

A Stable Fluorinated and Alkylated Lithium Malonatoborate Salt for Lithium Ion Battery Application

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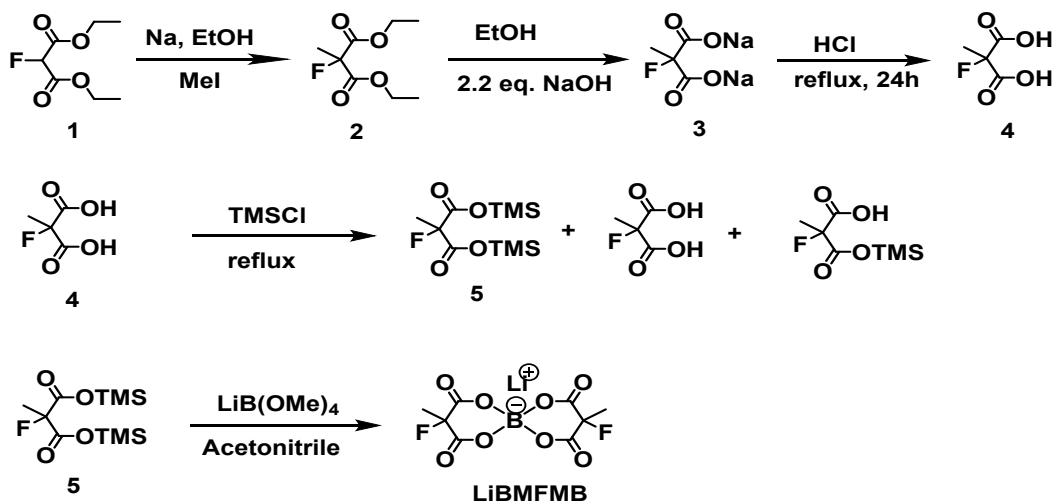
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1. Materials

All reactions involving trimethylsilyl functional groups were carried out under argon atmosphere. All solvents were of anhydrous grade (moisture less than 50 ppm) and were used without further purification. Diethyl fluoromalonate was purchased from Synnovator, Inc. Trimethyl borate and trimethylsilyl chloride were purchased from Aldrich. Ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and LiPF₆ were all purchased from Novolyte Technologies. LiB(OCH₃)₄ was synthesized according to literature procedures.¹ LiNi_{0.5}Mn_{1.5}O₄ was synthesized as described in the literature.² Natural graphite was obtained from MTI Coproration.



Scheme 1. Synthesis of LiBMFMB

Diethyl 2-methyl-2-fluoromalonate (compound 2): To a solution of sodium (2.3 g, 0.1 mol) in ethanol (100 ml), diethyl fluoromalonate (17.8 g, 0.1 mol) was added dropwise. The mixture was stirred at room temperature for 30 min and methyl iodide (14 g, 0.1 mol) was added dropwise and the resulting solution was refluxed for 1 h. The solvent was evaporated and the residue was distilled under reduced pressure to give pure diethyl methylfluoromalonate (2) (17.9 g, 75%). ^1H NMR (CD_3Cl , 400 MHz) δ ppm: 4.26 (q, $J = 7.2$ Hz, 4H, CH_2), 1.78 (d, $J = 22$ Hz, 3H, CFCH_3), 1.30 (t, 3H, $J = 7.2$ Hz, CH_3). ^{13}C NMR (CDCl_3 , 100 MHz) δ ppm: 13.76 (CH_3), 20.48 (d, $J = 23$ Hz, CFCH_3), 62.50 (CH_2), 92.30 (d, $J = 194$ Hz, CF), 166.90 (d, $J = 25$ Hz, $\text{C}=\text{O}$).

Sodium 2-methyl-2-fluoromalonate (compound 3): Compound 3 was synthesized by using the same procedure of our group.³ Yield: quantitative. ^1H NMR (D_2O , 400 MHz) δ ppm: 1.71 (d, 1H, $^2J_{\text{HF}} = 21.6$ Hz).

