

A novel flame-retardant lithium fluoroborate salt for LNMO-graphite-based Li-ion batteries

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Experimental details

Physical analysis

¹¹B{¹H} and ¹⁹F{¹H} NMR data were collected using a Bruker Avance III 400; ¹H at 400.13 MHz, ¹¹B at 128.39 MHz and ¹⁹F at 376.54 ppm. The moisture content of the salts was measured by making a 0.1 ml 1 M DME solution of the salts and measuring its water content by Karl Fischer titration in a Metrohm 831 coulometer. The moisture content of the DME was measured to be 7±3 ppm.

LiONFtb synthesis

0.289 g (0.0413 mol) Li metal strips were collected in a 100ml two neck round bottom flask with 15 ml dimethylcarbonate (DMC, Sigma-aldrich) solvent under Ar atmosphere. In another vial, 10.7 g (0.0454 mol) of nonafluoro *tert*-butanol [(CF₃)₃COH], HONFtb (Alfa Aesar) and 15 ml of DMC were mixed together. The mixing of HONFtb with DMC is exothermic, therefore the HONFtb were added to DMC dropwise. The flask with Li metal and DMC was stirred in a cold bath of dry ice and acetone, where the mixture of the HONFtb and DMC was slowly added to the Li metal over 3 h. After the addition of the HONFtb had been completed, the cold bath was removed, which allowed the solution to return to room temperature slowly, with subsequent release of hydrogen gas. The solution was further stirred for 2 h and the solvent was removed by distillation under vacuum (RT, 10-2 mbar). After obtaining the solid sample, the salt was sublimed at 100 °C under a vacuum, which was found to yield crystals of dry LiONFtb salt, which was stored under the Ar atmosphere. NMR spectra of the LiONFtb salt [LiOC(CF₃)₃] in DMSO-D₆: ¹⁹F NMR (376.54 MHz, DMSO-D₆, RT), d = -75 ppm (s, -CF₃). NMR analysis of the LiONFtb salt is consistent with literature.¹. The moisture content of the LiONFtb salt was tested as the 1 M LiONFtb solution in EC/DMC by Karl Fisher analysis to be < 20 ppm.

LiBF₂(ONFtb)₂ synthesis

Lithium tetrafluoroborate (LiBF₄) was obtained from Sigma-Aldrich. 0.468 g of LiBF₄ (5 mmol) was dissolved in 5 ml of EC/DMC (30:70, w/w) mixture to prepare the 1 M LiBF₄ in EC/DMC solution in three vials. 2 (10 mmol, 2.42 g), 3 (15 mmol, 3.63 g) and 4 (20 mmol, 4.84 g) equivalents of LiONFtb was added to the respective vials, and stirred at 40°C for 2 days, followed by centrifugation to isolate the white precipitate. Afterwards, the clear filtrates were tested by ¹¹B and ¹⁹F NMR analysis. Since both the prepared (LiONFtb) and the purchased (LiBF₄) precursors have <20 ppm of moisture, the filtrate solution did not contain any residual moisture and, therefore, has been directly used as electrolytes in Li batteries in the following section. The room temperature ionic conductivity of the 1 M LiBF₂(ONFtb)₂ in EC/DMC was found to be 6.2 ± 0.2 mS/cm, which was lesser than that of 1 M LiPF₆ in

EC/DMC (10.9 mS/cm). The Li plating stripping study of the 1 M LiBF₂(ONFtb)₂ in EC/DMC showed a lesser current density of Li stripping, which was found to be consistent with this observation (Fig. S14). However, as observed in Fig. 2a, the cell cycling performance of the LiBF₂(ONFtb)₂ is similar to that of LiPF₆ which further suggests that the lower ionic conductivity of the novel salt does not significantly affect its battery cycling due to its better oxidative stability and interface forming capability.

LiBF₂(ONFtb)₂ electrochemical characterisation

The electrochemical stability of the novel salt solution, as-synthesised, was tested in a VMP3 potentiostat. The Oxidative stability was tested in a configuration where glassy carbon (GC) was used and the working electrode (WE) and Pt and Li metal strips (Sigma Aldrich) were used as the counter and reference electrode (CE and RE) respectively at 1 mV/s scan rate. The oxidative stability was tested by a linear sweep voltammetry experiment from open circuit voltage (OCV) to 5 V vs. Li followed by a cyclic voltammetry between 3 V and 5 V vs. Li. Ni was used as a working electrode for the Li plating stripping study which was carried out using CV analysis starting from OCV and between -0.3 V and 0.5 V vs. Li. Pt and Li metals were used as CE and RE in the Li plating-stripping studies.

Coin cell cycling

LiNi_{0.5}Mn_{1.5}O₄ (or LNMO) powder was procured from Haldor Topsoe. The electrodes were prepared by preparing a slurry composed of LNMO powder, PVDF, and conductive carbon (C65, Timcal) in N-methyl 2-pyrrolidone (NMP) solvent in a 90:5:5 gravimetric ratio, followed by drying under vacuum at 70 °C. The charge and discharge capacities and C rates of the LNMO cell were calculated based on the theoretical capacity of LNMO (148 mAh/g). Graphite anode foil was purchased from Customcells with areal loading of 1.1 mAh/cm² areal loading (90% active material). 10 mm graphite anodes have been paired with 8 mm cathodes in all coin cells. All coin cells were prepared in 2032 cells with Celgard 3501 as the separator, 1 mm spacer, and 1.4 mm wave washer. 45 µl of electrolytes have been used in all coin cells. All cells were cycled in a Neware battery tester at room temperature with C/20 formation cycle (cc-cc) and 1C long-term cycling (cccv chg – cc dchg, C/20 cutoff chg). the cycling protocol in this work is consistent with the latest literature on LNMO battery cycling protocol at 1 mA/cm² current density.²⁻⁴

