

Supplementary Material

A low-cost inorganic oxide as dual-functional electrolyte additive towards long cycling Li-rich Mn-based cathode materials

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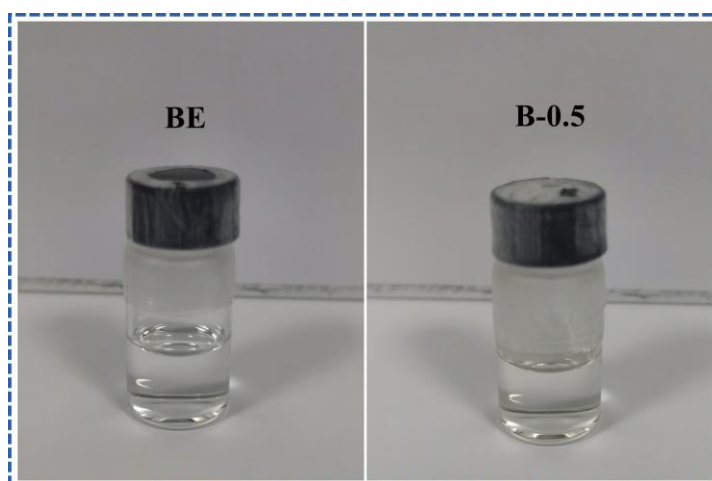
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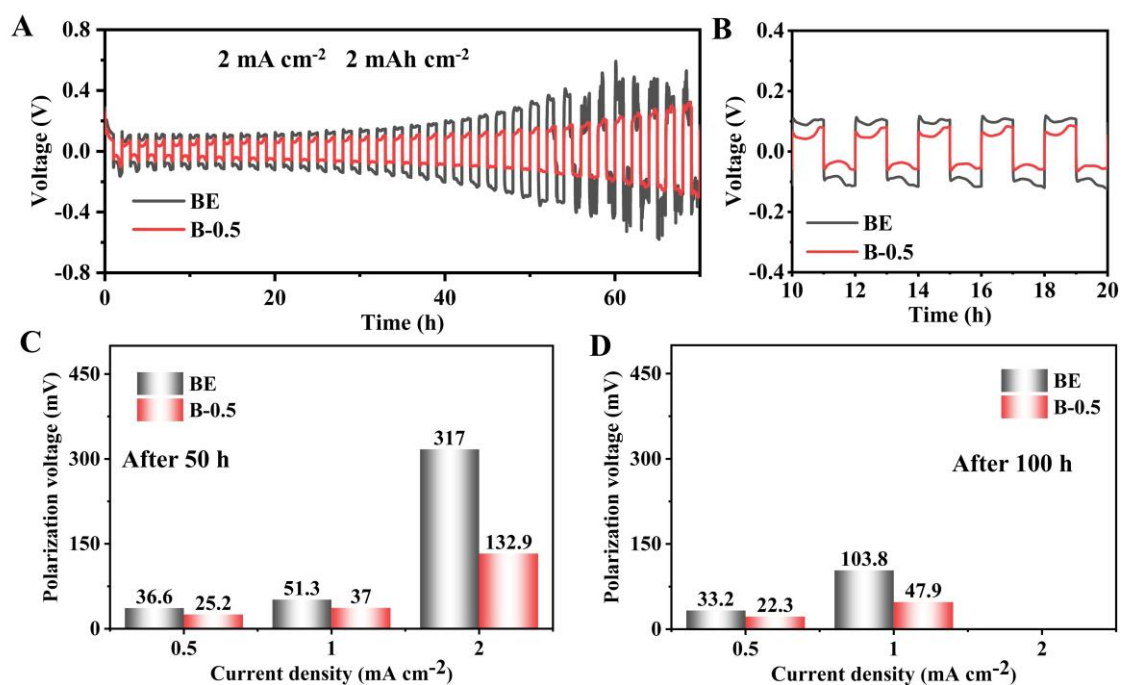
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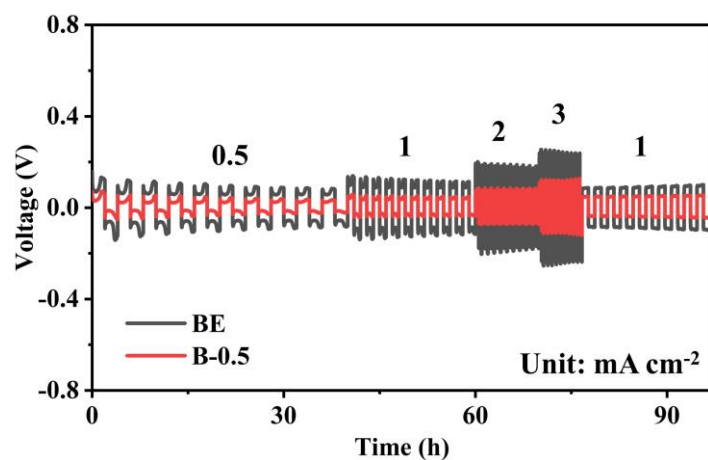
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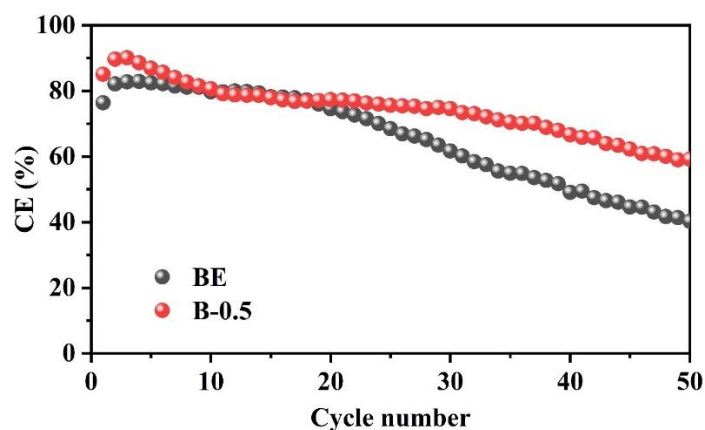
Supplementary Figure 1. Optical photos of BE and B-0.5 electrolytes.



