Understanding Structural and Electrochemical Degradation in Li-rich Cathodes

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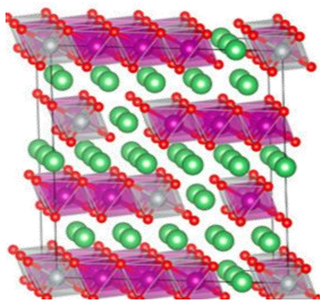
Introduction

Li-rich layered oxides (LRLOs) are among the most promising high-capacity cathode materials for next generation lithium-ion batteries, delivering capacities well above 200 mAh g^{-1} through the simultaneous exploitation of both cationic and anionic redox activity. However, severe structural and electrochemical instabilities such as transition metal redistribution, microstructural micro-cracking, and voltage decay hinder their commercial viability.



Aim

This work investigates a Co-free LRLO composition, $Li_{1.18}Mn_{0.52}Ni_{0.3}O_2$, comparing its degradation pathways when cycled in a conventional carbonate-based electrolyte versus an advanced ionic liquid-based alternative

Materials Synthesis

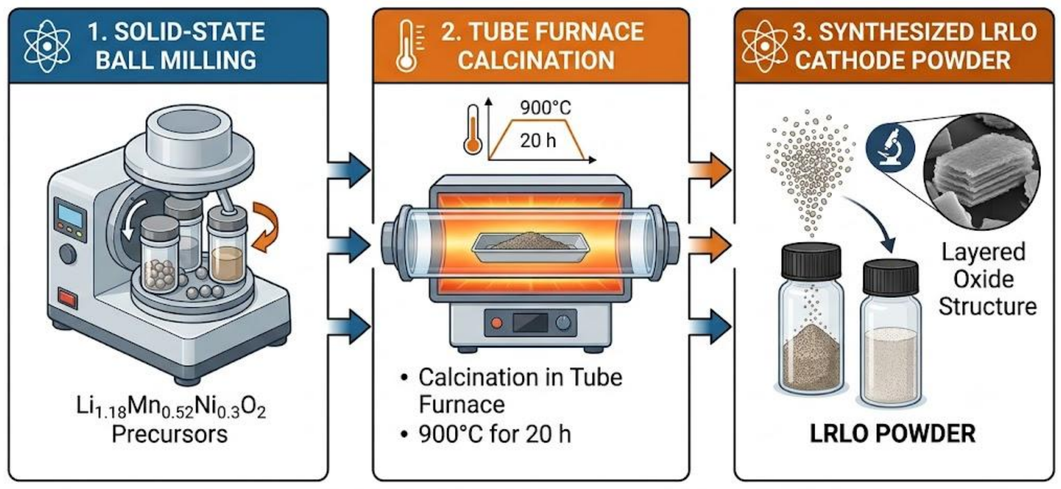
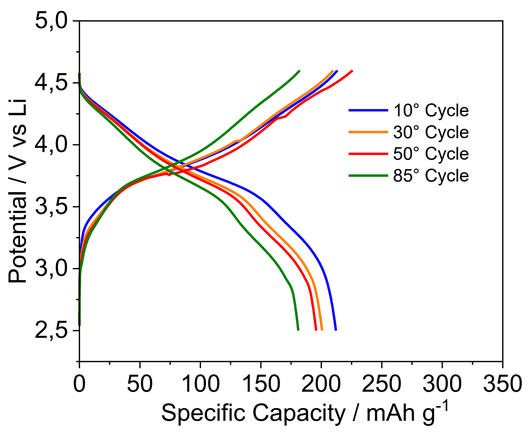
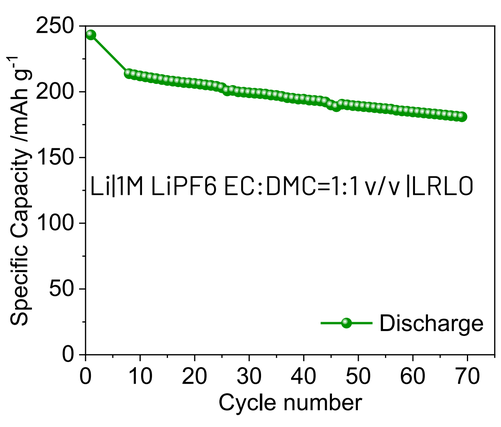