(a) Conventional Li salts for battery applications

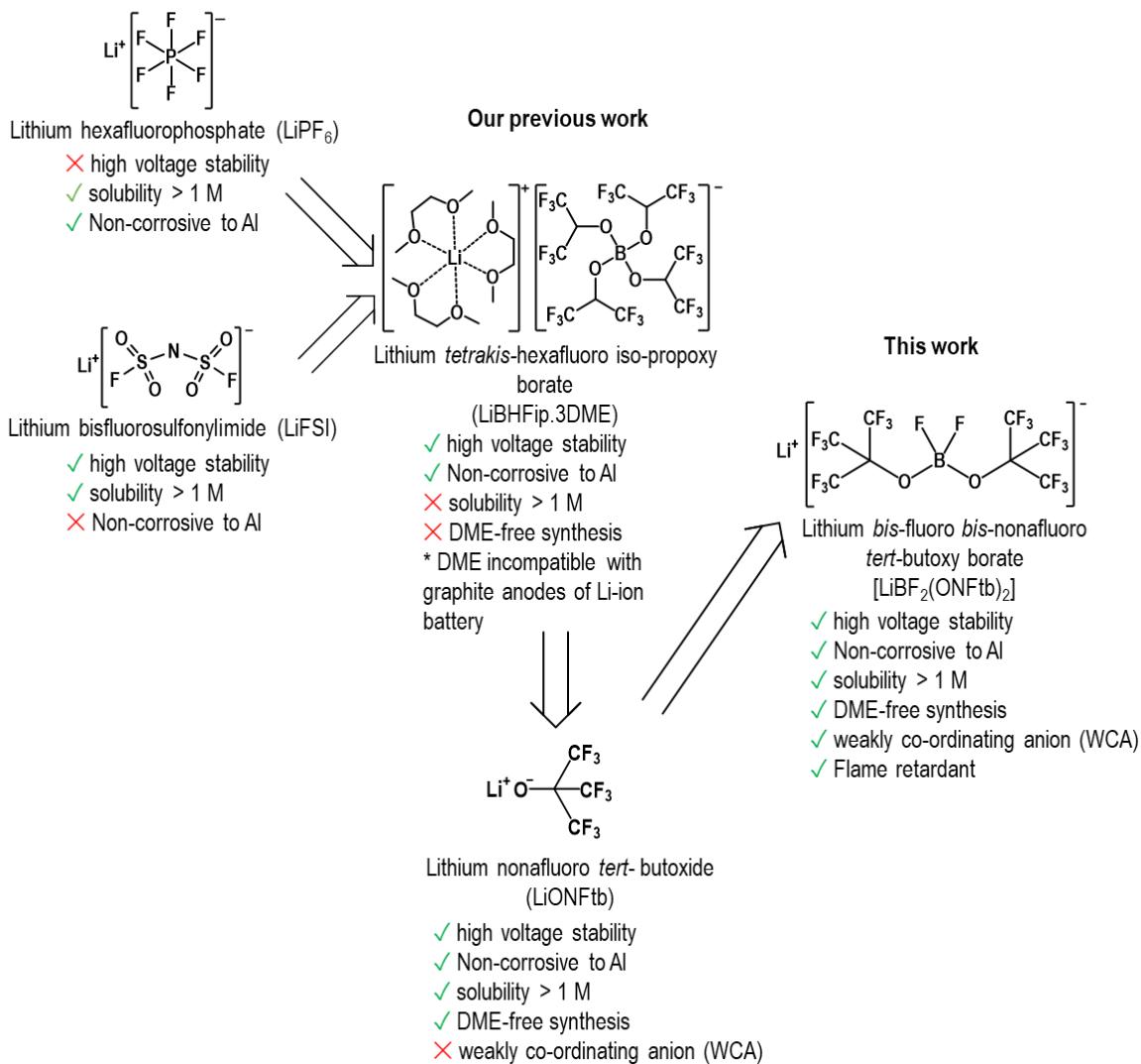


Figure S1: The limiting features of commercially available Li salts and the rationale for designing a novel Li salt in comparison to our previous work

