Comparative Degradation Study of Li-ion Battery Chemistries under Grid Services

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Introduction

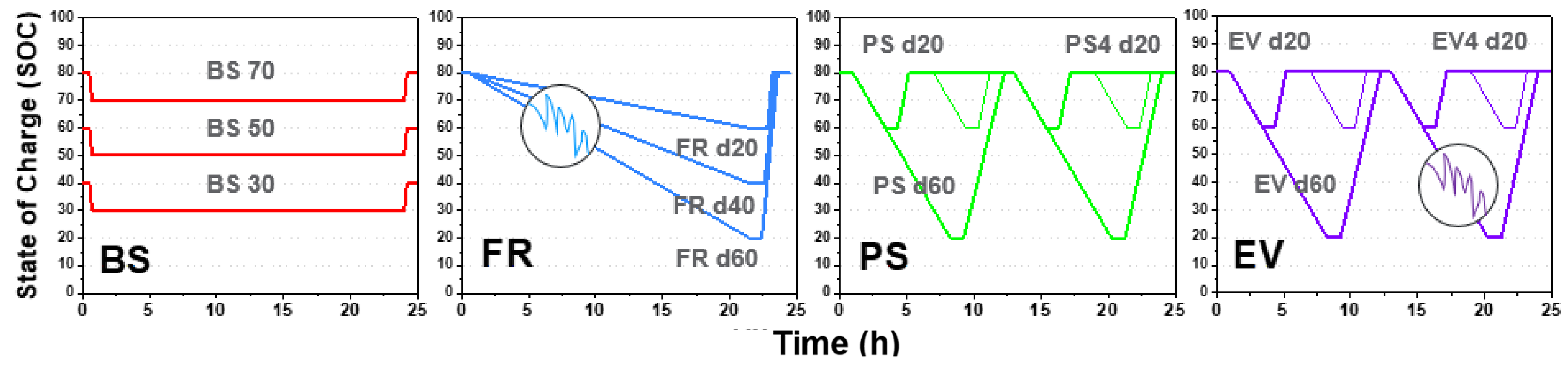
Various lithium-ion battery chemistries are currently deployed for stationary energy storage applications. However, state-of-the-art lithium-ion battery performance is not well explored and understood compared to vehicle application in terms of reliability.[1,2] In this work, four different Li-ion battery chemistries including NMC, NCA, and LFP types are subjected to one year of grid duty cycles specified to frequency regulation and peak shaving services. Our test setup, protocol and updated results will be compared and discussed.