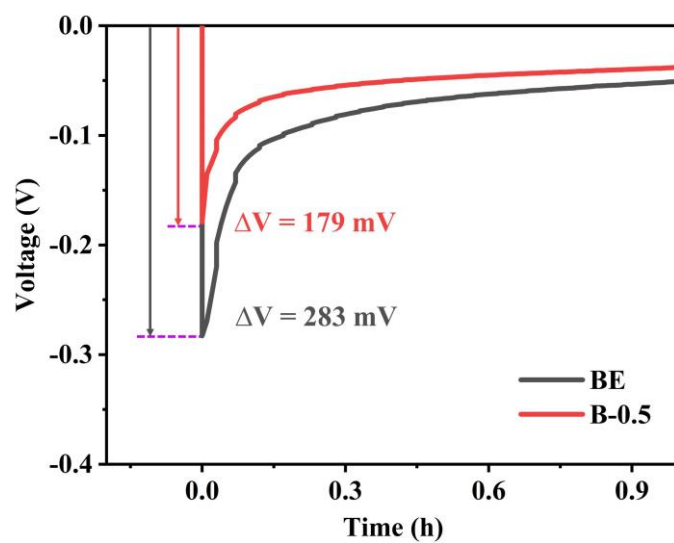
Supplementary Figure 2. (A, B) Cycling performance of Li||Li symmetric cells at 2 mA cm⁻² and 2 mAh cm⁻². (C, D) The polarization voltage of Li||Li symmetric cells after cycling different times: (C) 50 h, (D) 100 h.



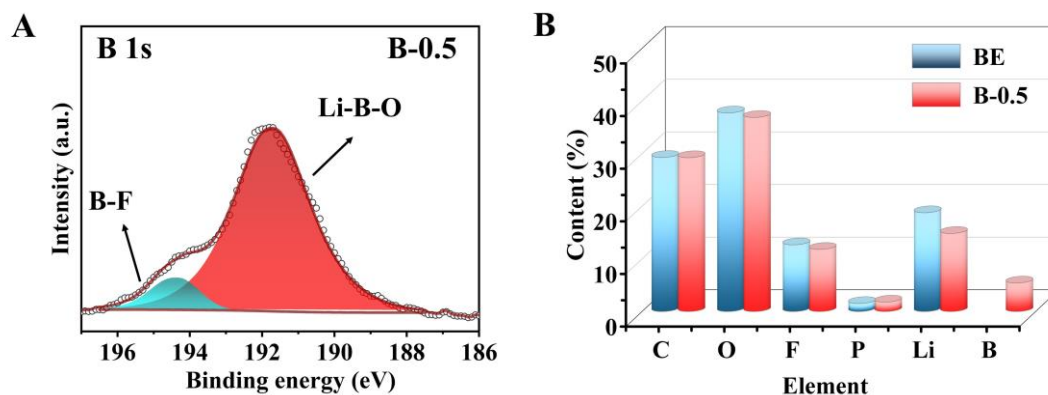
Supplementary Figure 3. Rate performance of Li||Li symmetric cells with different electrolytes at current densities ranging from 0.5 to 3 mA cm⁻² for 1 mAh cm⁻².