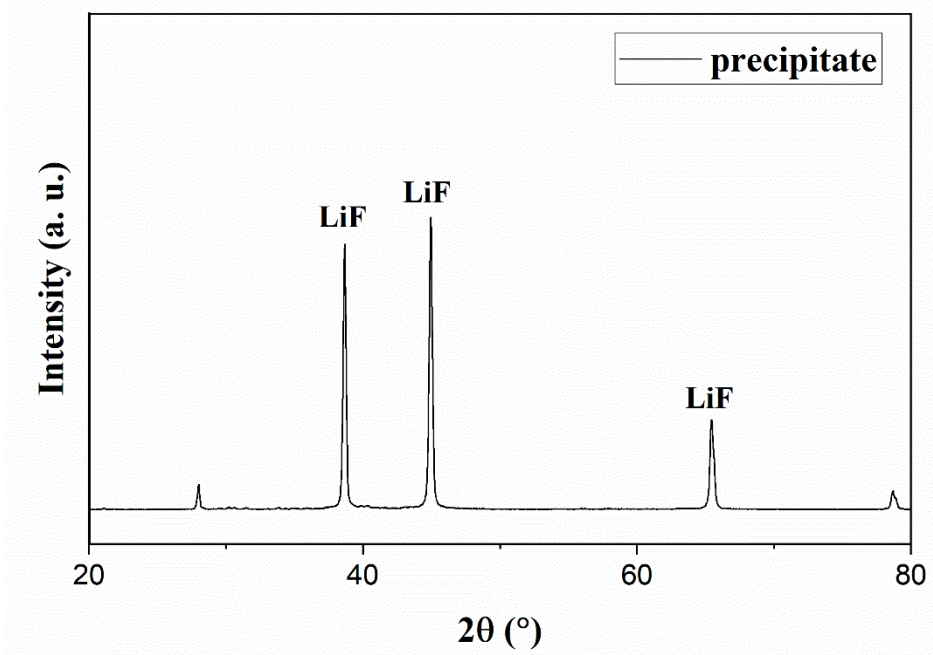


Figure S2: X-ray diffraction pattern of the precipitate

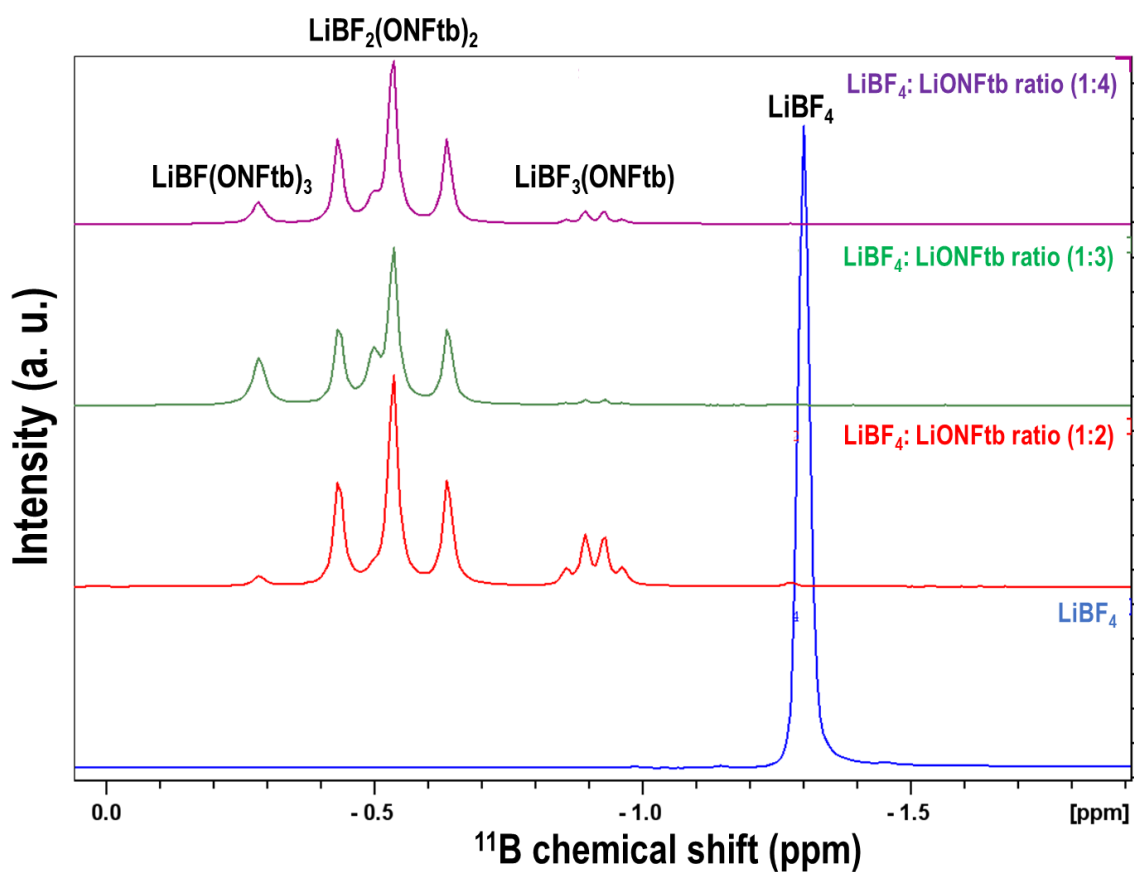


Figure S3: ^{11}B NMR spectra of the LiBF_4 precursor and solutions with various ratios of LiBF_4 and LiONFtb .

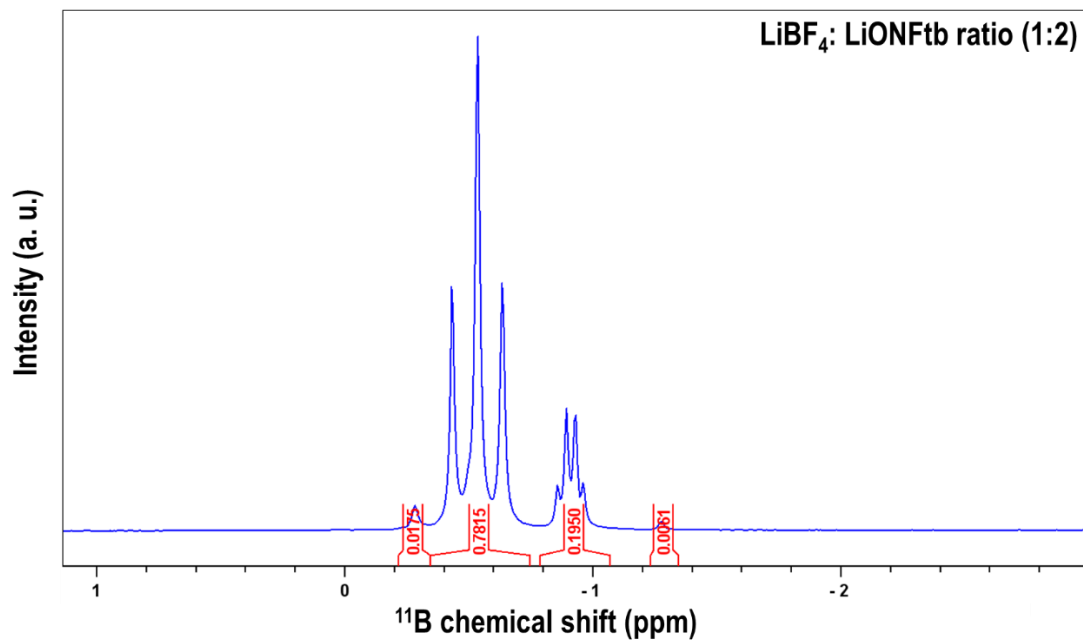


Figure S4: ¹¹B NMR spectra of the solution with 1:2 molar ratio of LiBF₄ and LiONFtb.

