Key Parameters in Determining the Reactivity of Lithium Metal Battery

Supporting Information

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Method

Electrolyte. Battery-grade lithium bis(fluorosulfonyl)imide (LiFSI) was purchased from Oakwood Products, Inc.; Bis(trifluoromethane)sulfonimide lithium 99.95% (LiTFSI) was purchased from Sigma-Aldrich. All salts were further dried at 120 °C under vacuum for 24 h before use; 1,2-dimethoxyethane (DME) anhydrous, 99.5% was purchased from Sigma-Aldrich; 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE, 99%) was ordered from SynQuest Laboratories. Solvents were dried with molecular sieves before use. LiFSI–DME–TTE were mixed in a molar ratio of 1:1.2:3 to prepare the LHCE. The carbonate electrolyte, 1.2 M Lithium hexafluorophosphate (LiPF6) dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 by weight) with 10% fluoroethylene carbonate (FEC) was purchased from Gotion. The All-F electrolyte was directly made by Gotion with formula provided by UCSD. All procedures were performed in an argon gas filled glove box (<0.1 ppm O_2, <0.1 ppm H_2O).

Electrochemical Testing. For Li||Cu cells, the cleaned Cu pieces was assembled in the 2032 coin cell as the working electrode while the Li metal (0.1 mm thick, China Energy Lithium Co., Ltd.) was the reference and counter electrode. Celgard 2325 separator was used as the separator and soaked in 55 µL of electrolyte. The Graphite and Silicon half cell were cycled at room temperature at a rate of C/20 during the first cycle and C/10 for subsequent cycles. The Graphite half cells are cycled between 0.05V to 2V while the Silicon half cells are cycled between 0.05V and 1.5V. For the full cell testing, the Graphite and Silicon electrode was paired with an LFP, NMC622, coated NMC622 or LNMO cathode and assembled in a 2032 type coin cell. The full cells were charged at room temperature at a rate of C/10 to 3.8V for LFP, 4.4V for NMC622 and coated NMC622 and 4.85V for LNMO. All cell makings were performed in an argon gas filled glove box (<0.1 ppm O_2, <0.1 ppm H_2O).

Pressure controlled split cells. A custom-made split cell that consists of two titanium plungers (1/2-inch diameter) and one polyether ether ketone (PEEK) die mold (1/2-inch inner diameter) is used for the pressure controlled Li plating. The Cu||Li cells were made by sandwiching the Li metal foil (7 mm diameter, 50 μm thick, China Energy Lithium Co., Ltd.), Celgard 2325 separator (1/2 inch diameter) and the cleaned Cu foil between the two titanium plungers inside the PEEK die mold. Only minimum amount of electrolyte (~5 μL) was added to the Cu||Li cells to wet the separator. After the assembly, the split cell and the load cell were put into the cell holder, which provided the uniaxial stacking pressure. The uniaxial stacking pressure was adjusted by the three screws on the cell holder. The screws were carefully adjusted to apply the desired stacking pressure to the split cell while keeping both the split cell and the load cell in vertical position. The cell was tested inside the glovebox using Landt CT2001A battery cycler (Wuhan, China). Various current densities and stacking pressure were applied to conduct the study as indicated in the main text.

Cryogenic Focused Ion Beam- Scanning electron Microscopy (Cryo-FIB/SEM). The copper foil with deposited Li was recovered from the split cell and then washed with DME to remove the residual electrolyte in the Ar-filled glovebox. The sample was mounted on a SEM stub (Ted Pella) in the glovebox, then transferred to a FEI Scios DualBeam FIB/SEM system with an Air-tight transfer holder to minimize air exposure[2]. Liquid N_2 was used to cooled down the sample stage to -180˚C to create a cryogenic environment which helps minimize beam damage to the sample. Gallium ion beam with a voltage of 30 kV, current of 7 nA and dwell time of 100 ns was used to roughly mill down the cross-section of the deposited lithium. After the rough milling, the cross-section was cleaned with ion beam at 1 nA. The SEM image of the cross-section was taken using Everhart-Thornley Detector (ETD) at 5 kV and 0.1 nA.

