Understanding the electrolyte additive properties of lithium nonafluoro-tert-butoxide for its application in high-voltage $LiNi_{0.5}Mn_{1.5}O_4$-graphite batteries

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Experimental section

Synthesis and purification of LiONFtb

The detailed synthesis of LiONFtb salt has been recently reported by our group(1) as an intermediate in the preparation of a novel Li borate salt, $LiBF_2(ONTfb)_2$. However, the properties of LiONFtb itself were not explored in that work. Briefly, the LiONFtb salt was synthesised by a reaction between equimolar amounts of Li metal and nonafluoro-*tert*-butyl alcohol in a mixture of ethylene carbonate-dimethyl carbonate (EC/DMC) solution in a dry ice-acetone bath. In a typical synthesis method, 0.289 g (0.0413 mol) Li metal strips, 10.7 g (0.0454 mol) of nonafluoro tert-butanol [$(CF_3)_3COH$], HONFtb (Alfa Aesar) and 15 ml of EC/DMC (30:70 w/w) were considered. The reaction is exothermic and involves hydrogen release, therefore addition of the fluorinated alcohol in a dry ice-acetone bath (-78°C) is crucial. The salt was synthesised in an EC/DMC solution mixture to make the salt compatible with the battery application. It is noteworthy here that the acetonitrile has also been tested as a replacement for the carbonate solution, however, was found to be incompatible with Li metal and undergo unwanted side reaction, resulting a brownish-green precipitate. The resulting solution was vacuum distilled to obtain the salt, which was purified by sublimation at ~110°C. The pure crystal LiONFtb salt was found to co-crystallise with EC solvent molecules. The purity of the LiONFtb yield was analysed by ^{19}F NMR analysis of a salt solution prepared in DMSO-D_6. (purity 99%, yield 82%). Thermal stability of the LiONFtb salt was studied using a Mettler Toledo TGA/DSC 1 STARe system. Samples were heated under dynamic TGA with heating rate of 10 °C min−1 over a temperature range of 20 to 180 °C under nitrogen. The FTIR spectra were acquired by a Bruker ATR-FTIR spectrometer, where each measurement consisted of 64 scans with 4 cm^{-1} resolution within the range of 4000–600 cm^{-1}.

Coin cell preparation

$LiNi_{0.5}Mn_{1.5}O_4$ (or LNMO) and graphite-coated foils with areal capacity of 2 mAh/cm^2 and 2.2 mAh/cm^2 respectively, were procured from Customcells. The active material loading of the cathodes has been 90%. The charge and discharge capacities and C rates of the LNMO cells were calculated based on the theoretical capacity of LNMO (148 mAh/g). 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, from a 2 g electrolyte batch of each samples.

All cells were cycled in a Neware battery tester at room temperature with C/20 formation cycle (cc-cc) and C/2 long-term cycling (cccv chg – cc dchg, C/20 cutoff chg).

Characterisation

The cyclic voltammetry, linear sweep voltammetry and chronoamperometry analysis were carried out by a Biologic VMP3 potentiostat. The LSV of the Al-Li cells were carried out from OCV to 5 V vs. Li at a 1 mV/s scan rate followed by CA analysis at 5 V for 180 min. The cyclic voltammetry of the LNMO-Li and graphite Li cells were studied in a 2032 coin cell with celgard 3501 separators and 380 mm thick Li foil (the coin cell preparation details were the same as that followed for long-term cycling). The CV tests were started from OCV and cycled between 4.9-3.5 V for the LNMO-Li cell and 0.01-3 V for the graphite Li cell at the scan rate of 0.2 mV/s. The morphological changes of the LNMO cathode post-cycling were studied by SEM analysis after recovering them from the cycled coin cells and washing them with DMC solvent. FEI Nova NanoSEM 450 FEG SEM and a JEOL JSM-7001F FEG SEM were used for the SEM, EDS and elemental mapping analysis at an accelerating voltage (HT) of 15 kV and energy dispersive spectrometer that was attached to the microscope. The post-cycling samples for SEM characterisation were prepared by adhering the samples to SEM specimen holders with double-sided conducting carbon tapes and maintaining them under an inert environment before being transferred into the microscope.