Objectives and Methodology

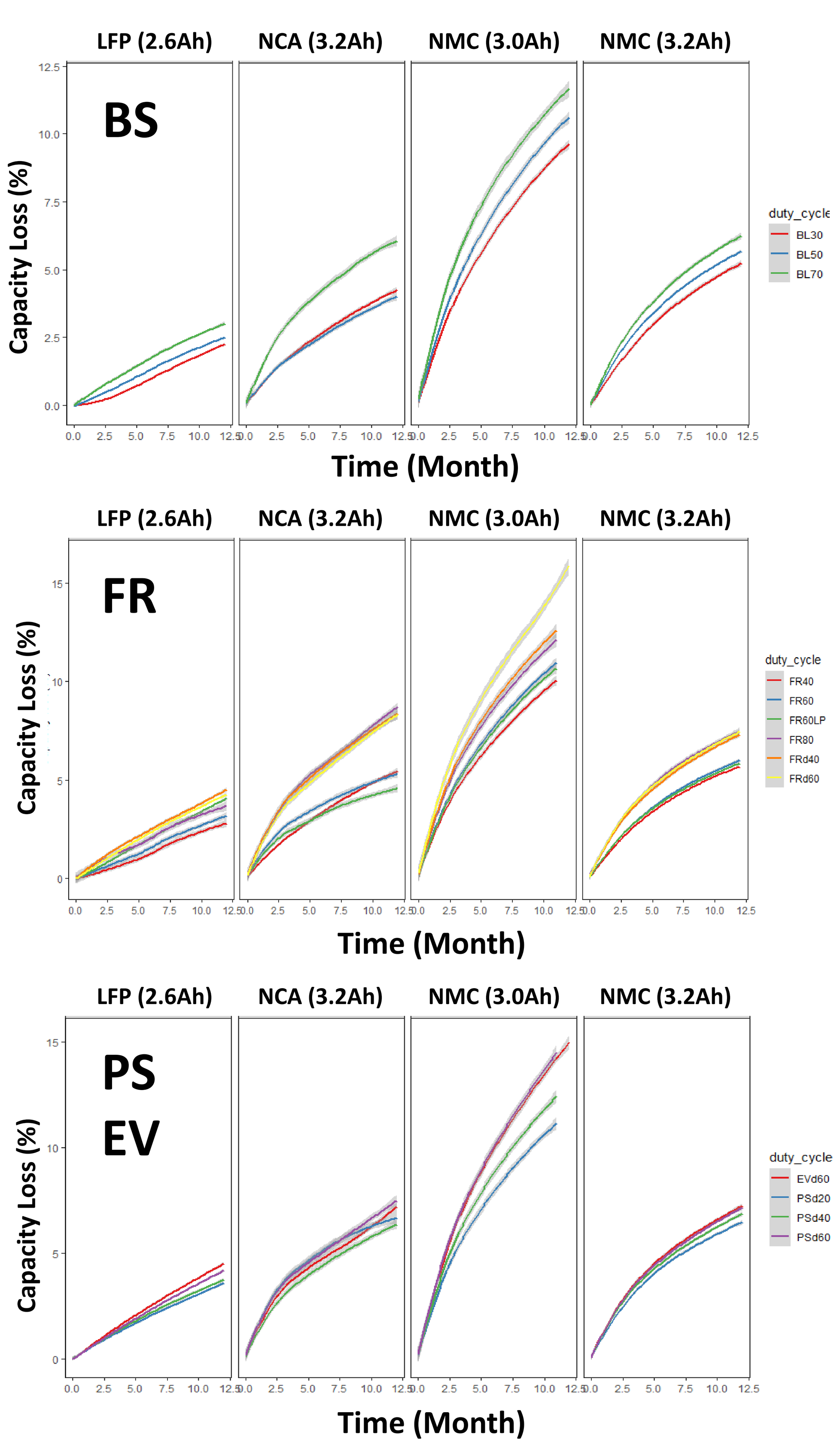
- **Develop standardized testing protocols for industry specific reliability.**
- **Testing under controlled and accelerated conditions: develop State of Health Model**

