High-Energy Batteries Additive-Driven Stability Compatible with Saudi Arabia's Climate and Power Demands

Layan Yahya Alamoudi, DR.Wandi Wahyudi, Prof. Hussam Alshareef

Layan.Alamoudi@kaust.edu.sa, Wandi.Wahyudi@kaust.edu.sa

Abstract

Lithium-ion batteries are essential for large-scale renewable-energy integration, particularly in regions such as Saudi Arabia that experience high ambient temperatures and rapidly growing electricity demand. However, ultra-high-nickel layered cathodes such as NMC955 ($LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$) suffer from structural and interfacial degradation under high-voltage and elevated-temperature operation. This study investigates electrolyte-additive engineering using tris(trimethylsilyl) phosphite (TMSPa) and a fluorinated boron-containing additive (TTFPB) to enhance the stability and performance of Ti-doped NMC955 cathodes at temperatures up to 60 °C. CR2032 coin cells with Ti-doped NMC955 cathodes and lithium-metal anodes were assembled using a baseline electrolyte (1 M LiPF in EC:EMC, 3:7 v/v) and additive-enhanced formulations. The cells were evaluated by galvanostatic cycling, electrochemical impedance spectroscopy (EIS), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD). The dual-additive electrolyte (1 wt% TTFPB + 1 wt% TMSPa) markedly suppressed impedance growth and improved capacity retention relative to the baseline, while maintaining high coulombic efficiency at 4.5 V and elevated temperature. EIS indicated the formation of a stable, passivating interphase, while XRD and NMR provided evidence of preserved layered structure and modified solvation and interfacial chemistry. Although constrained by time and the use of Li-metal counter electrodes, this work demonstrates that combining a structurally stabilized Ti-doped NMC955 cathode with a dual-additive electrolyte is a promising strategy for durable, high-energy storage under extreme thermal and electrochemical stress.

Date: August 24, 2026

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1 Introduction

Lithium-ion batteries (LIBs) are widely used in portable electronics, electric vehicles, backup-power systems, and large-scale energy-storage applications because of their high energy density, high efficiency, low self-discharge, and long cycle life [1]. In renewable-energy systems, LIBs can store excess electricity from intermittent sources such as solar and wind and deliver it when generation is insufficient, helping to balance supply and demand and improve grid reliability.

This storage capability is vital for regions experiencing rapid load growth and severe thermal stress, such as Saudi Arabia. Driven by extreme summer cooling demands and expanding industrial infrastructure, national electricity consumption reached 340.43 TWh in 2024 (a 4.1% increase over 2023), with peak demand hitting a record 77.08 GW in 2025. To manage peak load shifting and integrate ambitious solar expansion targets, Saudi Arabia is actively expanding its energy infrastructure, including procurement tenders for 12 GWh of battery energy storage capacity[2, 3]. Deploying energy storage at this scale under harsh desert climates requires LIBs that possess both high energy density and exceptional thermal stability[4].

Among the available cathode materials, layered nickel-manganese-cobalt oxides, $LiNi_xMn_yCo_zO_2$ (NMC), are attractive because they combine high specific capacity, high operating voltage, and relatively high energy density. Increasing the nickel content further improves capacity and reduces reliance on expensive cobalt. In particular, NMC955 $LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$ is a promising high-energy cathode; however, its high nickel content also increases its susceptibility to structural and interfacial degradation. Recent studies report that NMC955 can deliver theoretical capacities exceeding 220 mAh g^{-1} at a 4.3 V cutoff, but capacity retention decreases at higher voltage because of lattice distortion, microcrack formation, cation mixing, oxygen instability, and surface reconstruction[5, 6].

The stability challenge becomes particularly important at elevated temperatures and high states of charge. Ni-rich NMC cathodes may undergo transition-metal migration, oxygen release, electrolyte oxidation, transition-metal dissolution, cathode-electrolyte interphase (CEI) growth, and impedance increase. These processes reduce lithium-ion transport and active-material utilization, resulting in capacity loss and reduced cycle life.