ALD coating for NMC. For the ALD process, the calendared cathode was first stored in a 60 ℃ oven overnight to remove the moisture, then transferred to the ALD chamber. The deposition of Al_2O_3 requires trimethylaluminum (TMA) as the precursor and water as the reactor. The carrier gas was nitrogen in 300 mbar, and the reaction temperature was 100 °C. The deposition rate was 1.0 Å per cycle. The surface layer thickness on the electrodes was controlled through the number of cycles performed. To ensure the precursor gas could spread into the electrode, a pre-injection of TMA for 6 seconds was applied. In the rest of the cycles, the TMA dose time was 0.6 s, followed by 1 s TMA purge, and the moisture dose time was 0.2 s, followed by 1 s purge. A vacuum-drying process at 80 °C for at least 24 h was then applied to the surface-modified electrode before any electrochemical testing to remove any residual moisture.

Differential scanning calorimetry - Fourier-transform infrared spectroscopy (DSC-FTIR). The DSC-FTIR measurement was done on NETZSCH STA 449 F3 Jupiter with an in-line coupled system of Bruker ALPHA II FTIR. The cycled electrodes were first retrieved from the coin cells and seal in a Cu backed Al pan with controlled amount of electrolyte (~3 g/Ah). All sample preparations were performed in an argon gas filled glove box (<0.1 ppm O_2, <0.1 ppm H_2O). The Al pan was pierced by a needle after loading into the DSC chamber so that the evolved gas could be analyzed by the in-line FTIR. During the DSC-FITR measurement, the temperature was ramping up at a rate of 10°C/min to 400°C. All DSC-FTIR measurement were done under Ar and N_2 environment.

Solvent	Boiling Point (˚C)
DME	85.0
TTE	93.2
DEC	127.0
EC	243.0
FEC	212.0
FEMC	90.0

Table S1. The boiling point of all the electrolyte solvents used in the study.

