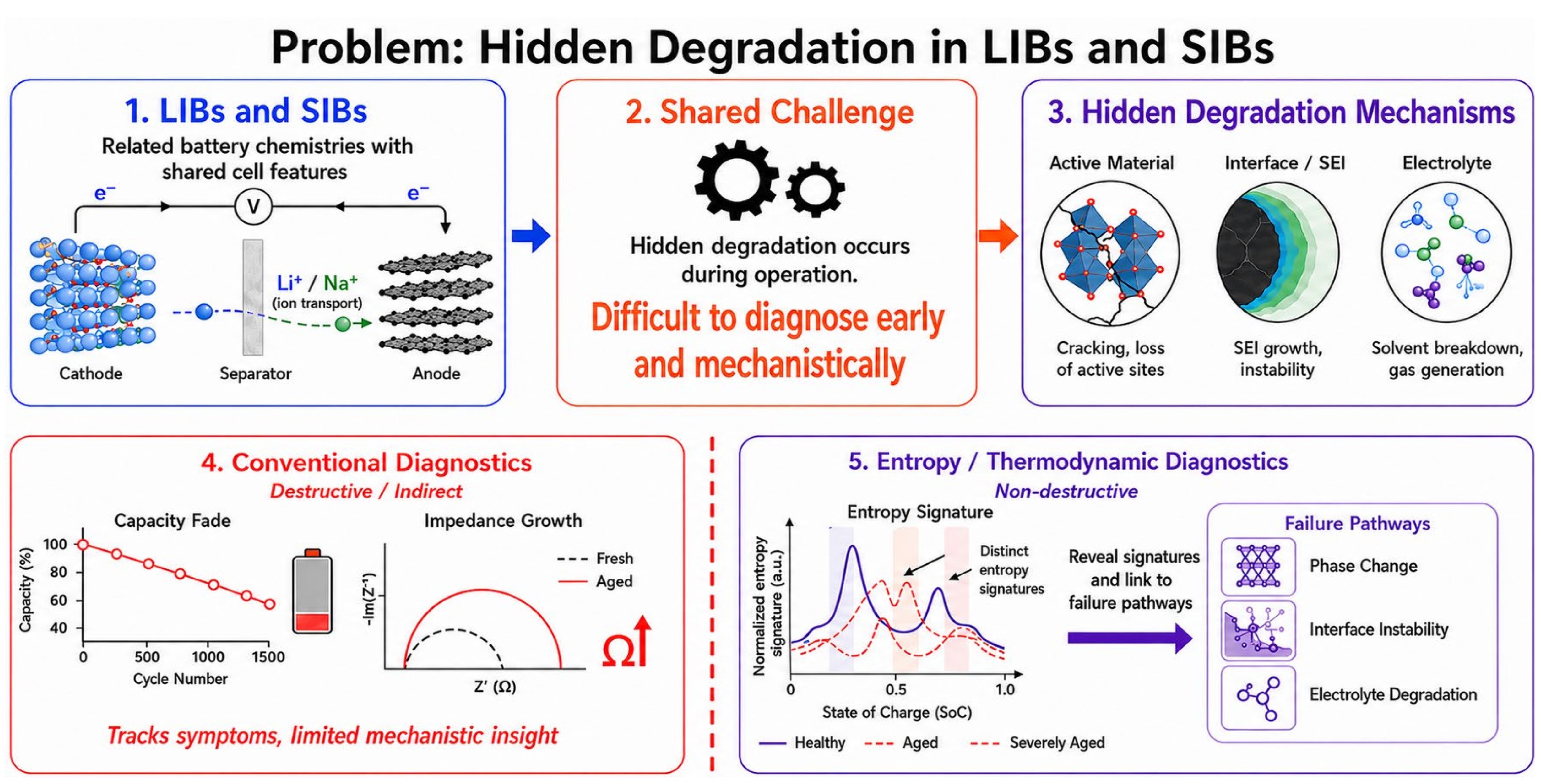


Figure 1. Overview of the problem: hidden degradation mechanisms and diagnostic gaps in LIBs and SIBs.

APPROACH

We use non-destructive entropy-change measurements to detect thermodynamic signatures of LIB/SIB degradation and link them to material-level failure pathways.