2-methyl-2-fluoromalonic acid (compound 4): Dried sodium methylfluoromalonate was dissolved in large excess of concentrated HCl solution and the heterogeneous solution was stirred at room temperature overnight. After the reaction was completed, HCl was removed by

vigorous nitrogen bubbling, followed by roto-evaporating at 80 °C. The concentrated liquid was dissolved in 500 mL of ether and the precipitated NaCl was removed by filtration. The product was obtained after removing solvent. Yield: 90%. ^1H NMR (acetone- d_6 , 400 MHz) δ ppm: 7.05 (s, 2H), 1.71 (d, $^2J_{\text{HF}} = 21.6$ Hz).

Bis(trimethylsilyl) 2-methyl-2-fluoromalonate (compound 5) (mixture with mono-ester): A mixture of methylfluoromalononic acid and trimethylsilyl chloride was reflux for 4 days, during which the by-product HCl was removed by vacuum and fresh trimethylsilyl chloride was added several times. The reaction was monitored by NMR, and when the highest ratio of the final product to the monoester was observed, the reaction was stopped. The excess amount of trimethylsilyl chloride was removed by rotovap and the crude product was further purified by distillation. Yield: 60 %. ^1H NMR (CDCl_3 , 400 MHz) δ ppm: 1.69 (d, 1H, $^2J_{\text{HF}} = 49.0$), 0.33 (s, 18H).

Lithium bis(2-methyl-2-fluoromalonato)borate (LiBMFMB):⁴ $\text{LiB}(\text{OCH}_3)_4$ (one equivalent) and bis(trimethylsilyl) (2-fluoro-2-methyl)malonate mixture with mono-ester (two equivalents) was mixed in argon-saturated anhydrous acetonitrile and stirred at room temperature for 12 h. After the reaction was completed, the mixture was filtered to remove insoluble part. The solvent was removed by rotary evaporation at 50 °C before drying in a vacuum oven at 75 °C for 24 h. Pure white powder was obtained after washed with ether. Yield: 70%. ^1H NMR ($\text{DMSO-}d_6$, 400 MHz) δ ppm: 1.83 (d, $^2J_{\text{HF}} = 20$ Hz). ^{11}B NMR ($\text{DMSO-}d_6$, 128.4 MHz) δ ppm: 1.27. ^{19}F NMR ($\text{DMSO-}d_6$, 376 MHz) δ ppm: -159.43 (q, $^2J_{\text{HF}} = 29.3$ Hz). ^7Li NMR ($\text{DMSO-}d_6$, 155.4 MHz) δ ppm: -1.04 .

2.3.Characterization

NMR measurements were performed using a 9.4 Tesla Bruker Avance NMR spectrometer at Larmor frequencies of 400.1, 376.4, 155.3, and 128.4 MHz for ^1H , ^{19}F , ^7Li , and ^{11}B , respectively. The chemical shifts of the proton NMR spectra were reported in ppm relative to tetramethylsilane (TMS) or residual protonated solvent peaks in ^1H NMR spectra. LiCl , $\text{BF}_3 \cdot \text{Et}_2\text{O}$, and CF_3Cl in DMSO-d_6 were used as a secondary external standard for ^7Li , ^{11}B , and ^{19}F NMR, respectively. Sample temperature was controlled by a resistance heater in the probe using air for the heat transfer gas. Sample temperatures were calibrated with 100% ethylene glycol according to the Bruker temperature calibration manual.