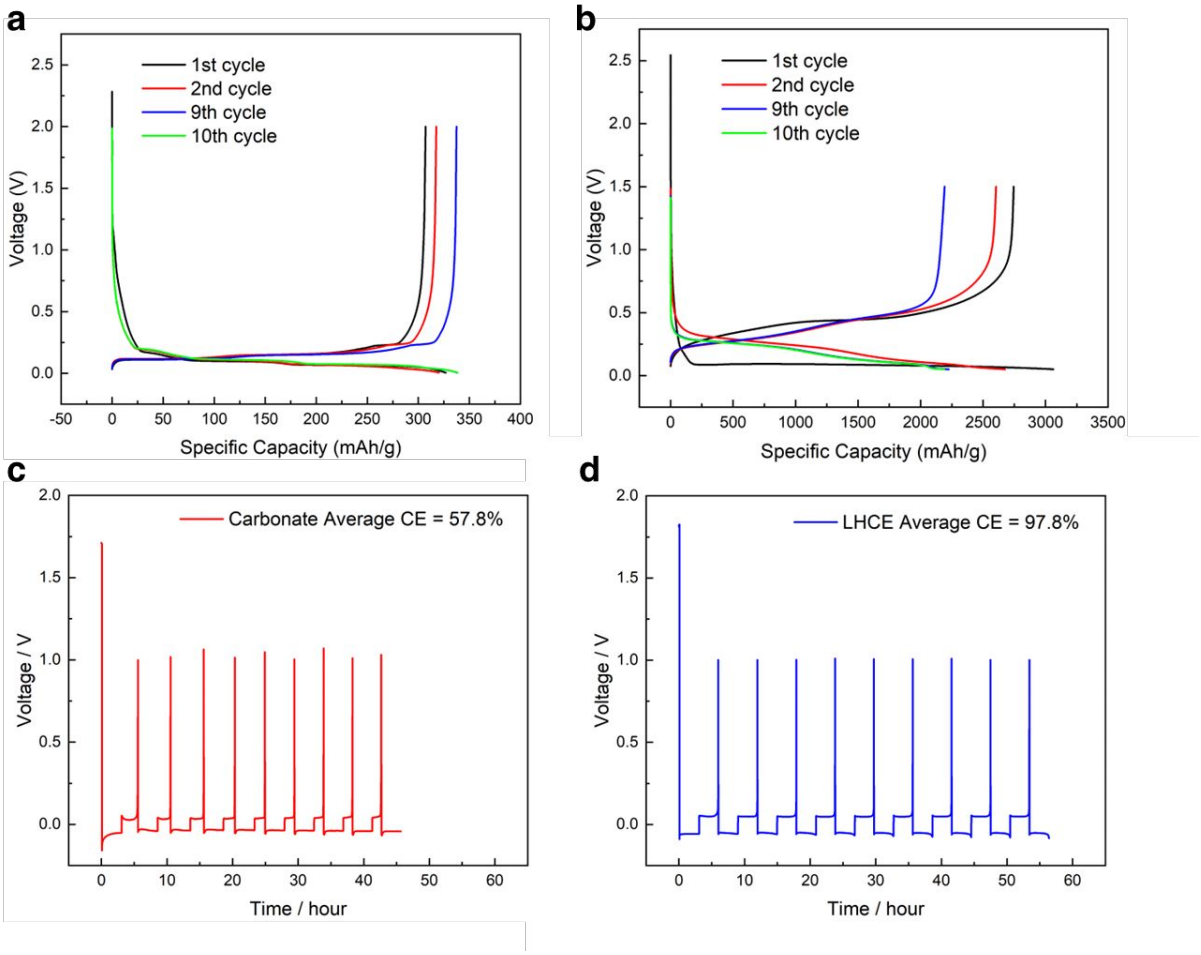

Figure S1. The cycling voltage profiles of (a)Graphite, (b)μSi, (c)Li||Cu in Carbonate and (d) Li||Cu in LHCE.

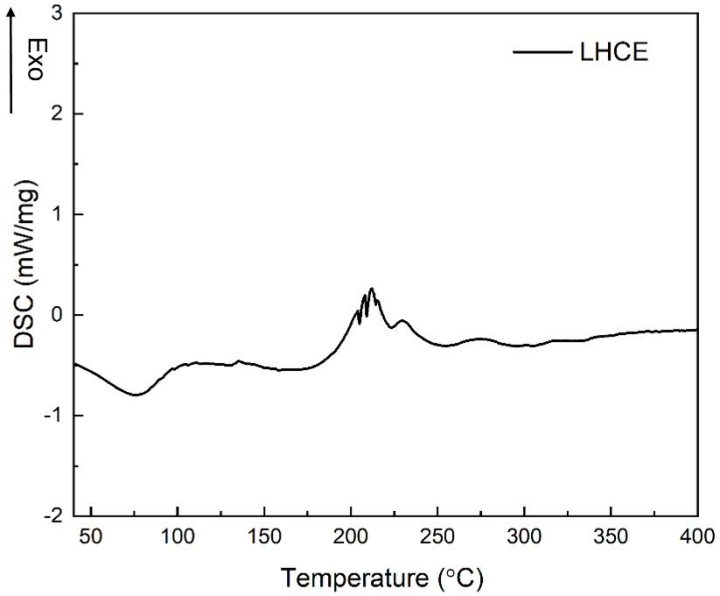

Figure S2. The DSC profile of LHCE.