In hot climates such as Saudi Arabia, battery systems may operate at elevated temperatures. In this project, the cells are evaluated at temperatures up to 60 °C to reflect realistic high-temperature operating conditions. Here, the baseline cathode material is 1 mol% Ti-doped NMC955, which is expected to provide improved bulk structural stability compared with undoped NMC955.

The primary focus is to further enhance electrochemical stability and cycle life through electrolyte-additive engineering. Film-forming additives can preferentially oxidize at the cathode surface and generate a thin, chemically stable CEI that suppresses electrolyte decomposition, transition-metal dissolution, surface reconstruction, and crack-related degradation. For example, Fluorinated additives have also been reported to improve interfacial passivation and limit impedance growth in high-nickel NMC cathodes[7].

Therefore, this project investigates electrolyte-additive strategies to improve the interfacial stability and cycling performance of Ti-doped NMC955 cathodes at temperatures up to 60 °C. By combining a stabilized bulk cathode structure with an optimized electrolyte formulation, this research aims to deliver durable, high-energy LIB configurations capable of reliable long-term operation in high-demand applications, including renewable-energy storage in hot environments.

2 Methodology

2.1 Method details

Coin cells (CR2032) were assembled inside an argon-filled glove box to investigate electrolyte additive effects on battery performance.

The cathode consisted of $LiNi_{0.9}Mn_{0.05}Co_{0.05}O_2$ (NMC 955) modified with Titanium (Ti) doping on an Aluminum-carbon-coated current collector, paired with a Lithium (Li) metal anode.

The Baseline Electrolyte (BE) comprised 1 M $LiPF_6$ dissolved in ethylene carbonate and ethyl methyl carbonate (EC:EMC, 3:7 vol%). Standard test additives were evaluated at different concentrations relative to the BE:

- TTFPB 1 wt%
- TMSPa 1 wt%
- 1 wt% TTFPB + 1 wt% TMSPa

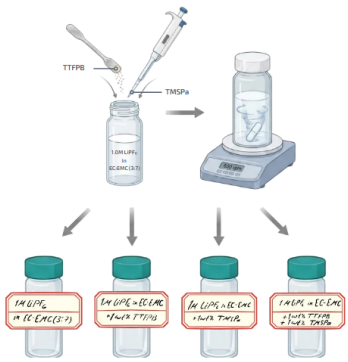


Figure 1 Electrolytes Formulation

2.1.1 Testing Protocols

Initial electrochemical performance was evaluated at room temperature (RT) within a voltage window of 2.8 V to 4.3 V. Cells underwent pre-cycling at 0.1C, Then cycled at 0.5C. The best-performing cells were further subjected to extreme operational stress tests:

- **High Voltage:** Upper cutoff increased to 4.5 V
- **High Temperature:** Elevated testing at 60°C
- **High C-Rate:** Accelerated testing at 1C and 3C

2.2 Evaluation Procedure

The electrochemical and structural properties of the cells were evaluated using the following techniques:

- **Galvanostatic charge/discharge (GCD):** Used to measure discharge capacity, capacity retention, coulombic efficiency, voltage profiles, and rate performance.
- **EIS (Electrochemical impedance spectroscopy):** Used to investigate changes in interfacial resistance, including ohmic resistance, interphase resistance, and charge-transfer resistance.
- **NMR (Nuclear magnetic resonance):** Used to probe changes in electrolyte chemistry and interfacial species.

- **XRD (X-ray diffraction):** Used to examine changes in the cathode crystal structure, phase stability, and structural degradation.

3 Results and Discussion

3.1 Electrochemical Performance

Figure 2a shows the cycling performance of cells containing different electrolyte additives at room temperature within the 2.8–4.3 V voltage window. Cells were pre-cycled at 0.1C and subsequently cycled at 0.5C. While the baseline electrolyte (BE) exhibits steady capacity fade (dropping to approximately 125 mAh/g by cycle 300), the dual-additive formulation (1 wt%TTFPB + 1 wt% TMSPa) significantly improves reversible capacity and stabilizes coulombic efficiency, maintaining superior capacity retention over the tested cycles. TTFPB alone also outperforms the baseline, whereas TMSPa alone exhibits rapid capacity decay after 50 cycles, demonstrating the synergistic benefit of using the dual-additive system rather than individual components.