Calculated amount of anhydrous lithium salts were dissolved in EC/DMC in an argon-filled glovebox and the solution was then subjected to high vacuum treatment (10 mtorr) at 50 °C for overnight, after which only EC was left. Based on the integration of the ^1H NMR peaks for the lithium salts and EC, calculated amounts of EC and EMC were subsequently added to prepare standard EC/EMC (1/2 by wt.) solutions of 0.8 M LiBMFMB. Cathode composite electrode was obtained by casting well-homogenized slurry of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (80 wt%), carbon black (10 wt%), and PVdF (10 wt %) in N-methylpyrrolidone (NMP) on aluminum foil with a doctor blade. Graphite electrode was obtained by casting well homogenized slurry of graphite (85 wt%), carbon black (5 wt%), and PVdF (10 wt %) in N-methylpyrrolidone (NMP) on copper foil with a doctor blade. After solvent evaporation the electrodes were cut into discs with a diameter of 12 mm and further dried at 110 °C for 24 h. All the samples for the electrochemical tests were assembled in a glove-box with oxygen and moisture level below 0.5 ppm. The coin cells were cycled on an Arbin instrument between 3.0 and 4.9 V for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and between 0.005 and 2.0 V for graphite electrode under different current rates. CV data were recorded with respective cathodes or graphite as the working electrode and lithium as both counter and reference electrode

under a scan rate of 0.1 mV s⁻¹. The bulk ionic conductivity of the electrolyte solutions were measured as described earlier.^{5, 6} Electrochemical impedance spectroscopy was measured on a Gamry Instrument in the frequency range from 3 × 10⁵ Hz to 1 Hz with perturbation amplitude of 10 mV.

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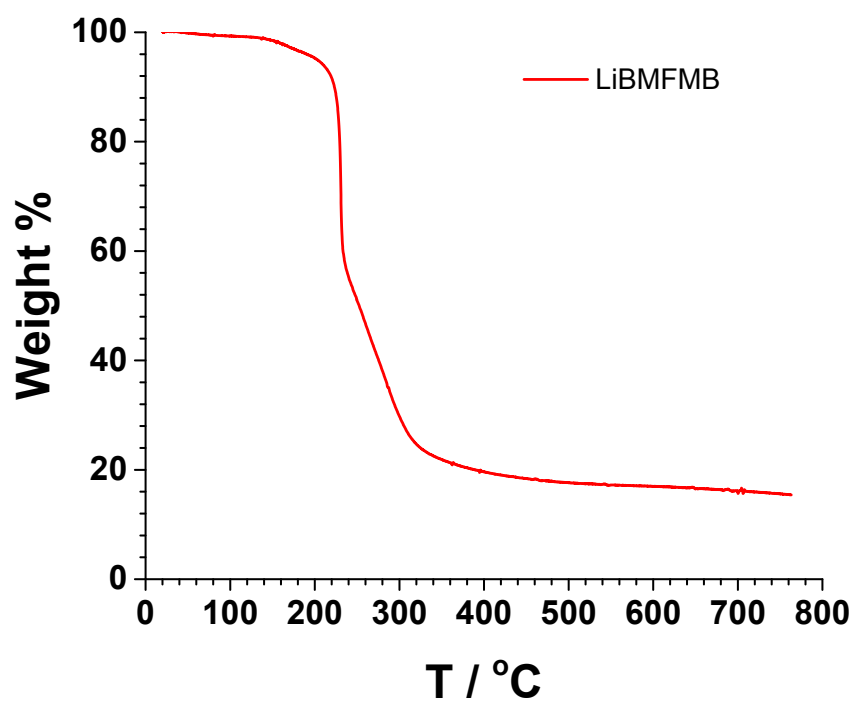
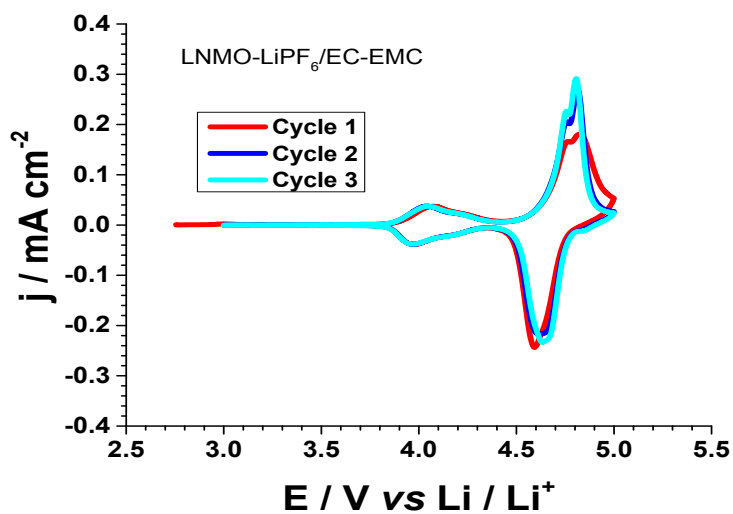


Fig. S1. TGA trace of LiBMFMB under nitrogen atmosphere at a heating rate of 10°C/min.