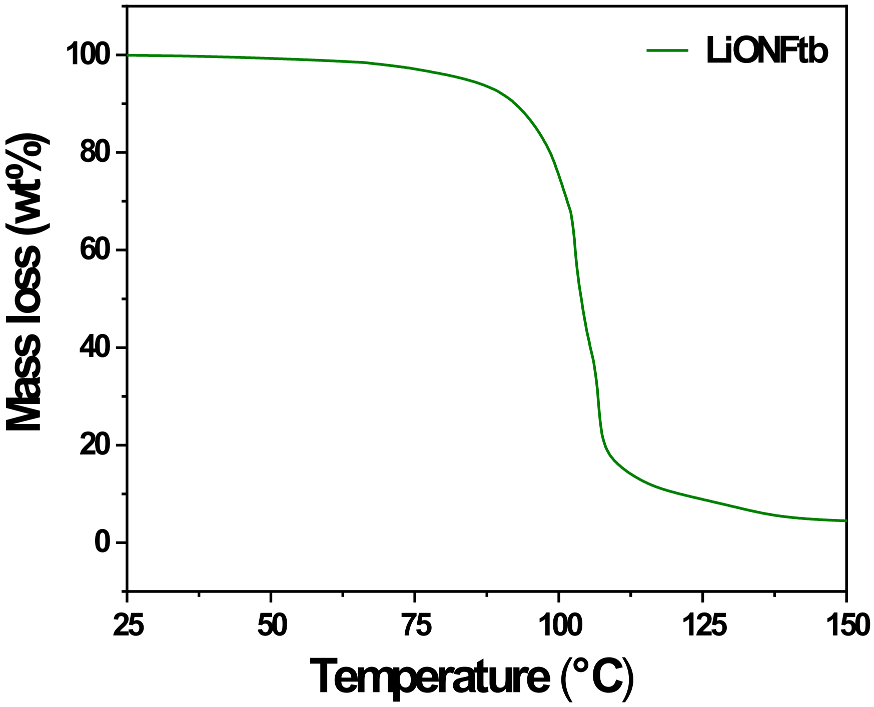

Figure S1: Thermogravimetric analysis (TGA) of the LiONFtb salt at 10°C/min scan rate

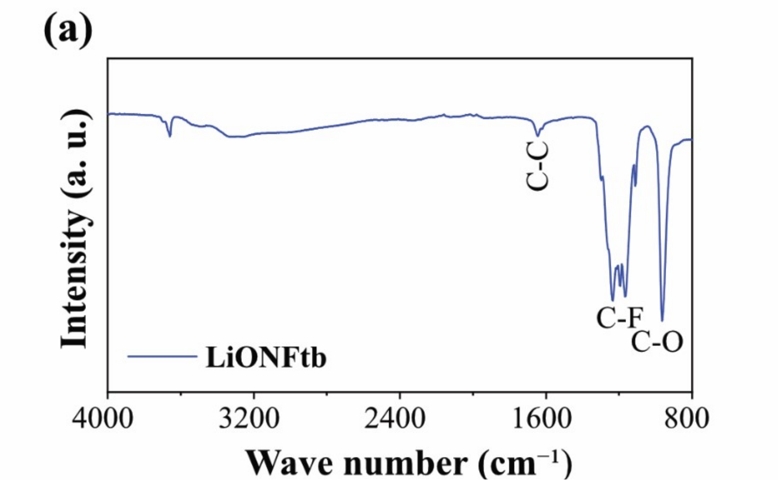

Figure S2: The FTIR spectra of the LiONFtb salt show its characteristic features.

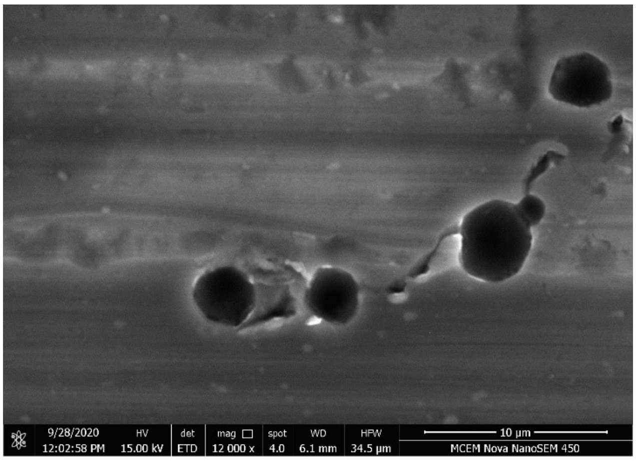

Figure S3: SEM image of Al foil recovered from LSV-CA analysis of Al-Li cell with LP30 electrolyte