Figure 2b presents the cycling performance when the upper cutoff voltage is increased to 4.5 V, a condition that imposes greater oxidative stress on the electrolyte and cathode–electrolyte interface. As expected under high voltage, the baseline electrolyte experiences pronounced degradation, with capacity falling sharply to roughly 125 mAh/g by cycle 140. In contrast, the TTFPB + TMSPa dual-additive effectively forms a robust, protective cathode–electrolyte interphase (CEI) on the Ti-doped NMC955 surface. This protective layer successfully suppresses parasitic reactions, allowing the cell to retain a much higher capacity (around 180 mAh/g at 100 cycles) compared to both the baseline and the single-additive TTFPB formulation.

Figure 2c shows the cycling behavior at an elevated temperature of 60 °C (with a 4.5 V cutoff), which typically accelerates parasitic reactions such as electrolyte decomposition, transition-metal dissolution, and CEI growth. The baseline electrolyte suffers heavily from these temperature-induced increases in interfacial resistance, dropping near 155 mAh/g after 100 cycles. The dual-additive formulation (TTFPB + TMSPa) proves highly stable, yielding a noticeably higher initial capacity (280 mAh/g) and maintaining roughly 200 mAh/g after 75 cycles. This indicates that the additive blend successfully limits high-temperature interfacial degradation and preserves reversible lithium-ion transfer under extreme thermal stress.

Figure 2d illustrates the rate capability of the best-performing dual-additive formulation (TTFPB + TMSPa) evaluated at 0.5C, 1C, and 3C. While higher current rates increase the demand on lithium-ion transport and amplify the impact of interfacial resistance, the dual-additive system maintains excellent capacity and stable coulombic efficiency. Remarkably, the capacity retention at 1C remains highly comparable to the 0.5C baseline, and even under the aggressive 3C rate, the cell retains functional capacity (above 110 mAh/g) up to 200 cycles. This confirms that the protective interphase formed by the additives is highly ionically conductive and does not excessively impede lithium-ion transport.