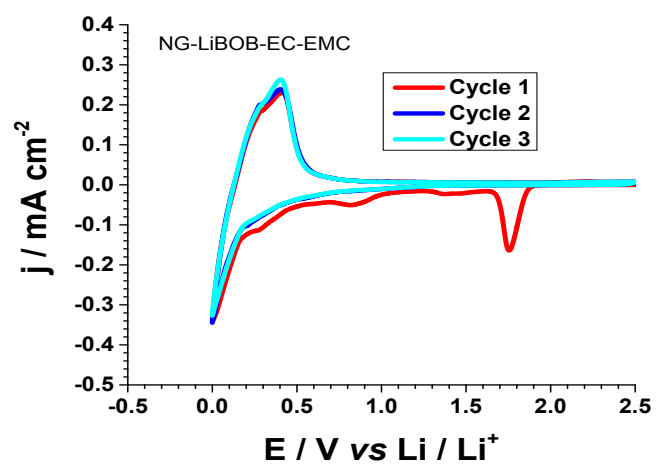
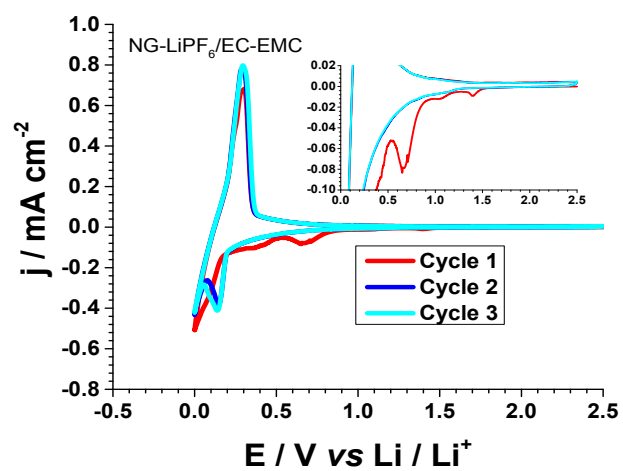
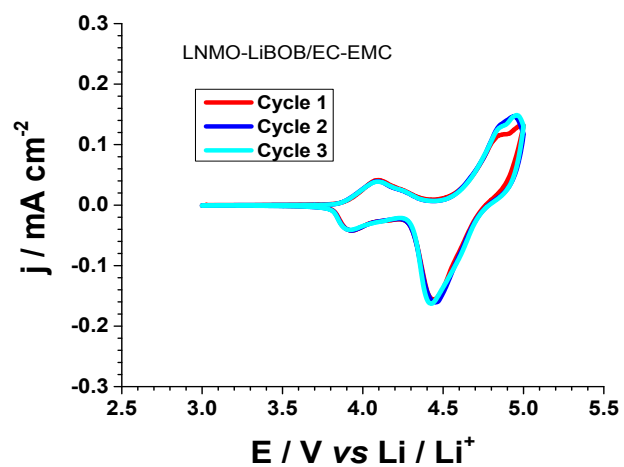
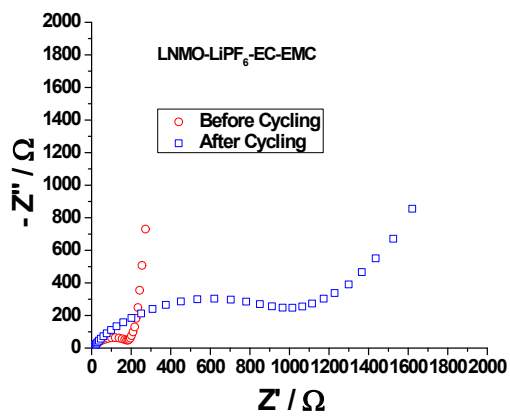
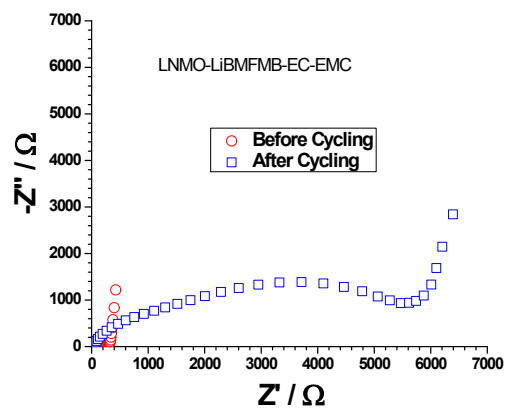