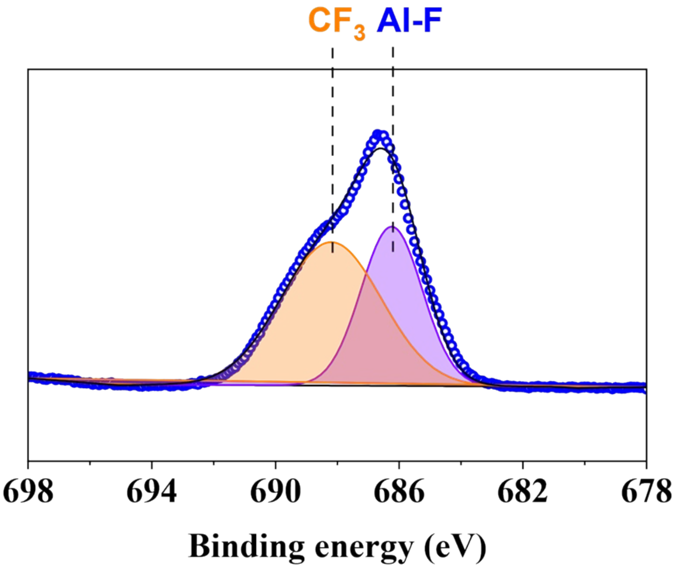

Figure S4: F 1s XPS analysis of the Al surface recovered from the Al-Li cells with 1 M LiONFtb in EC/DMC electrolyte

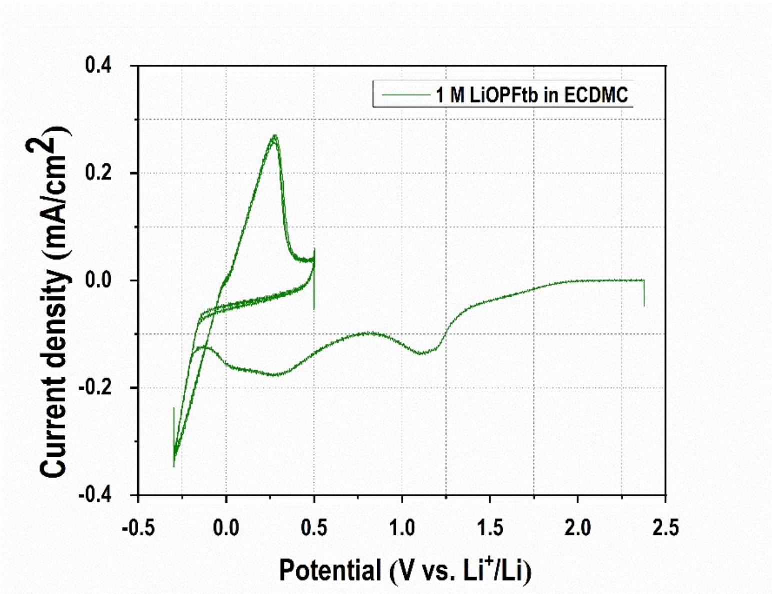

Figure S5: The cyclic voltammetry of 1 M LiONFtb in EC/DMC (30:70, w/w) on Ni working electrode, Pt counter and Li reference electrode at a 1 mV/s scan rate.