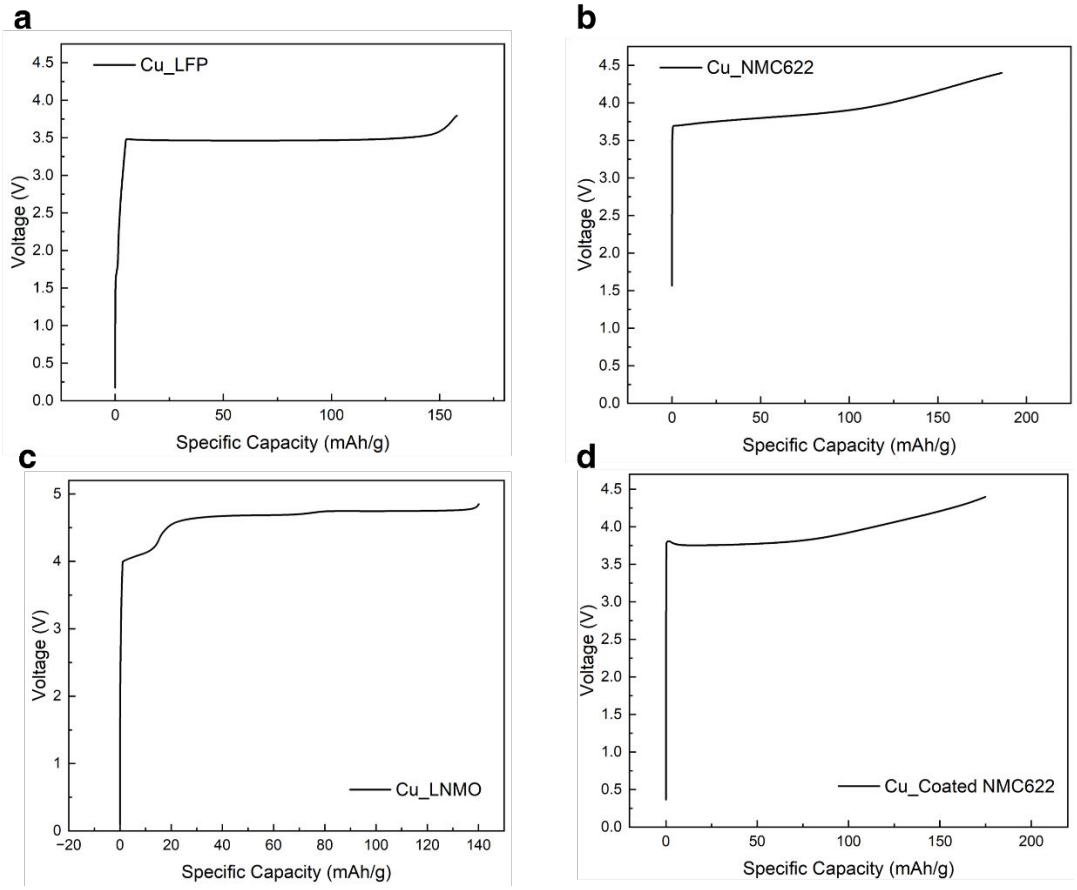

Figure S3. The cycling voltage profiles of (a) Cu||LFP, (b) Cu||NMC622, (c) Cu||LNMO and (d) Cu||Coated NMC622.

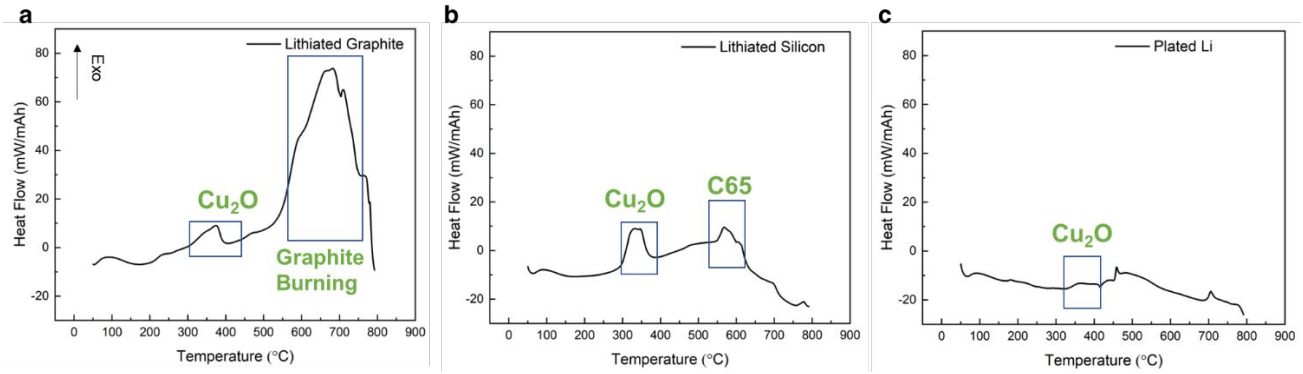

Figure S4. The DSC profiles of (a) Li-Gr (b) Li-Si and (c) plated-Li in Carbonate. All DSC is done in air. Graphite and Si anodes are cycled in half cell configuration at rate of C/20 and Li metal anodes are cycled in Li||Cu cells at rate of 0.5mA/cm^2. Carbonate electrolyte is used for all cells.