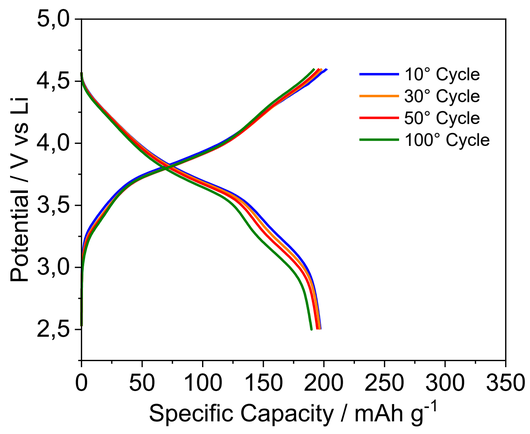
Image generated using AI (Google Gemini)

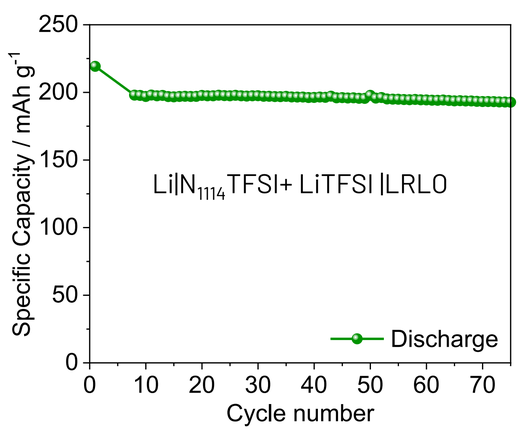
Electrochemistry





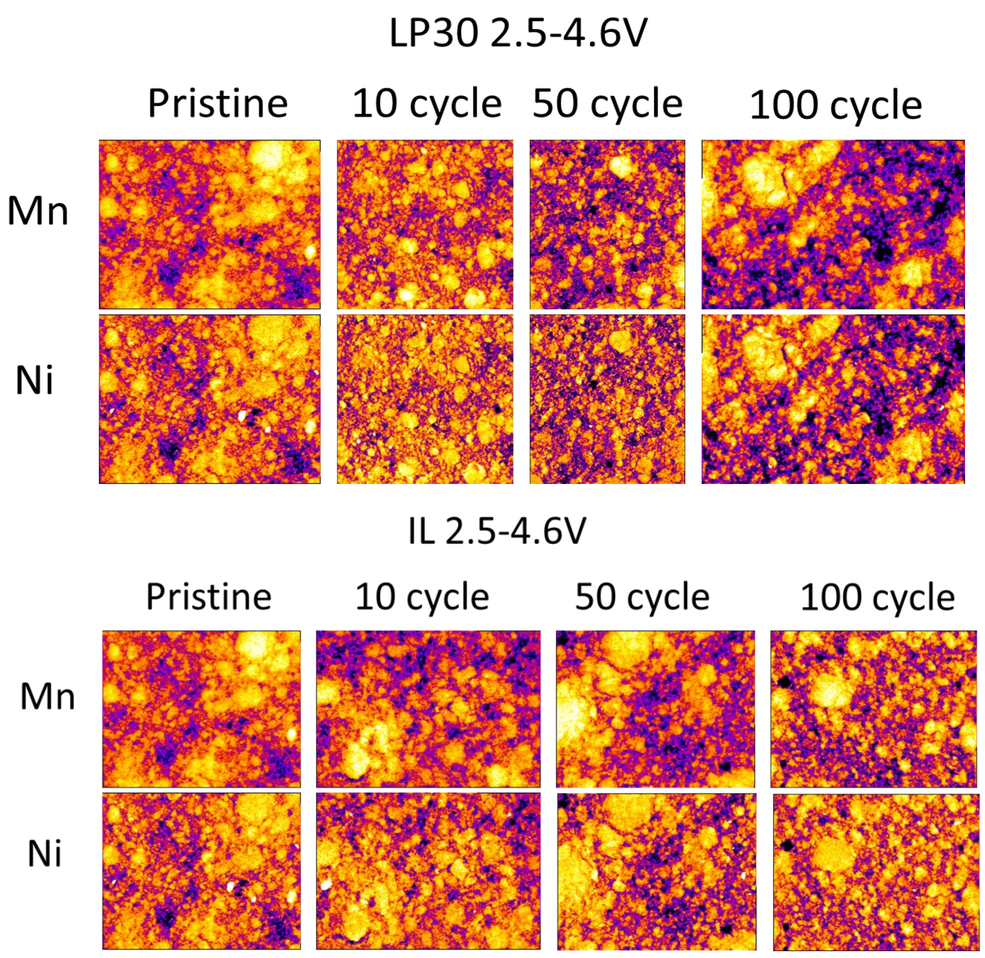
Galvanostatic Cycling
Voltage Range: 2.5-4.6 V
Current Density: 75 mA/g