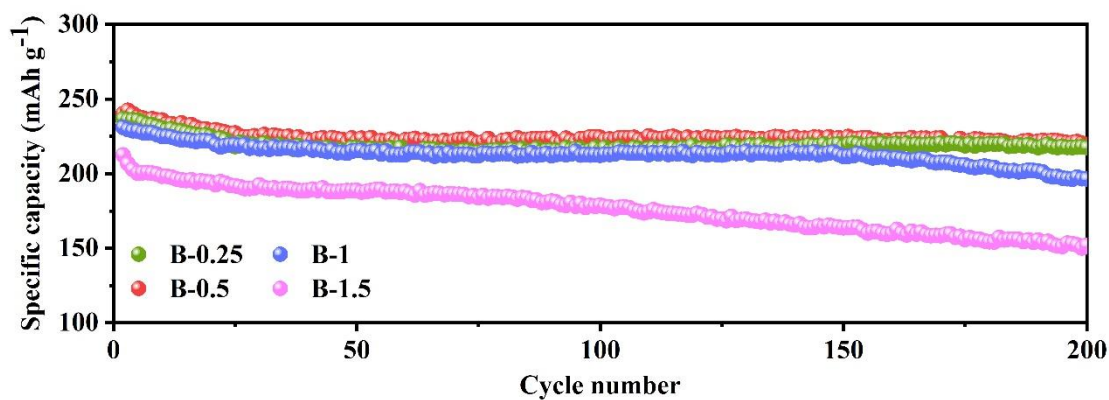
Supplementary Figure 4. CEs of Li plating/stripping in Li||Cu cells at the conditions of 1 mA cm⁻² and 1 mAh cm⁻².



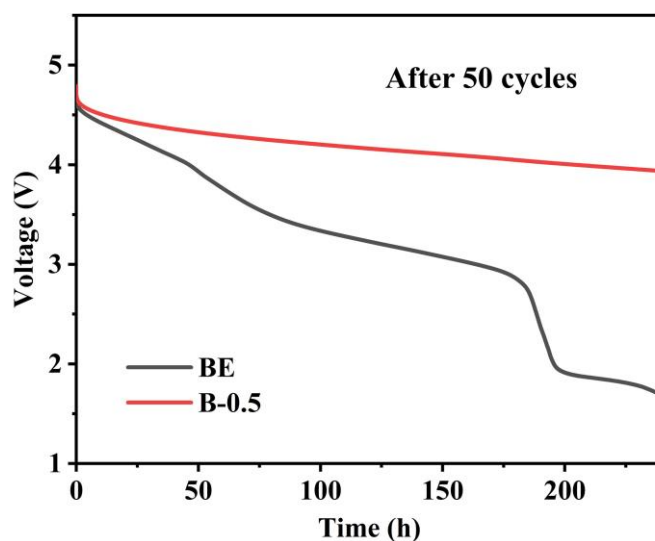
Supplementary Figure 5. Li nucleation overpotential of Li||Cu cells with the electrolytes of BE and B-0.5.



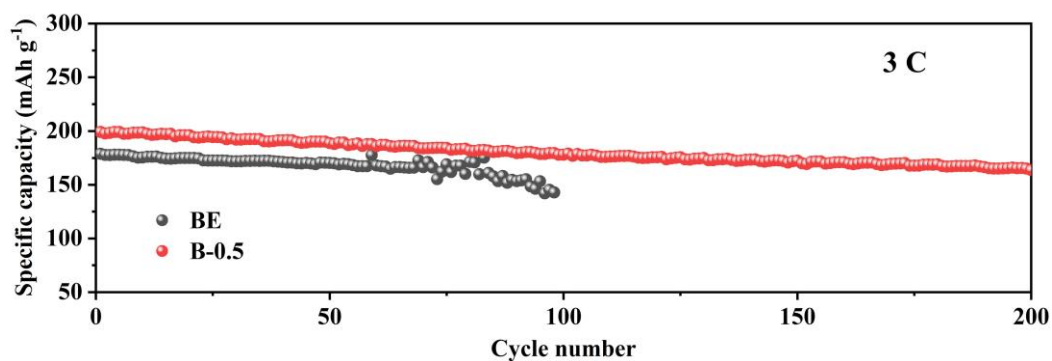
Supplementary Figure 6. (A) XPS spectra of B 1s for Li||Li symmetric cells after 10 cycles with B-0.5. (B) Comparison of element contents in SEI layer at different electrolytes.



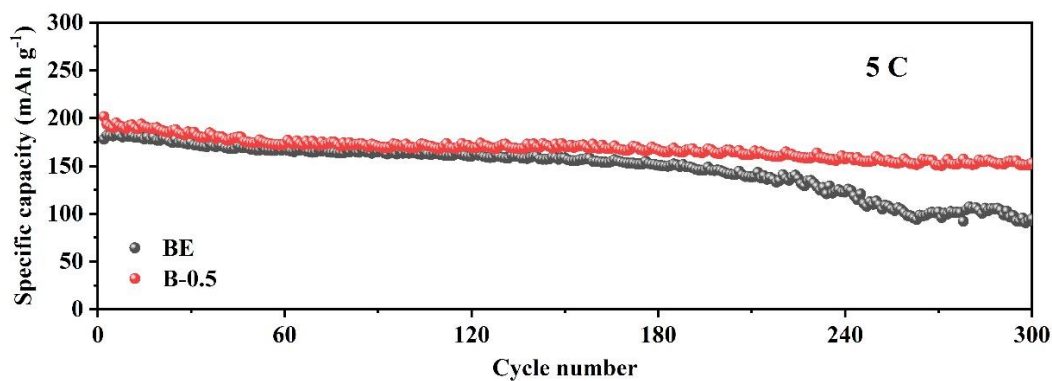
Supplementary Figure 7. Cycling performance of Li||LRM cells using the electrolytes with different amounts of additive between 2 and 4.8 V at 1 C.