- **High-throughput (HTP) entropy platform**: multi-zone temperature control + electrochemical testing.
- **Entropy profiling**: open-circuit voltage (OCV)–temperature response over 0–100% SOC for pristine and used cells.
- **Cells & Testing conditions**: standard constant current-constant voltage (CC-CV) cycling for lab-scale SIBs; grid peak shaving profiles for commercial LIBs.
- **Mechanism mapping** (future work): combine entropy shifts, performance data, and post-characterization.

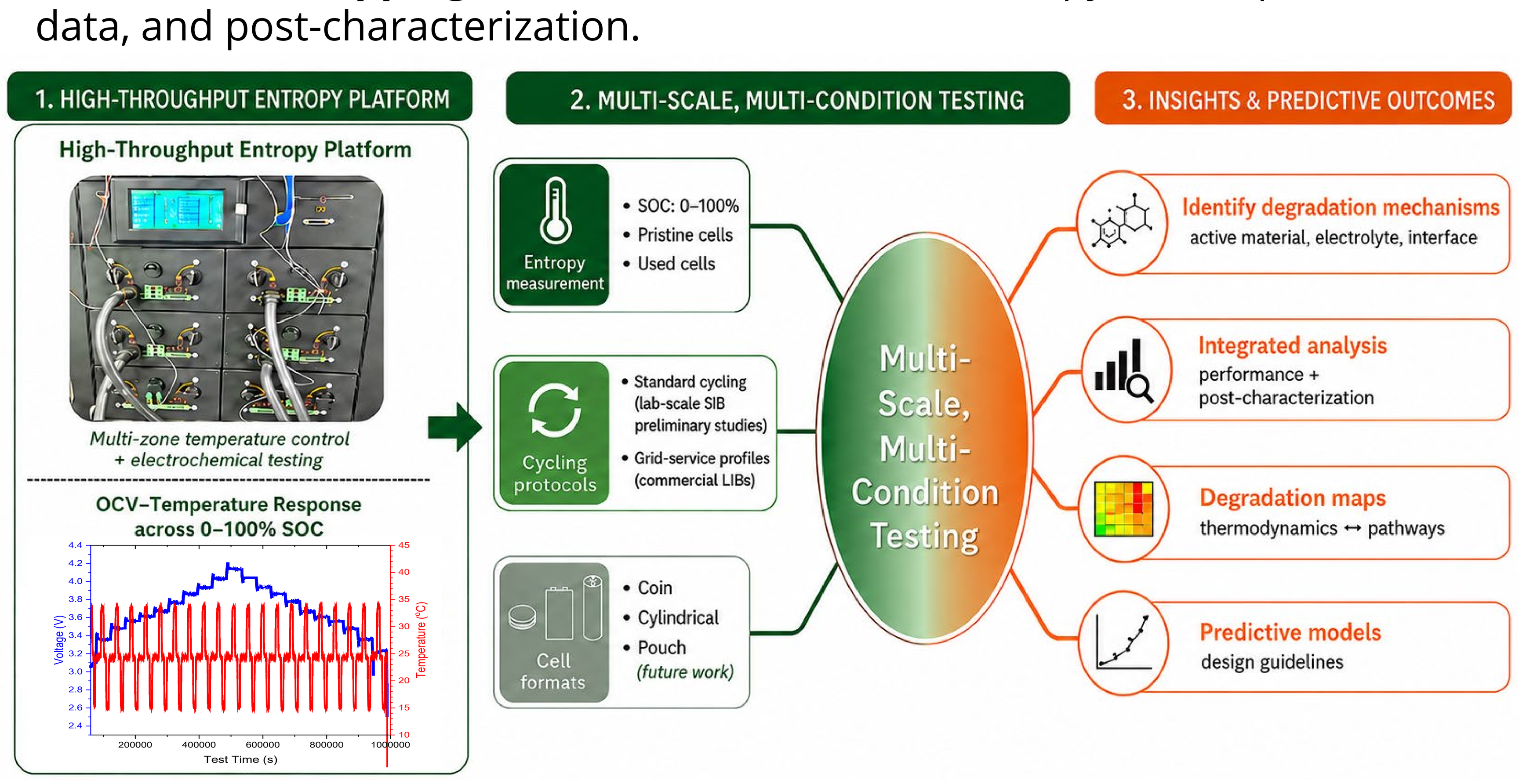
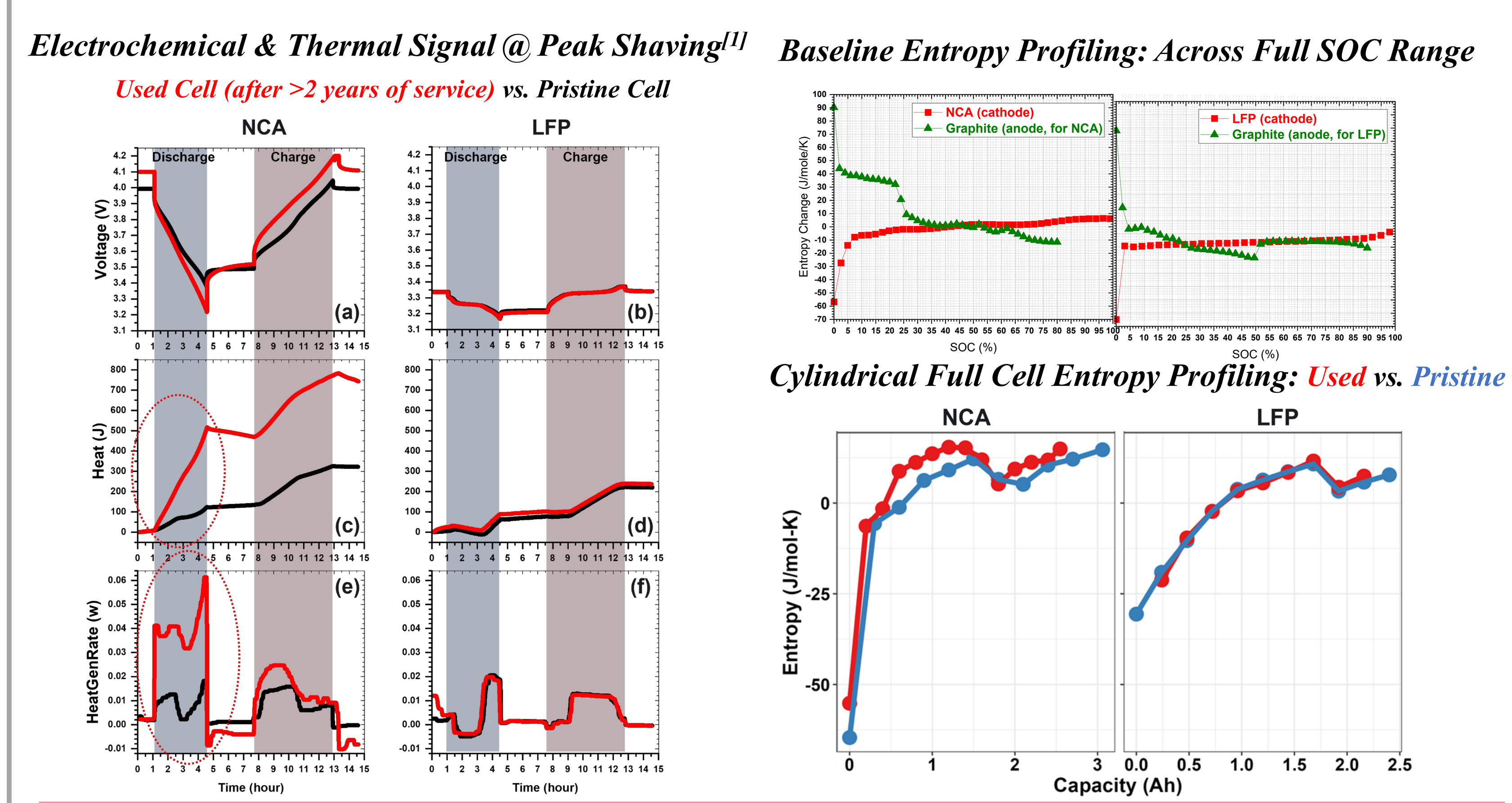


Figure 2. Overview of the non-destructive entropy-diagnostics workflow for probing degradation in LIBs and SIBs.