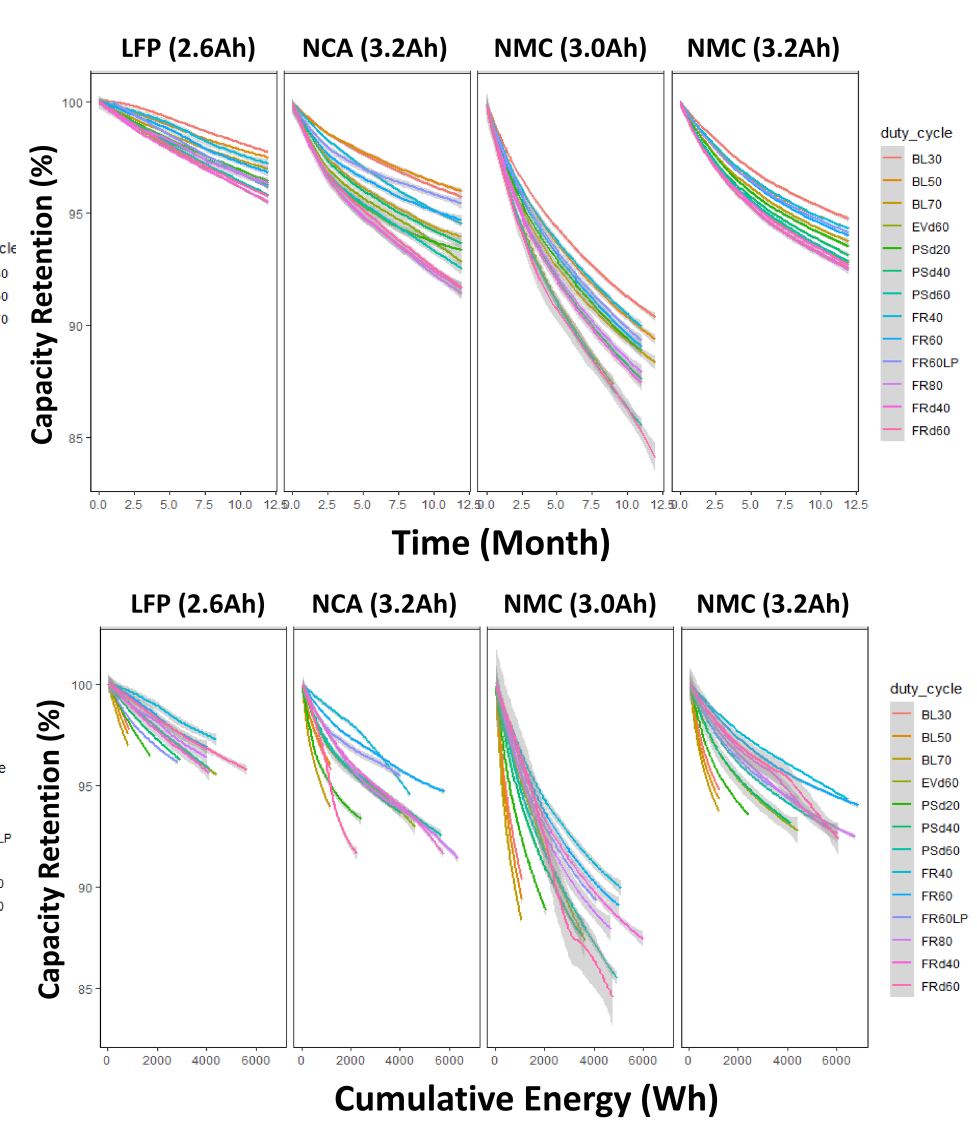
Variables
- **Time :** 24h grid cycle (1day)
- **State-of-Charge (SOC) :** 20~80%
- **Depth of Discharge (DOD or ΔSOC) :** 20, 40, 60%
- **Power (C-rate):** within cell specifications (voltage window)
- **Temperature :** 25°C
- **Number of cells:** 4 under same test condition (total: 156 cells)

Schedules (# of conditions)
- **BS : Baseline (3) –** aging at different SOC levels
- **FR : Frequency Regulation (4)**
- **PS : Peak Shaving (3)**
- **EV : Electric Vehicle (3)**