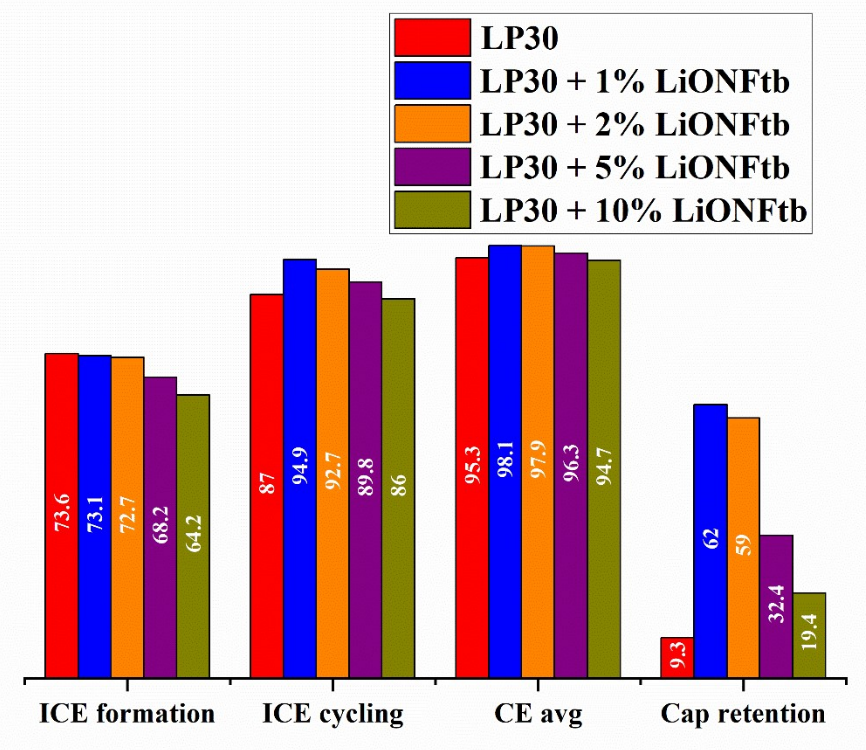

Figure S6: Summary of the initial coulombic efficiency during formation (ICE formation of the C/20 cycle), first cycle (i.e., C/2 cycling) coulombic efficiency (ICE cycling), average coulombic efficiency over 100 cycles (CE avg) and capacity retention after 100 cycles (Cap retention) of the LNMO graphite cells reported in this work with LP30 and different LiONFtb additive ratio (1, 2 5 and 10%)

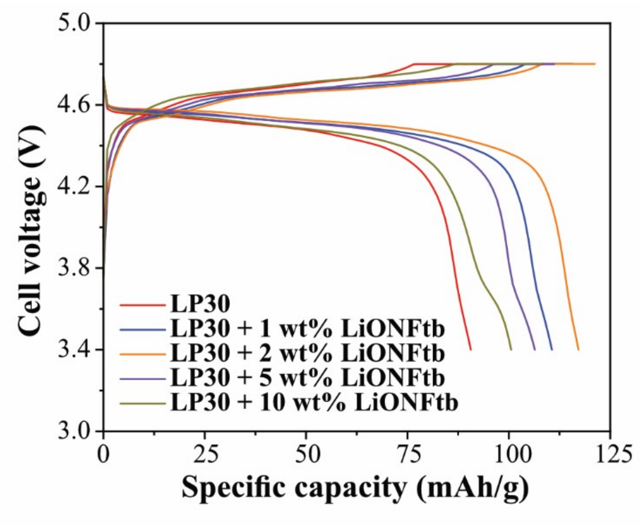

Figure S7: Charge discharge profile of the LNMO-graphite cell of the 5th cycle of C/2 cycling (with LNMO of areal capacity 2 mAh/cm^2).

Table S1: Recent literature on performance improvement of LNMO-graphite batteries with electrolyte additive application

	additive	Cathode areal capacity	Anode areal capacity	Cycling rate	Voltage range	Baseline electrolyte performance		Additive electrolyte performance	
		mAh/cm^2	mAh/cm^2			Initial dchg capacity (mAh/g)	Capacity retention (100 cycles)	Initial dchg capacity (mAh/g)	Capacity retention (100 cycles)
Hofmann et al.(2)	LiDFOB (0.5 M)	1.5	2.2	1C	3.5 - 5	120	92%	123	97.5%
Kim et al.(3)	LiTMSP(0.1 wt%)	0.24	0.45	0.1C	3.3-4.9	95	21%	103	39%
Gui et al.(4)	Flavone 91 wt%)	0.5	-	0.5C-1D	3.4-4.8	93	77%	100	90%
Lu et al.(5)	Triallyl phosphate (1 wt%)	1.1	1.2	0.2C	3.5-4.9	117	71%	-	84%
Wang et al.(6)	Triethyl borate (1 wt%)	-	-	0.3C	3.4-4.9	82	81%	110	86.5%
Zhu et al.(7)	tosylmethyl isocyanide (0.3 wt%)	-	-	0.3C	3.5-4.9	95	52%	115	70%
Xia et al.(8)	Trifluoromethylpyridine (LTFMP)-trimethyl borate (TMB) (0.2 wt%)	0.5	-	0.5C	3.5-4.8V	110	68%	110	87%
Li et al. (9)	3, 3, 3-trifluoropropylmethyldimethoxysilane (1 wt%)	0.3	-	1C	3-4.9V	-	60%	-	81%
Mu et al.(10)	4-methyl-1,3,2-dioxathiolane-2,2-dioxide (0.5 wt%)	~0.7	~1.2	0.5C	3.4-4.9V	88	71%	110	82%
Kazzazi et al.(11)	tris(trimethylsilyl) phosphite (TTSPi) and bis(2,2,2-trifluoroethyl) carbonate (TFEC)	~0.5	~0.5	0.5C	3-4.75V	110	18%	120	79%
Jamal et al.(12)	Tris(trimethylsilyl) Phosphite and Lithium Difluoro(oxalato)borate	1.5	1.8-2	0.3C	3.5-4.8V	110	45%	110	82%
This work	**LiONFtb (1 wt%)**	**2**	**2.2**	**0.5C**	**3.4-4.8V**	**105**	**9.2%**	**120**	**62%**