RESULTS

LIBs: Commercial Cell in Grid Service

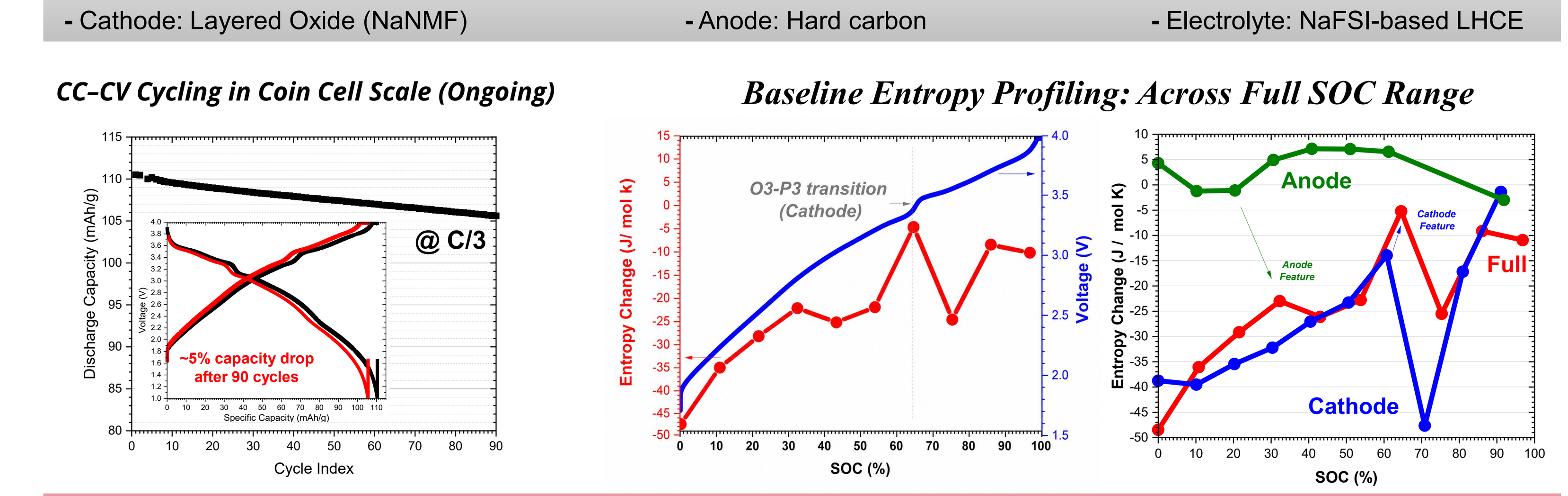


- NCA: performance loss → larger ΔS shifts (cathode, anode, and interfacial degradation);
- LFP: insignificant loss → consistent entropy profiles during operation (stable chemistry).

SIBs: Lab-Scale Cell in Preliminary Study

SIB Chemistry

- Cathode: Layered Oxide (NaNMF) - Anode: Hard carbon - Electrolyte: NaFSI-based LHCE



- SIB full-cell entropy reflects both cathode and anode contributions, capturing the NaNMF cathode transition → Demonstrate electrode-sensitive diagnostic.
- Long-term cycling-induced entropy shifts are under investigation.

CONCLUSIONS & IMPACT

- **Validated entropy diagnostics** in commercial LIBs operated under grid-service peak-shaving conditions for 2+ years.
- **Observed measurable entropy shifts** that correlate with battery performance loss, indicating thermodynamic changes associated with active-material degradation.
- **Extended the LIB-validated workflow toward SIBs**, with preliminary lab-scale studies demonstrating entropy profiling as an electrode-sensitive diagnostic for phase evolution in emerging sodium-ion systems.
- **Entropy features** can be linked to SOC-specific electrode processes, providing mechanistic insight beyond conventional voltage–capacity analysis.
- **Expected impact**: enable mechanism-informed degradation assessment, improve lifetime prediction, and accelerate development of reliable LIB and SIB systems for grid-scale energy storage.

FUTURE DIRECTIONS

- **Focus on SIB validation** using entropy diagnostics under controlled cycling and grid-relevant operating conditions.
- **Scale testing from coin cells to pouch and cylindrical formats** to evaluate format-dependent degradation behavior.
- **Integrate entropy, electrochemical, and post-characterization data** to identify active-material, interface/SEI, and electrolyte degradation pathways.
- **Develop SIB degradation maps and predictive diagnostics** to support reliable grid-scale energy storage.

References

[1] Q. Huang et al., J. Power Sources, 2024, 608, 234628

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