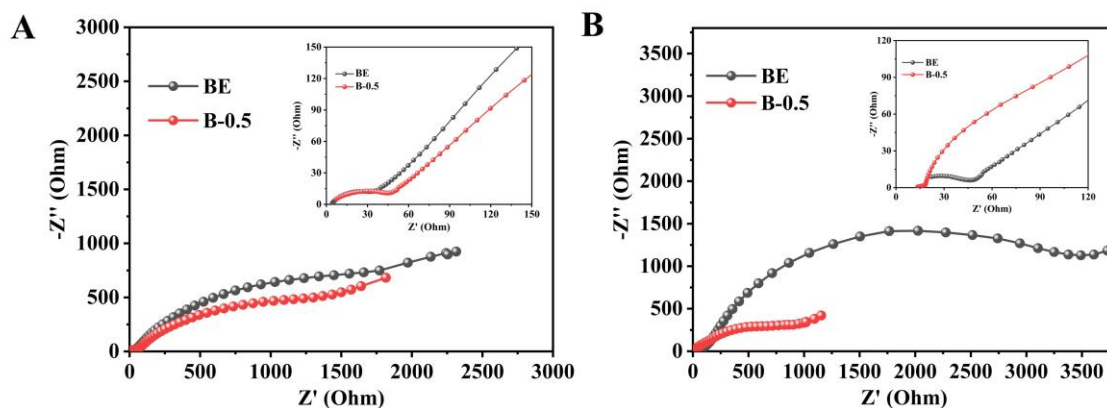
Supplementary Figure 8. Self-discharge curves of Li||LRM cells after 50 cycles at 4.8 V in different electrolytes.



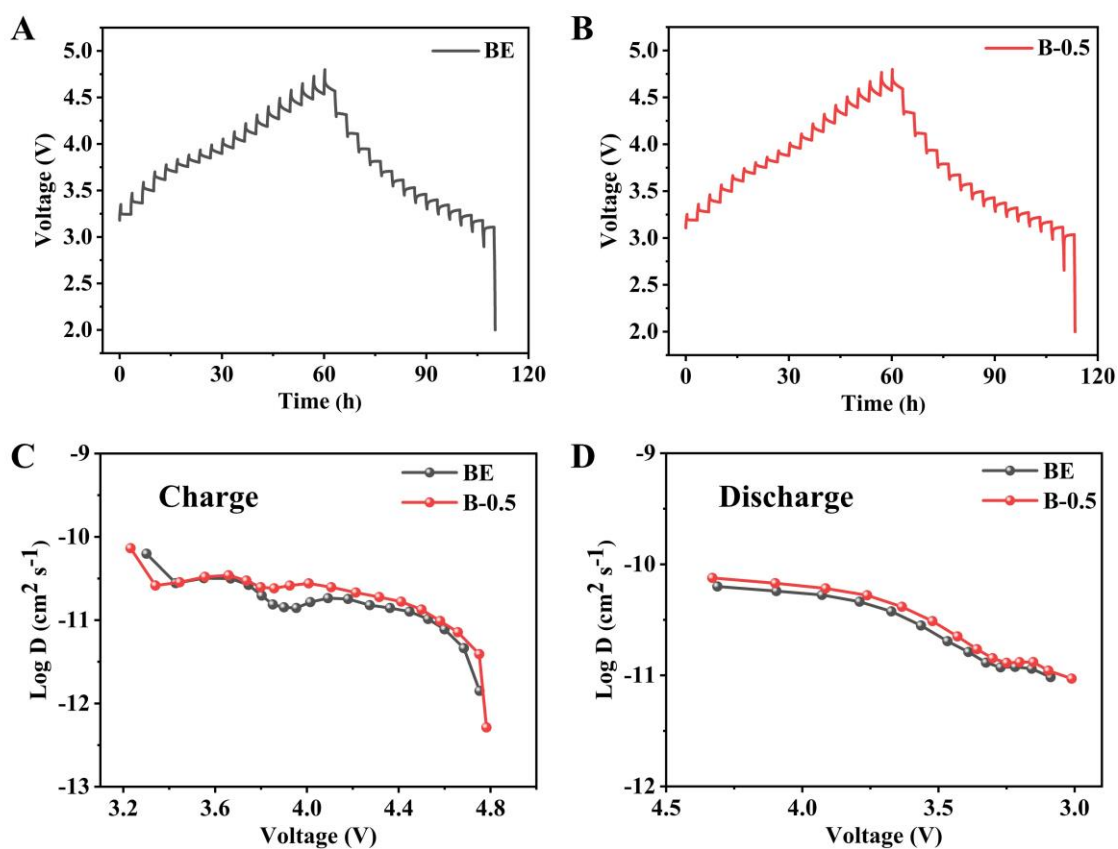
Supplementary Figure 9. Cycling performance of Li||LRM cells with different electrolytes at 3 C.