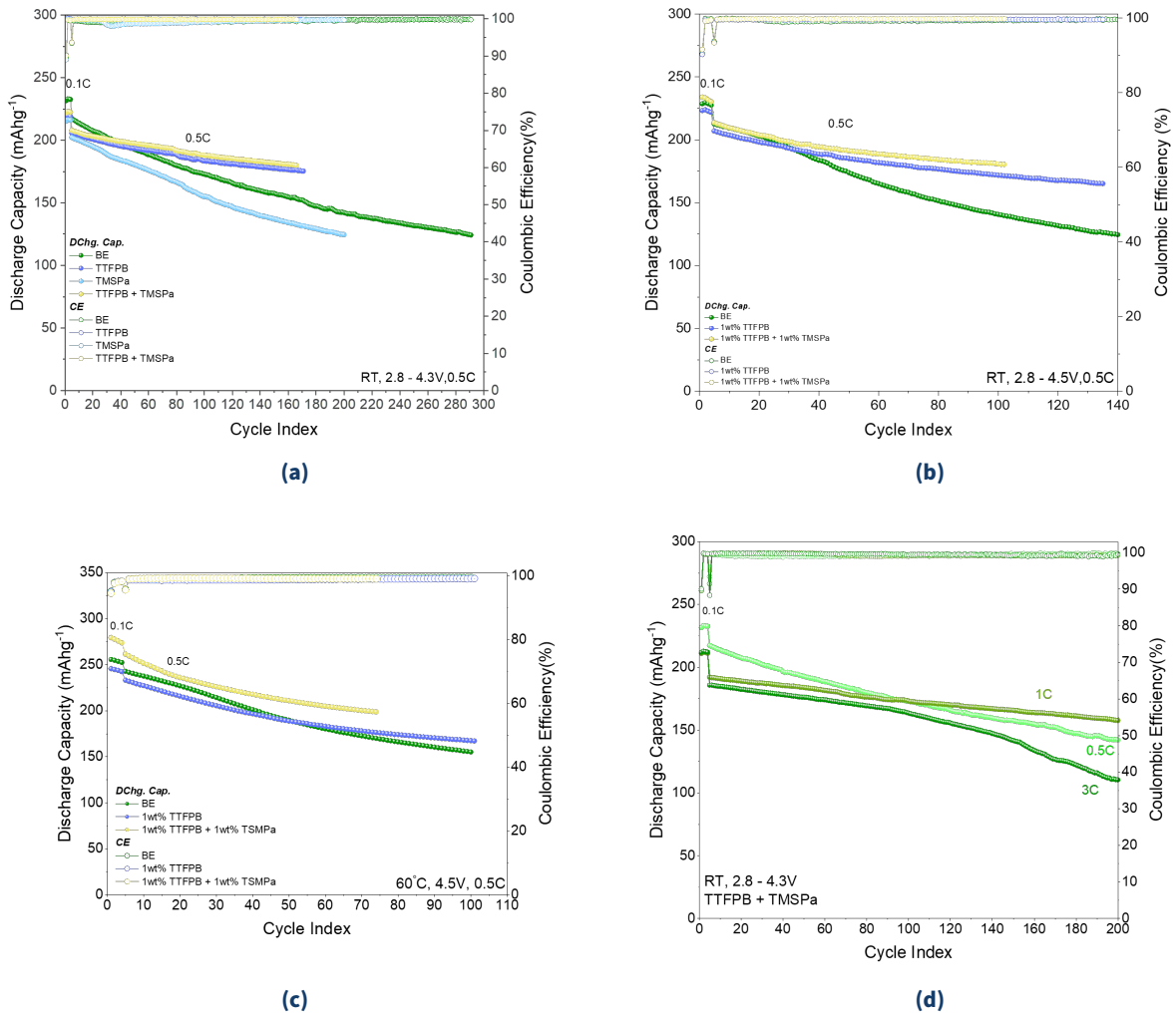


Figure 2 (a) Discharge capacity and coulombic efficiency the cells with different electrolyte formulations at room temperature (2.8–4.3 V, 0.5C after 0.1C pre-cycling). (b) High-voltage cycling at 4.5 V. (c) High-temperature cycling at 60 °C. (d) High-rate cycling at 0.5C, 1C, and 3C.

Figure 3 displays the initial charge–discharge voltage profiles of the cells across three distinct conditions, highlighting the kinetic benefits of the electrolyte additives. At room temperature within the standard 2.8–4.3 V window (Fig. 2a), the baseline electrolyte (BE) yields a slightly higher initial capacity (230 mAh/g), but the TTFPB + TMSPa dual-additive formulation improves the initial coulombic efficiency (ICE) to 90.07% compared to the BE's 89.56% . When the upper voltage cutoff is pushed to 4.5 V (Fig. 2b), the dual-additive system achieves the highest ICE (91.50% versus the BE's 90.61%) and exhibits tighter voltage polarization, indicating reduced interfacial resistance. Most notably, under the combined extreme stress of 60 °C and 4.5 V (Fig. 2c), the dual-additive formulation proves highly resilient; it unlocks a massive discharge capacity of roughly 280 mAh/g, significantly outperforming the baseline (approximately 255 mAh/g) and demonstrating maximized active material utilization under harsh thermal conditions.