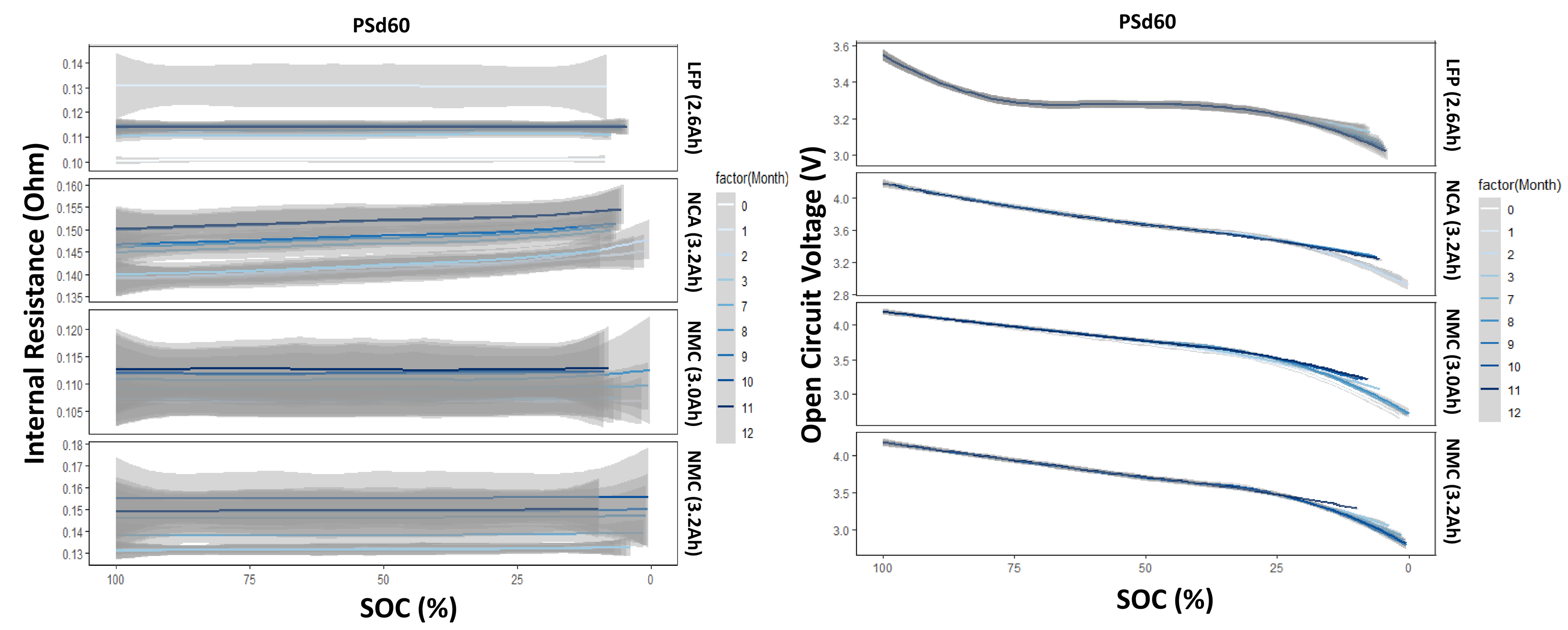


Results and Discussion

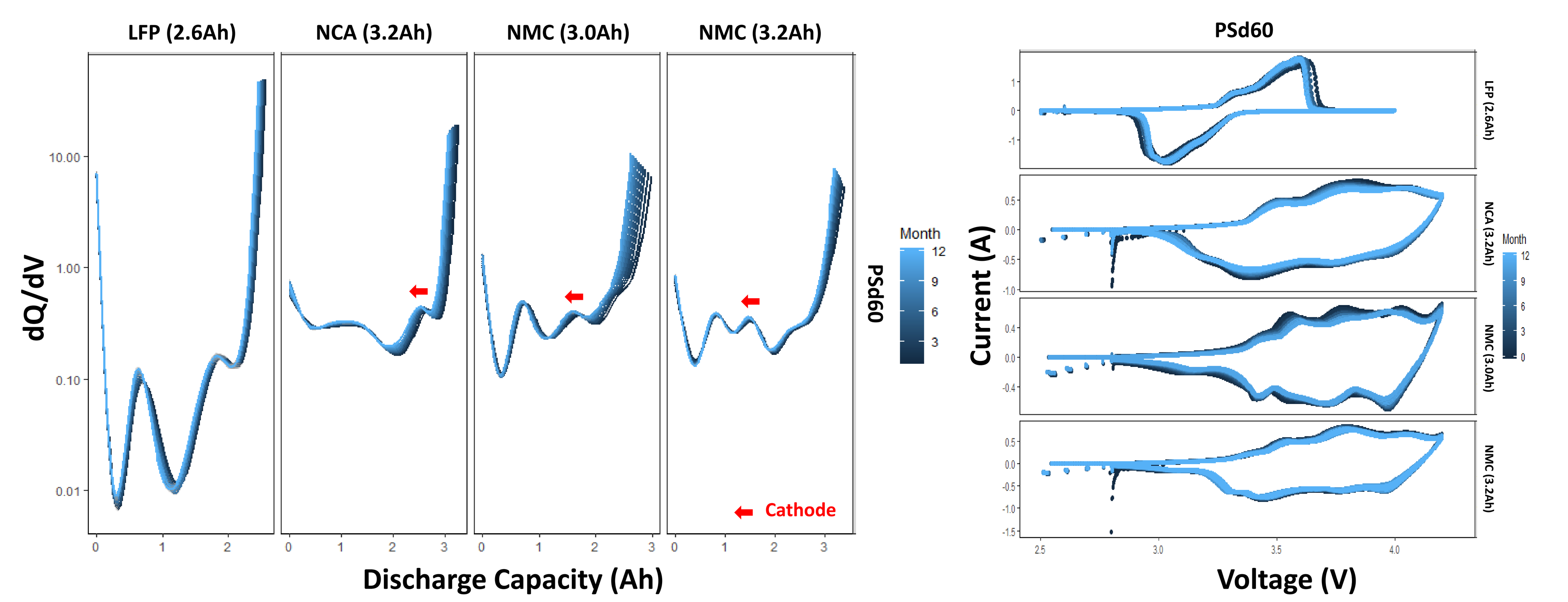




- LFP degraded the least (<5%) irrespective of service conditions.
- High energy NCA and NMC was comparable in terms of stability.
- Low energy NMC degraded 15% after one year of continuous peak shaving (PSd60).
- Higher SOC and larger DOD operation degrades the battery most.



- Internal resistance, open circuit voltage, dQ/dV and cyclic voltammetry was recorded for all cells.
- The most degraded grid service was peak shaving PSd60.



- Internal resistance increases with degradation of the cell.
- LFP cathode degradation is negligible even after one year of cycling.
- Cathode degradation is higher than graphite anode for NCA and NMC cells.
- Peak shaving service degrades the most per energy utilized.
- Even with same battery chemistry, cycling stability varies with cell engineering.

Summary and Perspective

- LFP cells have better aging, capacity, and energy retention.
- Frequency regulation service degrades the least per energy utilized.
- dV/dQ analyses and be applied for *in-situ* battery health monitoring
- Higher SOC level degrades the battery the most.
- Cathode dissolution occurs for NCA and NMC cells

Future Work