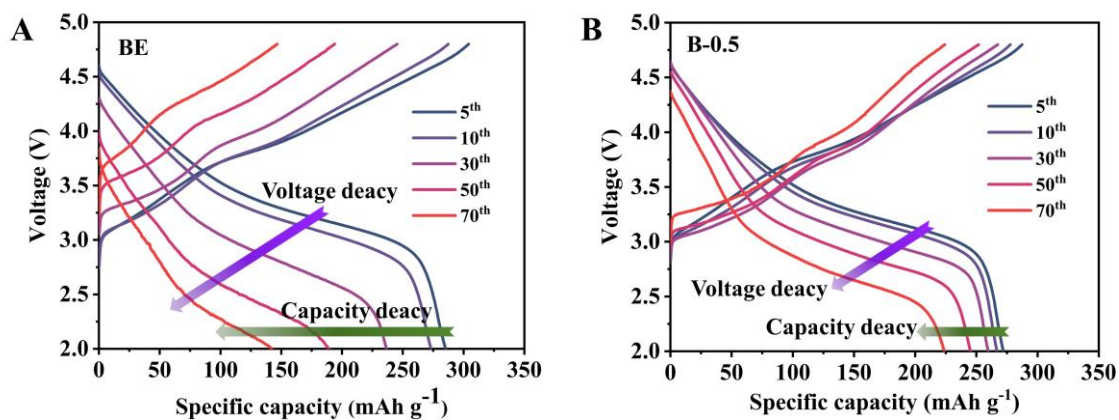
Supplementary Figure 10. Cycling properties of Li||LRM cells with different electrolytes at 5 C.



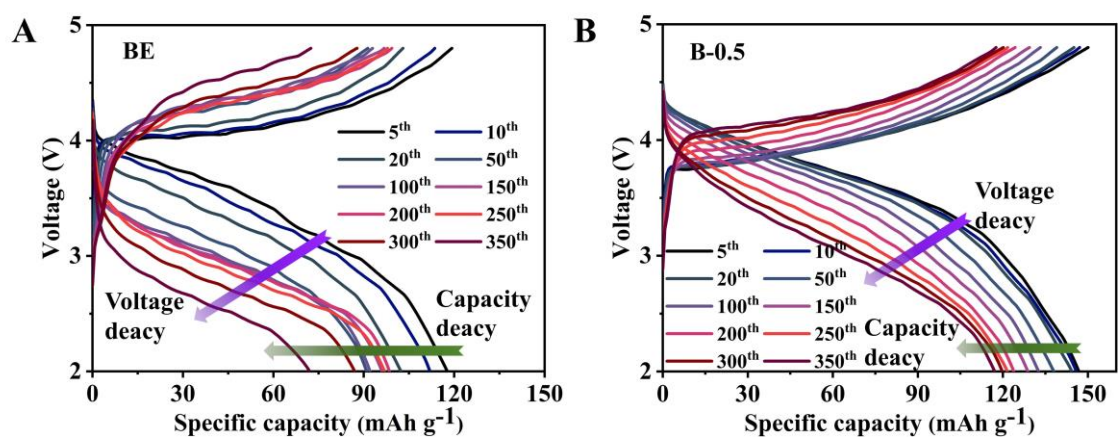
Supplementary Figure 11. Nyquist plots of Li||LRM cells after (A) 5 cycles and (B) 100 cycles.