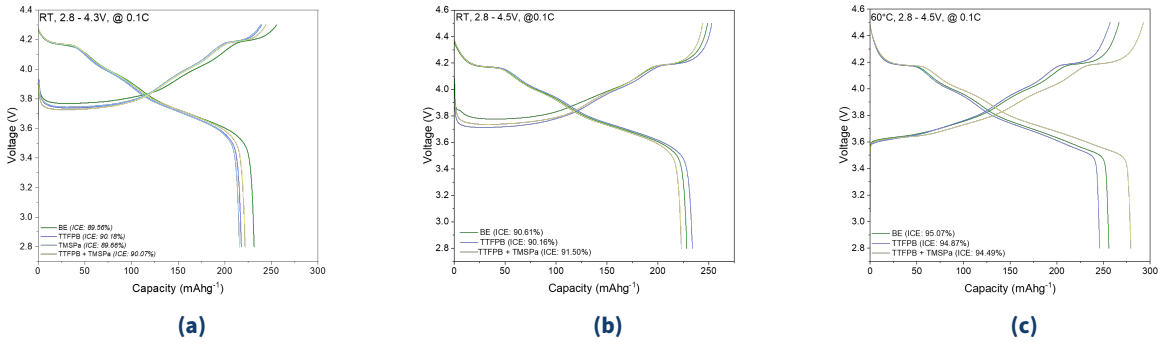


Figure 3 Charge–discharge voltage profiles of the cells: (a) RT, 2.8–4.3 V, 0.1C; (b) high upper cutoff voltage, RT, 2.8–4.5 V, 0.1C; (c) elevated temperature (60°C), 2.8–4.5 V, 0.1C.

Figure 5 presents the Nyquist plots for Ti-doped NMC955 | | Li cells cycled at room temperature with a 4.5 V upper cutoff at a 1C rate. As illustrated by the equivalent circuit model ,in figure 3, the high-frequency intercept on the x-axis corresponds to the bulk ohmic resistance (R_b). The semicircles in the high- and mid-frequency regions represent the solid electrolyte interphase resistance (R_{sei}) and charge-transfer resistance (R_{ct}), respectively. The low-frequency diagonal line represents solid-state lithium-ion diffusion (Warburg impedance)[8].

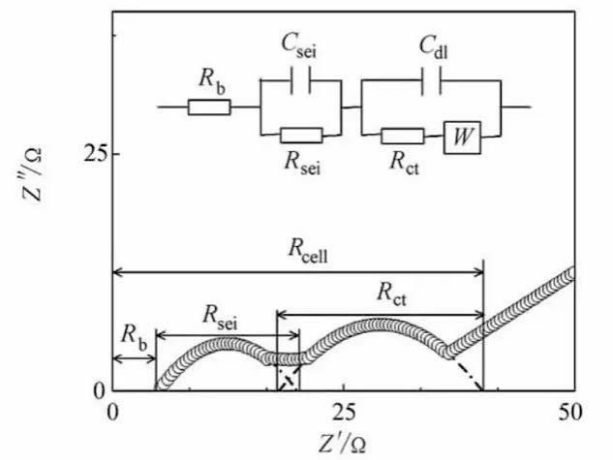


Figure 4 Lithium-ion battery EIS spectrum and equivalent circuit model showing Rs, Rsei, Csei, Rct, Cdl, and Warburg impedance. [8]

Stable Interphase with Additives:

For both the 1 wt% TTFPB and the 1 wt% TTFPB + 1 wt% TMSPa dual-additive formulations, the impedance spectra exhibit excellent stability. In the dual-additive sample, early cycles (Pre-cycle and 25 cycles) display distinct, wider semicircles, indicating the initial wetting and formation of a complex, multi-layered interphase. However, from cycle 50 to 125, the semicircles for both additive formulations tightly cluster together. This stabilization confirms that the additives successfully form a robust, passivating cathode–electrolyte interphase (CEI) that halts continuous electrolyte decomposition and prevents severe impedance growth.

Interfacial Failure in the Baseline (BE):

The baseline electrolyte displays highly unexpected impedance behavior for a battery. At 25 cycles, the cell experiences a massive spike in interfacial resistance (the semicircle expands far beyond 350 Ohms). In subsequent cycles (75 to 125), the apparent resistance collapses to

abnormally low values. Rather than indicating improved kinetics, this drastic, unnatural shrinkage is a classic signature of severe interfacial degradation—most likely severe lithium plating at the anode, which creates micro-shorts and artificial "leakage" currents that distort the EIS signal.