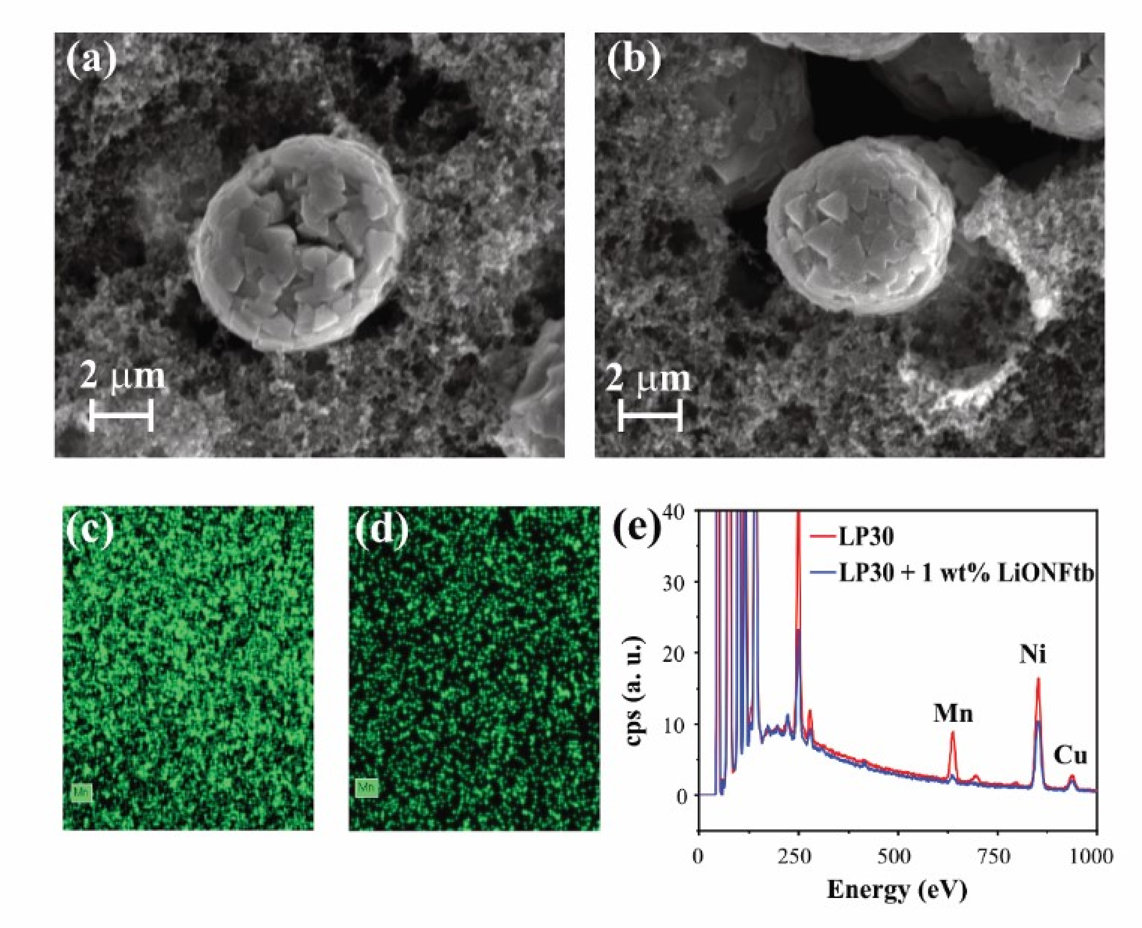

Figure S8: SEM image of the post cycling LNMO cathode particle recovered from LNMO-graphite cell with (a) LP30 and (b) LP30 + 1% LiONFtb electrolyte. Mn elemental mapping of the graphite anode recovered after cycling from the LNMO graphite cell with (c) LP30 and (d) LP30 + 1% LiONFtb electrolyte. (e) The energy dispersive spectroscopic (EDS) analysis of graphite recovered from the LNMO graphite cell with LP30 and LP30 + 1% LiONFtb electrolyte. The peak corresponding to Cu (anode current collector) may be used as a standard calibration parameter.

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