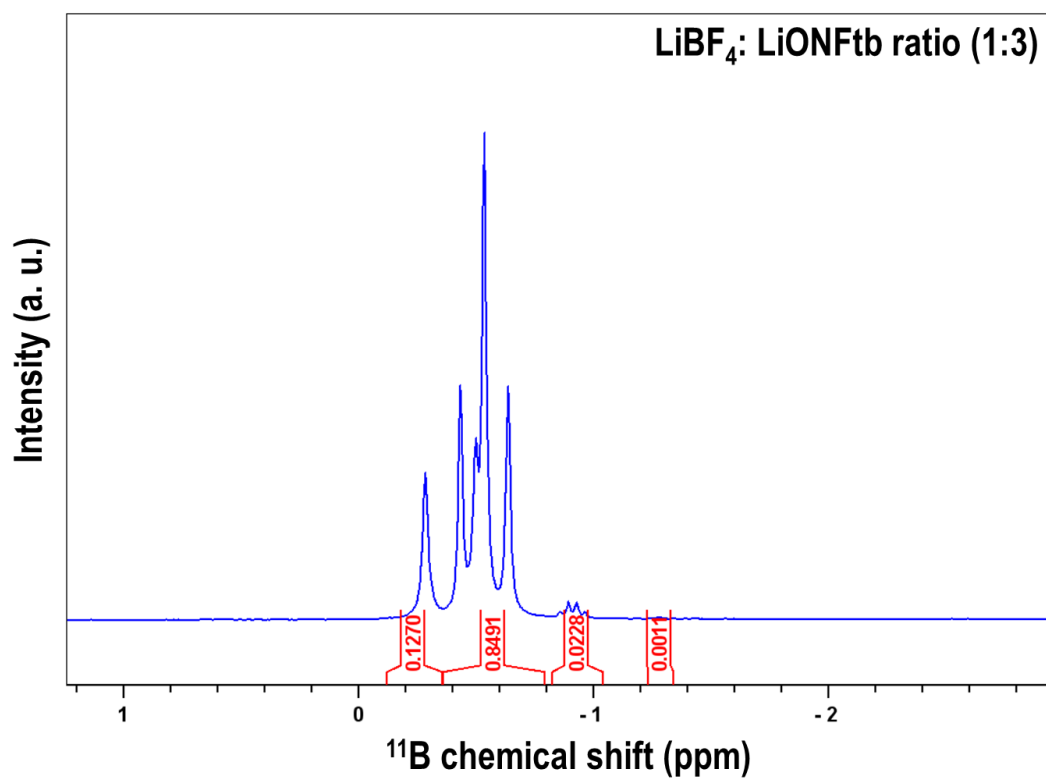


Figure S5: ¹¹B NMR spectra of the solution with 1:3 molar ratio of LiBF₄ and LiONFtb.

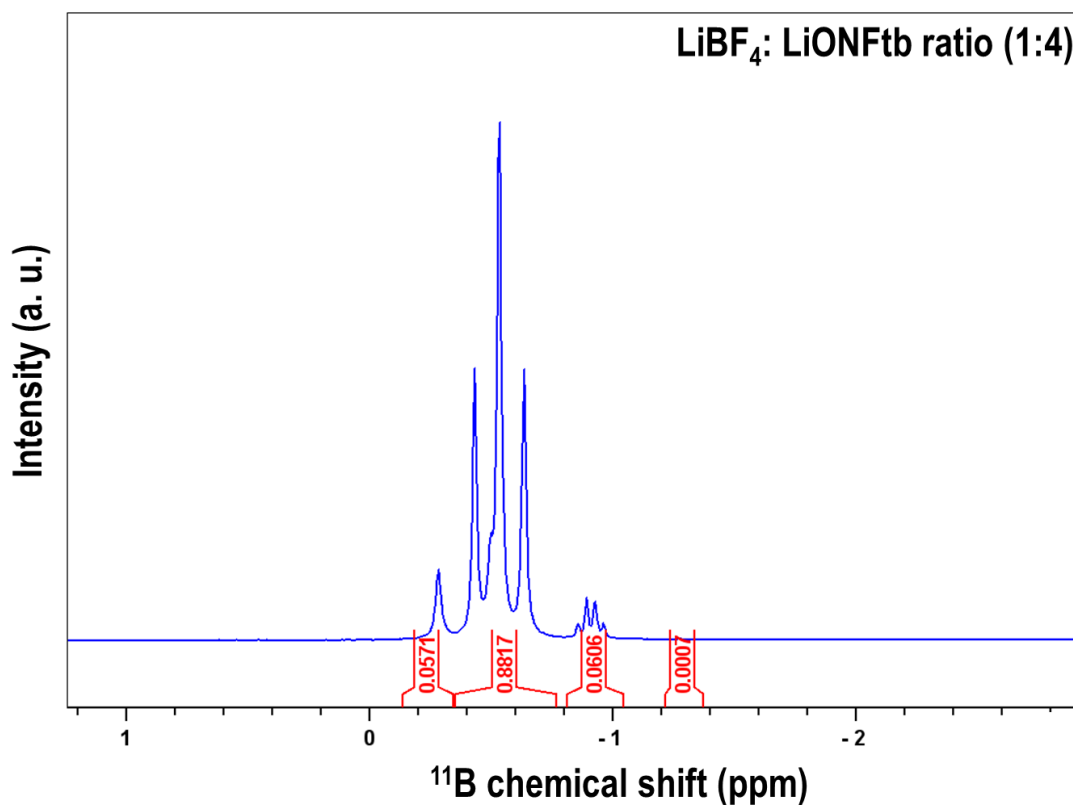


Figure S6: ¹¹B NMR spectra of the solution with 1:3 molar ratio of LiBF₄ and LiONFtb.