The impedance data visually confirm that the baseline electrolyte completely fails to passivate the electrodes under 4.5 V stress, leading to runaway parasitic reactions and likely Li-plating. In contrast, the tight clustering of the impedance curves in the later cycles for the additive-containing cells proves that TTFPB and TMSPa actively construct a durable, protective interphase that guaranties long-term kinetic stability.

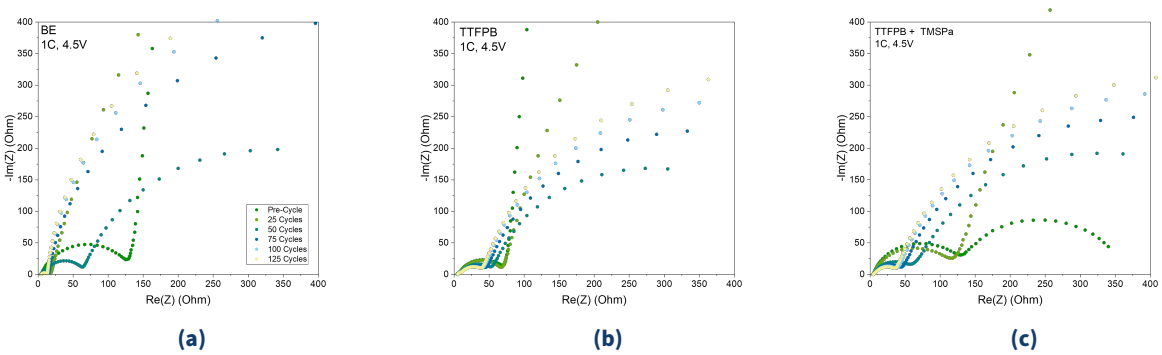


Figure 5 EIS spectra of cells with different electrolyte formulations after cycling at room temperature, 4.5 V, and 1 C: (a) Baseline Electrolyte (BE), (b)1 $wt\%$ TTFPB, and (c) 1 $wt\%$ TTFPB + 1 $wt\%$ TMSPa.

3.2 Structural and Chemical Characterization

XRD Analysis (Structural Stability)

X-ray diffraction (XRD) was utilized to monitor the physical stability of the single-crystal NMC955 cathode during a full charge and discharge cycle.

Lattice Flexibility: As the battery charges and lithium ions are extracted, the primary XRD peak shifts. This shift reflects the natural, expected contraction of the crystal lattice under voltage stress.

Complete Reversibility: Upon discharging, the XRD peak returns perfectly to its original starting position. This complete recovery demonstrates that the single-crystal material is highly elastic. It successfully avoids permanent structural deformation, detrimental phase changes, and internal microcracking, which are primary causes of failure in standard conventional cathodes at high voltages.

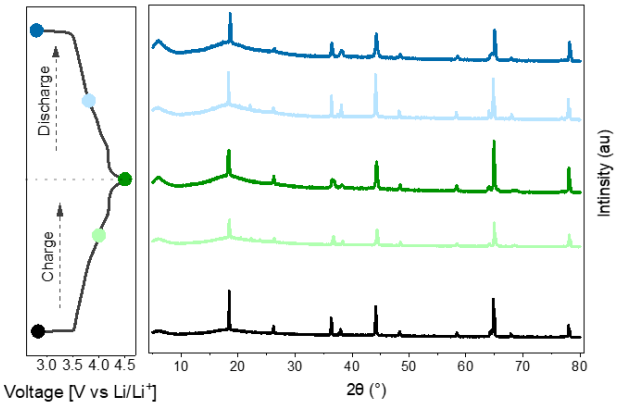


Figure 6 XRD patterns of Ti-doped NMC955 cathodes at various charge/discharge states at room temperature.

NMR Analysis (Electrolyte Chemistry)

Nuclear Magnetic Resonance (NMR) spectroscopy was employed to observe how the newly introduced additives interact with the electrolyte solvents and the lithium ions.

^{1}H NMR (Solvent Interaction):. The proton (^{1}H) spectra track the main liquid solvents in the battery. When the TTFPB and TMSPa additives are introduced, the solvent peaks show a distinct shift. This confirms that the additives are not inert; they actively alter and stabilize the chemical environment of the bulk electrolyte.