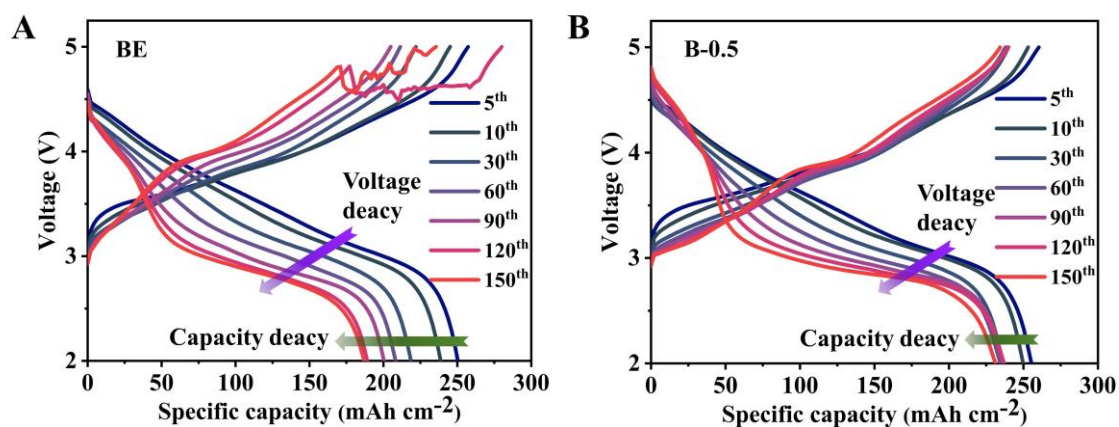
Supplementary Figure 12. The voltage curves of the GITT after 10 cycles in (A) BE and (B) B-0.5. The corresponding calculated Li^+ diffusion coefficient during the (C) charging and (D) discharging process.



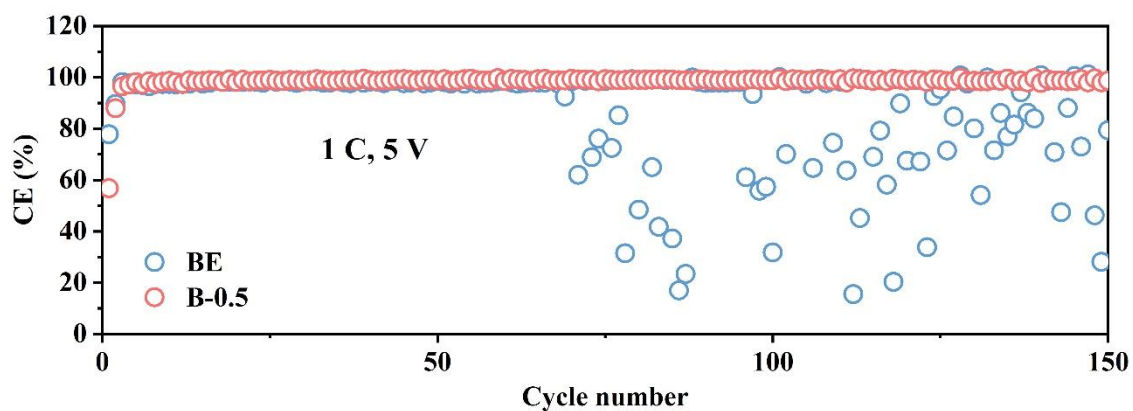
Supplementary Figure 13. Charge-discharge curves (A) without and (B) with the additive in the voltage range of 2-4.8 V at 1 C and 55 °C.



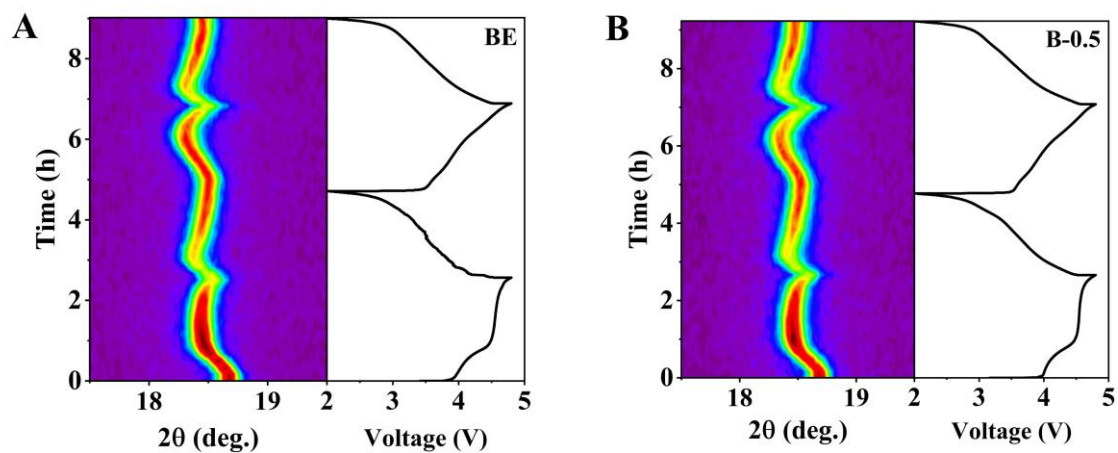
Supplementary Figure 14. Charge-discharge curves (A) without and (B) with the additive in the voltage range of 2-4.8 V at 0.33 C and -15 °C.