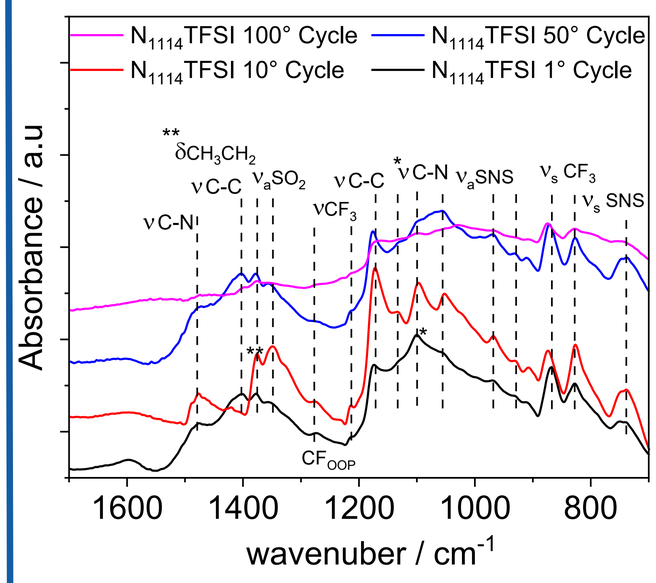
The conventional carbonate electrolyte (LP30) exhibits pronounced capacity fading (dropping from ~230 to <180 mAh/g) and noticeable voltage decay within 70 cycles due to electrolyte instability. In contrast, the ionic liquid system (IL: N_{1114}TFSI + LiTFSI) demonstrates outstanding electrochemical stability, maintaining a constant specific capacity of ~200 mAh/g and perfectly overlapping charge/discharge profiles up to 100 cycles.

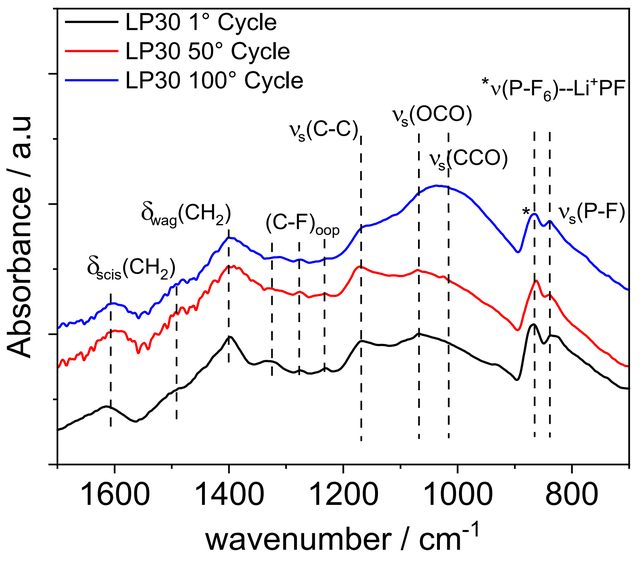
Synchrotron 2D XRF Imaging



Cycling in conventional LP30 electrolyte causes severe, progressive Mn degradation and lateral heterogeneity due to high-voltage Mn dissolution. Conversely, the Ni distribution remains comparatively stable with negligible fluorescence loss under the same carbonate-based conditions. In contrast, the ionic liquid-based electrolyte strongly suppresses Mn dissolution, maintaining a homogeneous elemental distribution even after 100 cycles.

FTIR





•LP30 system: Significant changes in band intensity as the number of cycles increases reveal the continuous decomposition of carbonate solvents and $LiPF_6$ salt, indicating the growth of a thick, resistive CEI layer.

•Ionic Liquid system**:** The spectra are dominated by stable $TFSI^-$ and N^+_{1114} features (CF_3, SNS, and C-N bands). The excellent overlap from the 1st to the 100th cycle proves high anodic stability and the formation of a thin, highly protective, and non-evolving CEI layer.

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