- Data accumulated here will be applied to modeling battery degradation and state-of health analyses for larger energy storage modules and systems.
- <u>Additional five chemistries including LFP, NMC and LTO cells (192 test channels) from different vendors will be installed since even with same battery chemistry, cycling stability varies with cell engineering.</u>
- In-operando/post-mortem cell characterization using advanced techniques.

Acknowledgements

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References

1. Choi D., N. Shamim, A.J. Crawford, Q. Huang, C.K. Vartanian, V.V. Viswanathan, and M.D. Paiss, et al. 2021. "Li-ion Battery Technology for Grid Application." Journal of Power Sources 511.(2021)
2. Crawford, Alasdair J. Choi, Daiwon, Balducci, Patrick J.; Subramanian, Venkat R.; Viswanathan, Vilayanur V. "Lithium-ion battery physics and statistics-based state of health model" Journal of Power Sources, 501, p.185-193 (2021).
3. A. Crawford, Q. Huang, M.CW Kintner-Meyer, J.-G. Zhang, D. Reed, V.L. Sprenkle, V.V. Viswanathan*, D. Choi*, "Lifecycle Comparison of Selected Li-ion Battery Chemistries under Grid Duty Cycle Combinations", *Journal of Power Sources*, 380, p.185-193 (2018).

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