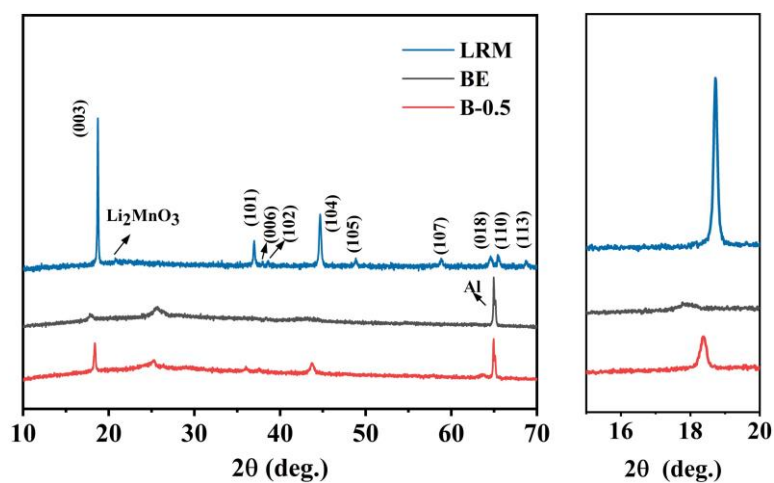
Supplementary Figure 15. Charge-discharge curves (A) without and (B) with the additive at 1 C in the voltage range of 2-5 V.



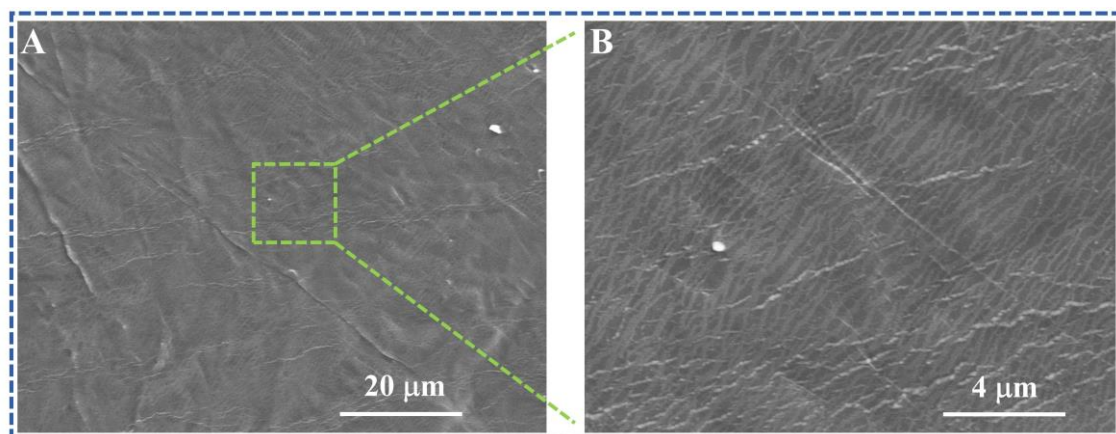
Supplementary Figure 16. The CEs of Li||LRM cells with different electrolytes during cycling at 1 C and 2-5 V.



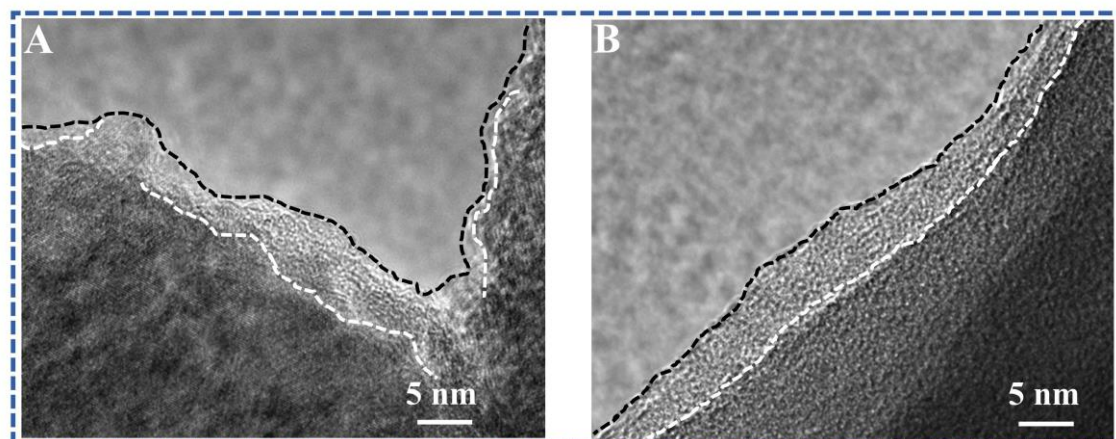
Supplementary Figure 17. The 2D contour plots and charge-discharge curves of the in-situ XRD patterns using (A) BE and (B) B-0.5 electrolytes.