Fig. S2. Cyclic voltammetries of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \parallel \text{Li}$ and $\text{NG} \parallel \text{Li}$ half cells under a scan rate of 0.1mV/s .



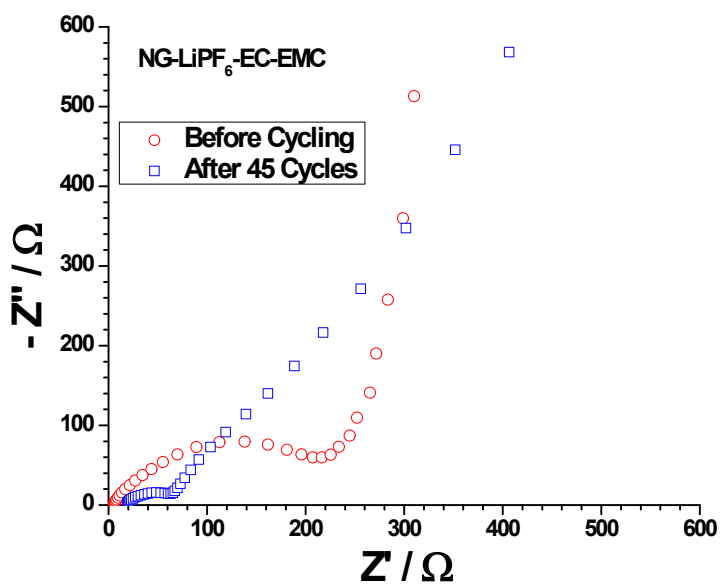
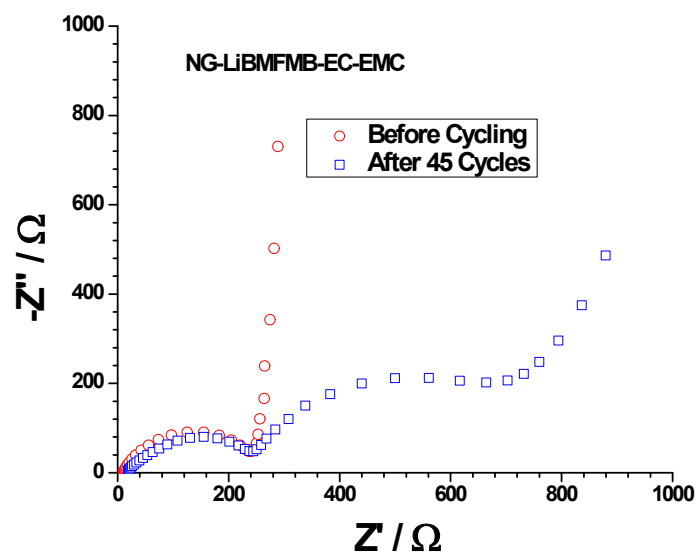


Fig. S3. Electrochemical impedance spectroscopies of the half cells at room temperature before and after cycling at 60°C.