^{7}Li NMR (Lithium Ion Solvation): . The lithium (^{7}Li) spectra track the behavior of the lithium ions themselves. Compared to the baseline electrolyte, the addition of the dual-additive formulation causes the primary lithium peak to shift noticeably. This indicates that the additive molecules directly surround and coordinate with the lithium ions as they move. By modifying how the lithium ions are transported, the additives facilitate the formation of a highly protective interphase layer on the battery's surface, effectively shielding the electrolyte from severe degradation.

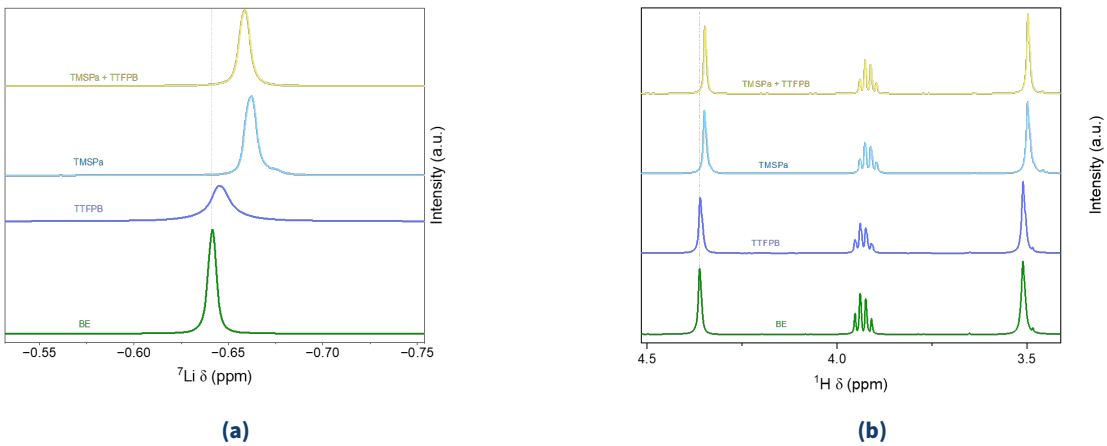


Figure 7 (a) ^{7}Li NMR spectra and (b) related proton NMR data for different electrolytes formulation.

4 Limitations and Future Work

Navigating a complex field like battery electrochemistry within strict program time constraints made mastering advanced characterization techniques and accelerating data collection a notable challenge. Consequently, several limitations remain to be addressed in future research:

- **Long-Term High-Temperature Cycling:**
  Due to tight time constraints, the extreme stress tests at 60 °C were limited to 100 cycles. Future testing should extend past 500 cycles to properly simulate multi-year grid-storage operation.
- **Microscopic Visual Inspection:**
  While structural stability was confirmed, time limitations prevented comprehensive visual post-mortem analyzes. Future research should employ Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM) on cycled electrodes to visually map CEI layer thickness and microcrack suppression.

5 Conclusion

This study evaluated additive-enhanced batteries to meet the high energy demands and severe thermal stresses characteristic of Saudi Arabia's climate. This work successfully demonstrated The dual-additive formulation (TTFPB + TMSPa) significantly enhanced both interfacial and bulk stability compared with the baseline electrolyte. Electrochemical testing and EIS showed that the dual-additive electrolyte forms a robust interphase that suppresses decomposition, while XRD confirmed that the single-crystal cathode inherently resists lattice collapse. Ultimately, these results show that coupling a resilient single-crystal cathode architecture with targeted film-forming additives offers a viable pathway toward reliable, long-life lithium-ion batteries for renewable-energy storage in high-temperature environments.

Acknowledgments

I would like to express my sincere gratitude to Dr. Wandi Wahyudi and Prof. Husam Alshareef for their invaluable mentorship and guidance throughout this summer internship. I am deeply thankful for this opportunity, which would not have been possible without the KAUST Academy. Furthermore, I extend my appreciation to KAUST for hosting this internship, and to the sponsors, KA.CARE and CREST, for their generous support.

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