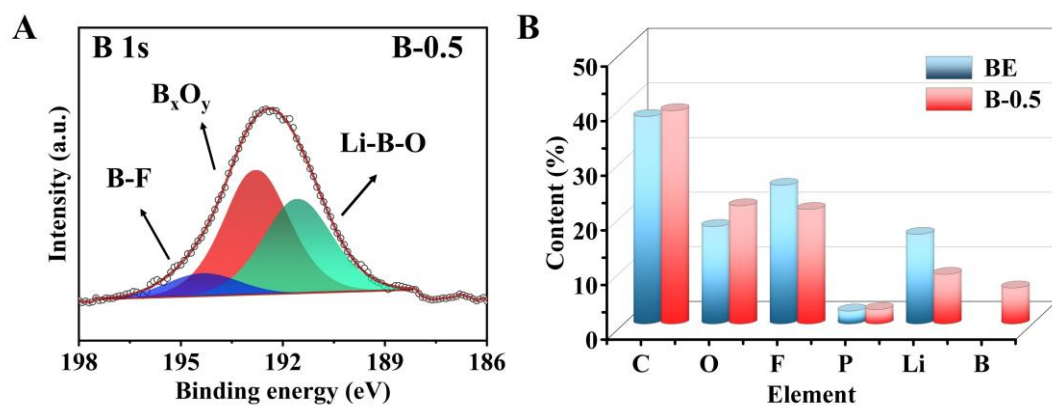
Supplementary Figure 18. XRD patterns of pristine LRM cathode and the cycled electrodes in different electrolytes.



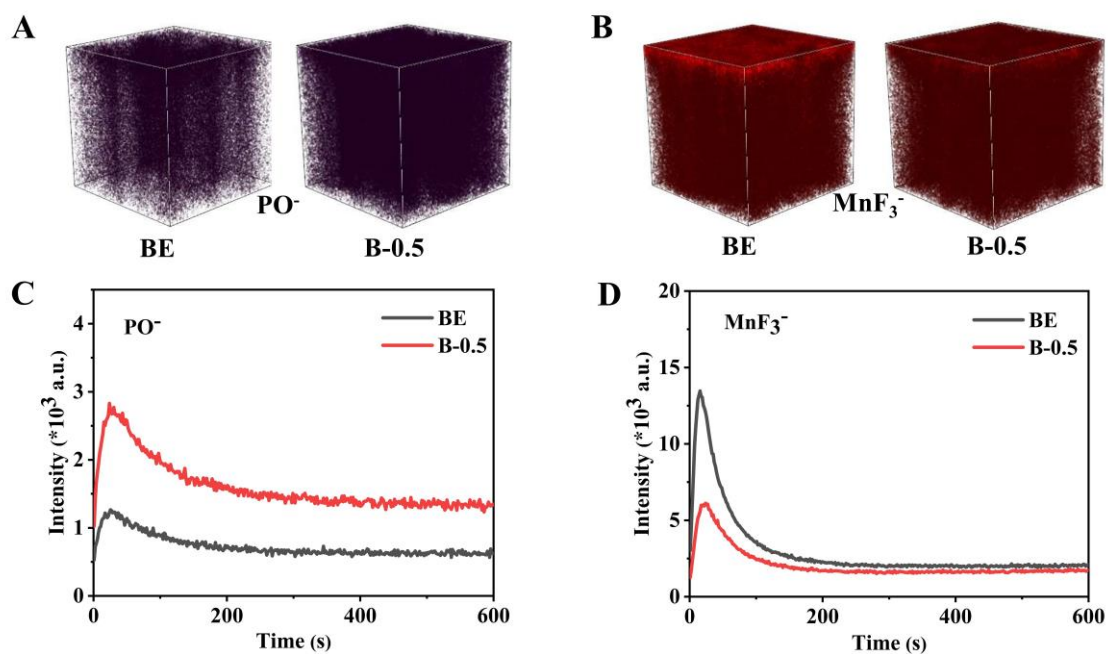
Supplementary Figure 19. (A) SEM image of fresh Li metal. (B) The corresponding local enlarged image.



Supplementary Figure 20. TEM images of the cycled LRM cathodes using (A) BE and (B) B-0.5 electrolytes.



Supplementary Figure 21. (A) XPS spectra of B 1s for the cycled cathode in B-0.5. (B) Comparison of element contents in CEI layer at different electrolytes.



Supplementary Figure 22. (A, B) TOF-SIMS 3D render images of fragments onto the cycled cathodes in BE and B-0.5. (C, D) The corresponding depth curves of (C) PO^- and (D) MnF_3^- species.

Supplementary Table 1. The prices of commonly used B-contained additives

Additives	Product No.	Purity	Cost (\$ kg ⁻¹)
LiODFB	L303675	99%	1056.4
LiBOB	L120347	99%	594.3
LiBF ₄	L107397	98%	529.5
B ₂ O ₃	B278635	98%	68.8

Note: data from Manufacturer of Shanghai Aladdin Co., Ltd.