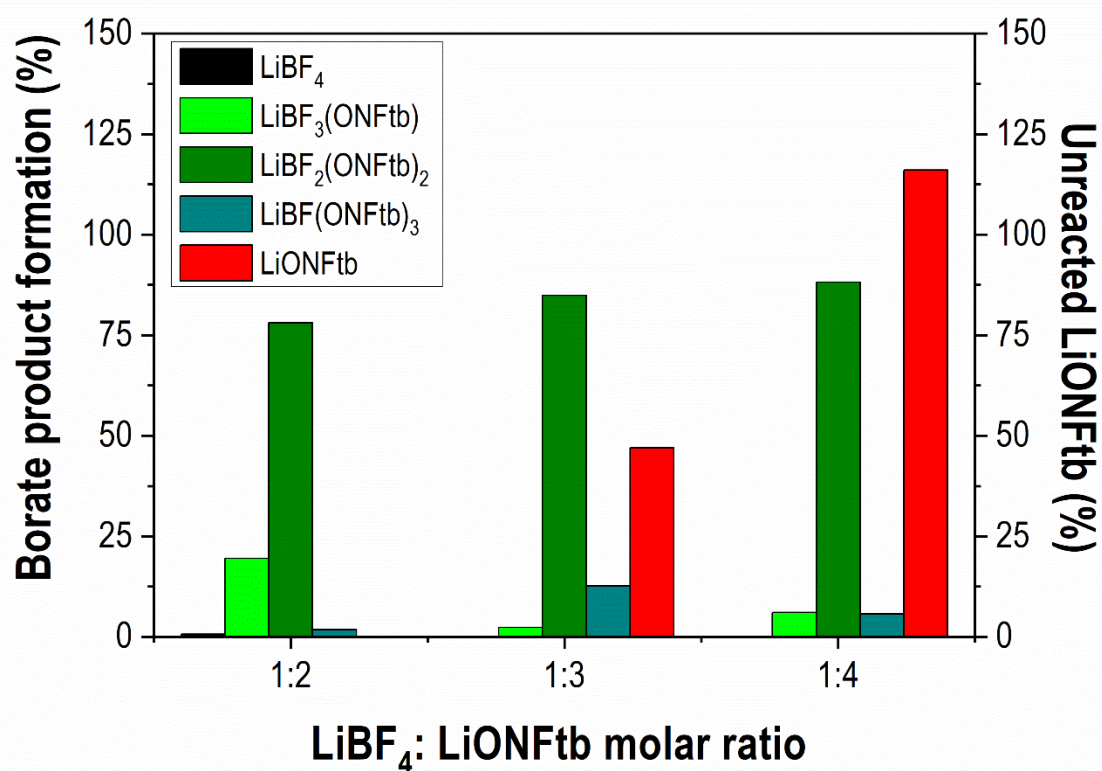


Figure S7: (a) Synthesis pathway of LiBF₂(ONFtb)₂ from the solution of LiBF₄ and LiONFtb. (b) Reaction by-products formed during the synthesis of LiBF₂(ONFtb)₂. (c) The ratio of different borate species (LiBF₄, LiBF₃(ONFtb), LiBF₂(ONFtb)₂, LiBF(ONFtb)₃) according to the peak integration

analysis of ^{11}B NMR spectra. Remnant LiONFtb in the solution, as detected in the ^{19}F NMR analysis, is represented in the red bar charts along the right Y axis.

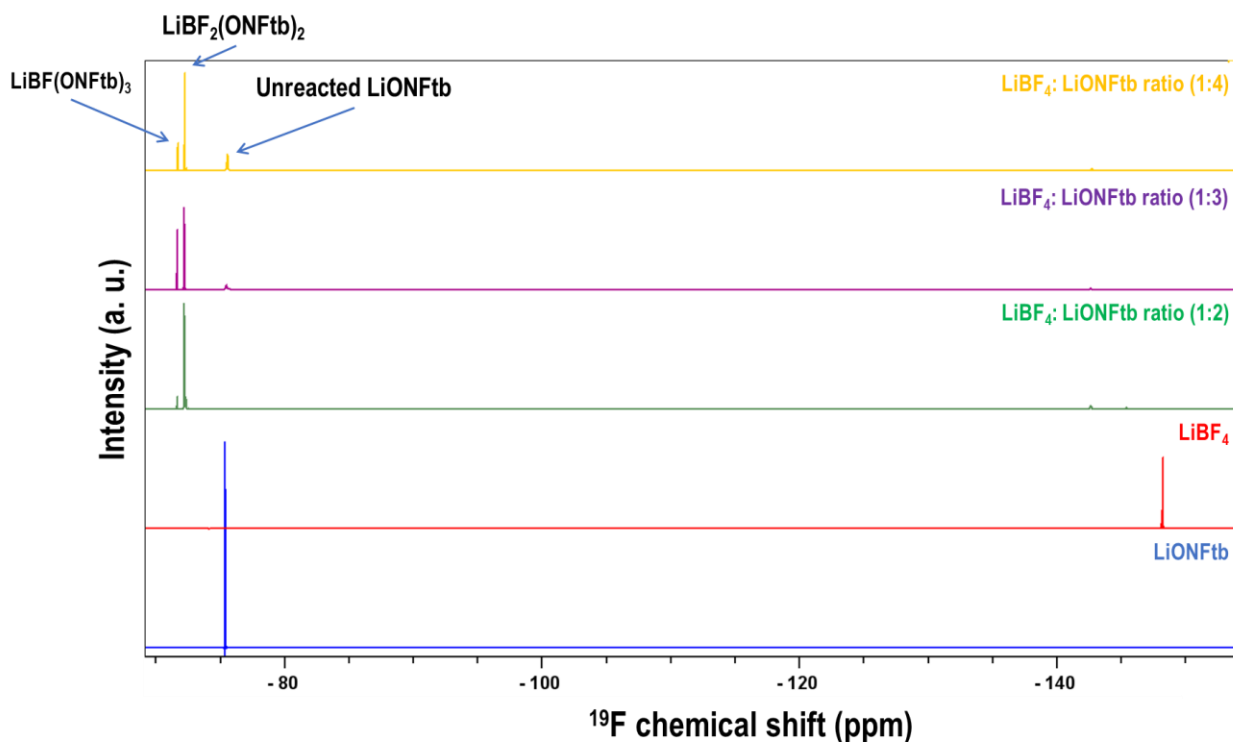


Figure S8: ^{19}F NMR spectra of the LiBF_4 precursor and solutions with various ratios of LiBF_4 and LiONFtb.

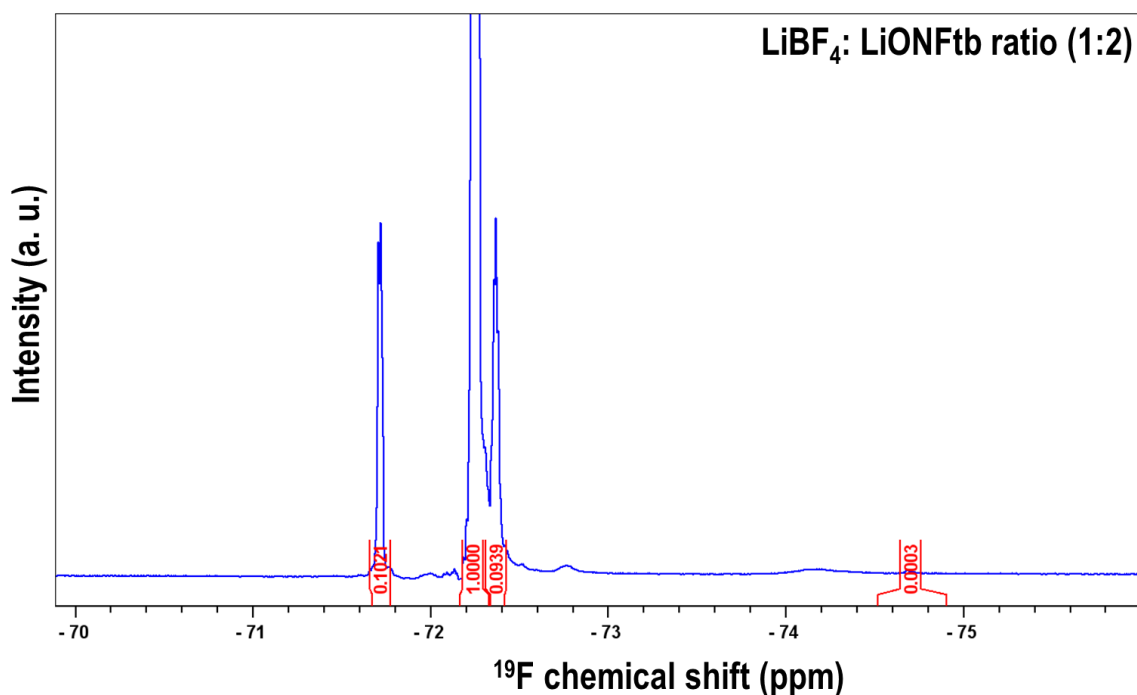


Figure S9: ^{19}F NMR spectra of the solution with 1:2 molar ratio of LiBF_4 and LiONFtb.

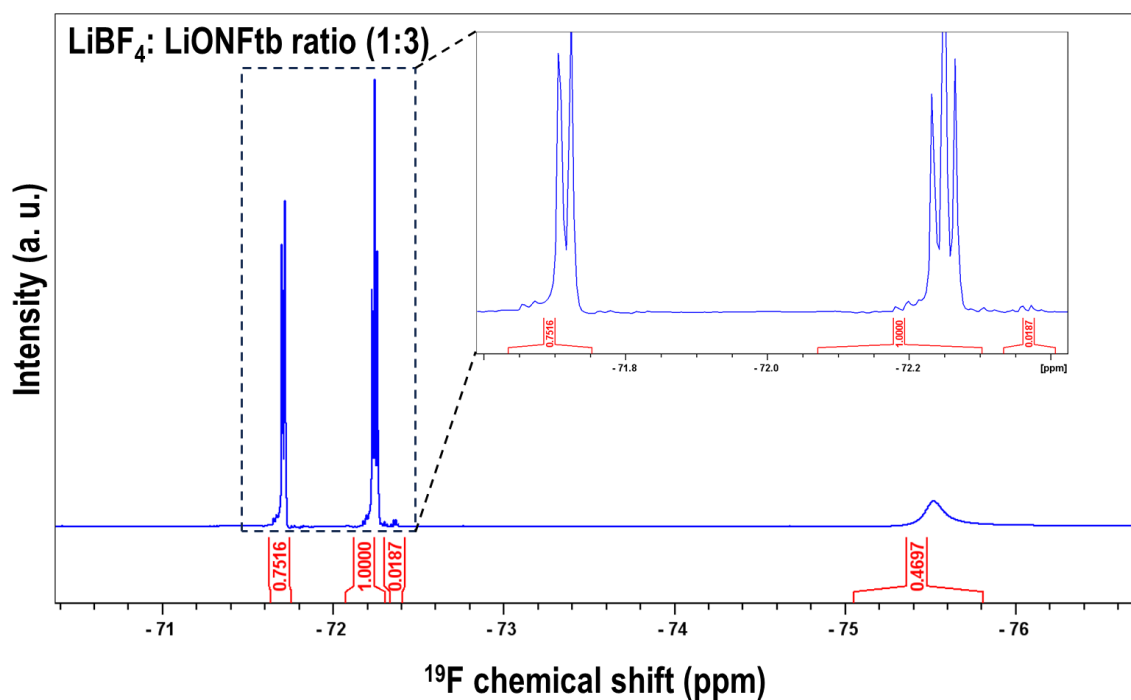


Figure S10: ¹⁹F NMR spectra of the solution with 1:2 molar ratio of LiBF₄ and LiONFtb. The weak quarter around -72.4 ppm can be assigned to the (-ONFtb) group of the LiBF₃ONFtb, as suggested by Qiao et al.¹ Therefore the triplet and doublet at -72.25 ppm and -71.7 ppm can be assigned to LiBF₂(ONFtb)₂ and LiBF(ONFtb)₃ respectively.

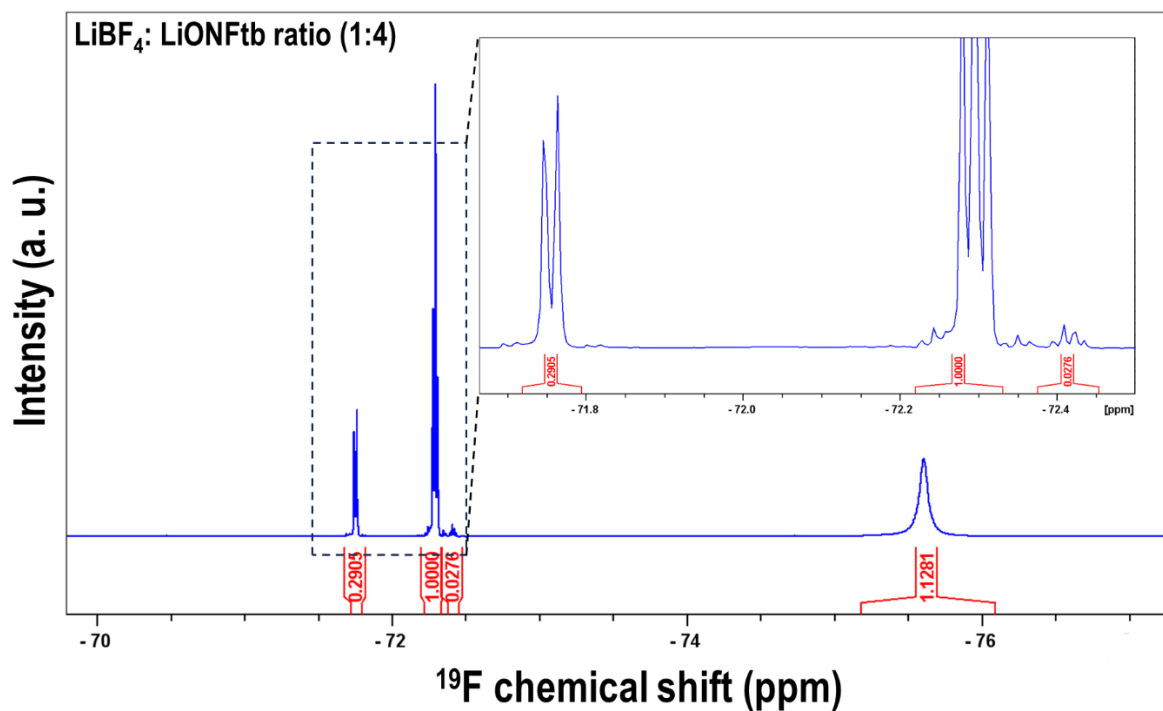


Figure S11: ¹⁹F NMR spectra of the solution with 1:4 molar ratio of LiBF₄ and LiONFtb.

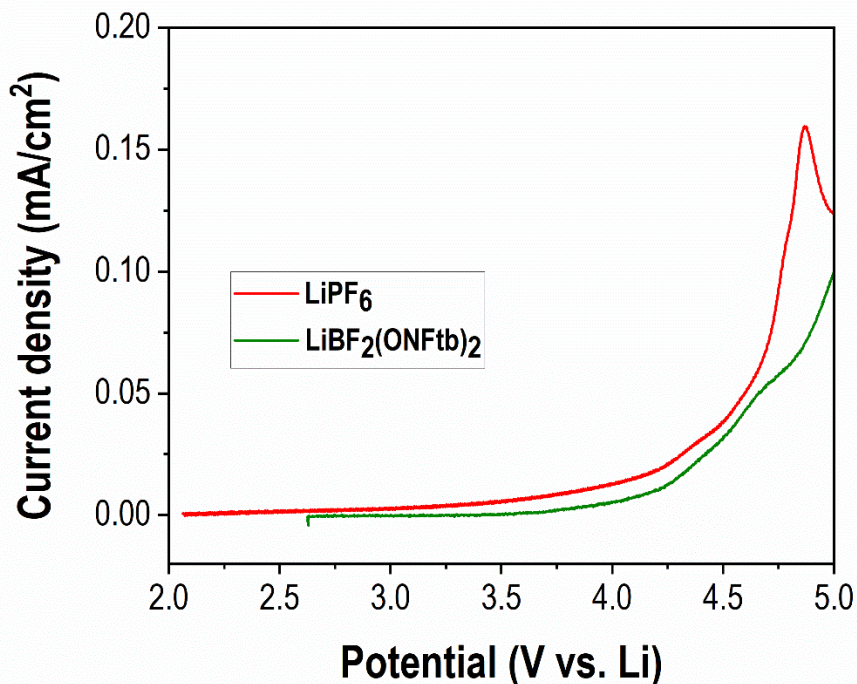


Figure S12: Oxidative stability analysis by linear sweep voltammetry of 1 M $\text{LiBF}_2(\text{ONFtb})_2$ (green trace) and 1 M LiPF_6 (red trace) in EC/DMC solution on a glassy carbon working electrode, Pt counter and Li reference electrode at 1 mV/s scan rate between open circuit potential (OCV) and 5 V vs. Li.

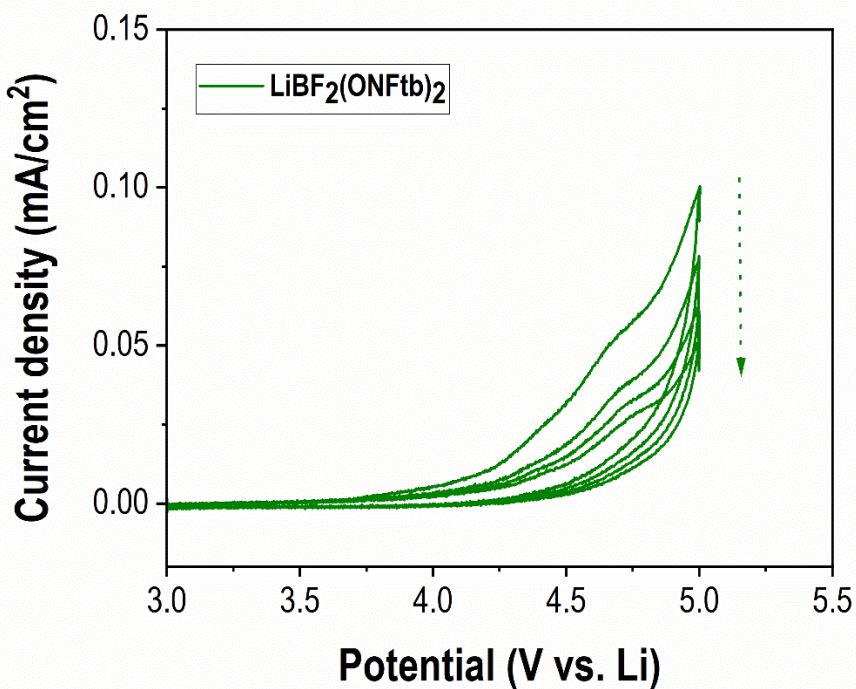


Figure S13: Cyclic voltammetry of 1 M $\text{LiBF}_2(\text{ONFtb})_2$ (green trace) in EC/DMC solution on a glassy carbon working electrode, Pt counter and Li reference electrode at 1 mV/s scan rate between 3 V and 5 V vs. Li.

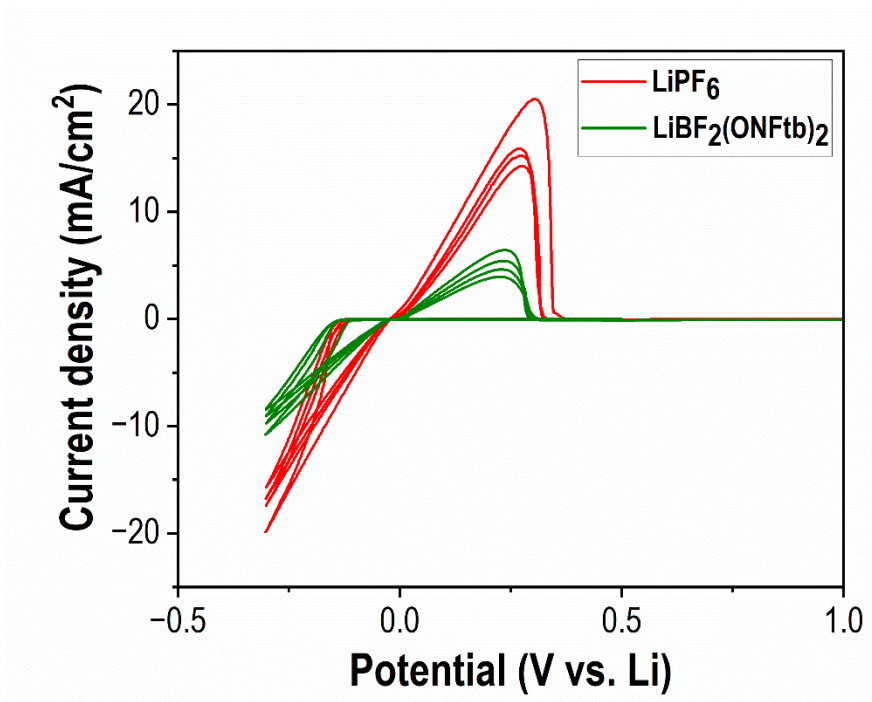


Figure S14: Li plating stripping cyclic voltammetry analysis of 1 M $\text{LiBF}_2(\text{ONFtb})_2$ (green trace) and 1 M LiPF_6 in EC/DMC solution on a glassy carbon working electrode, Pt counter and Li reference electrode at 1 mV/s scan rate between -0.3 V and 0.5 V vs. Li.

References

1. L. Qiao, Z. Cui, B. Chen, G. Xu, Z. Zhang, J. Ma, H. Du, X. Liu, S. Huang, K. Tang, S. Dong, X. Zhou and G. Cui, *Chem Sci*, 2018, **9**, 3451-3458.
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