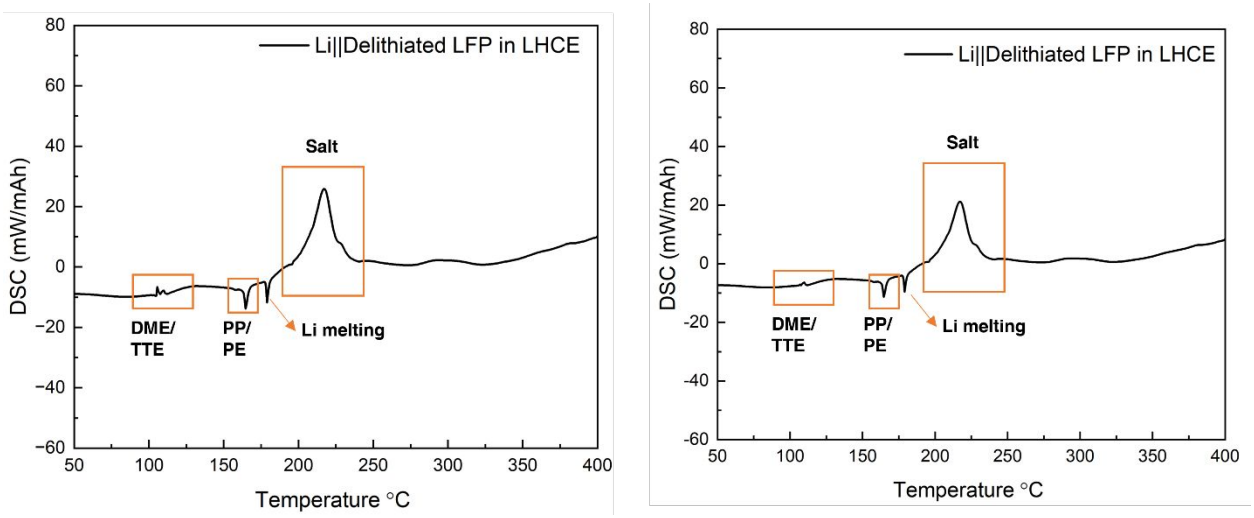

Figure S5. The DSC profiles of duplicated tests of delithiated LFP in LHCE to show the reproducibility of the DSC tests.

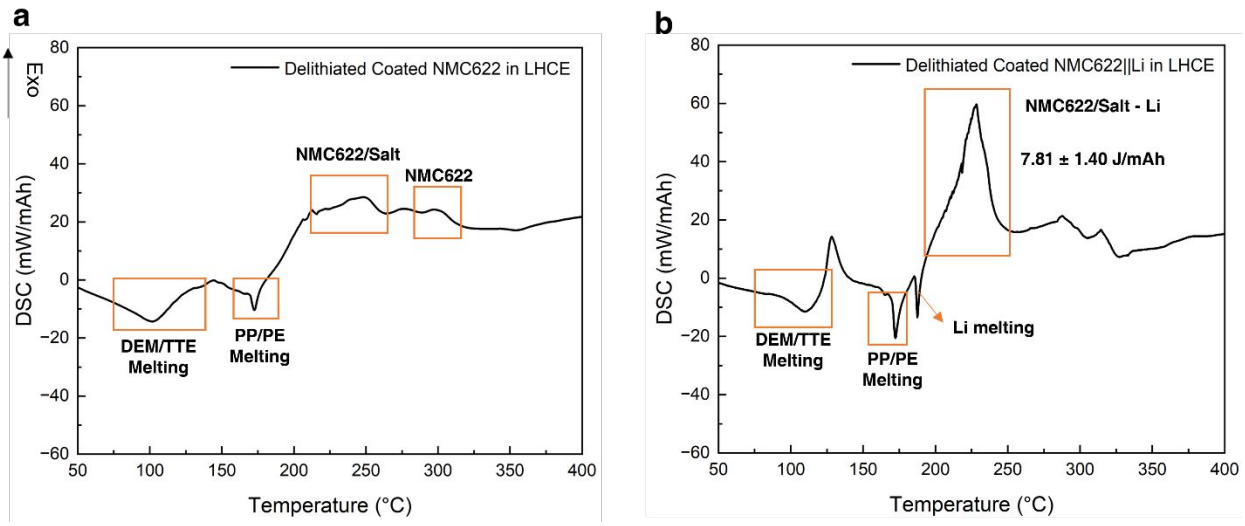

Figure S6. The DSC curves of (a) delithiated coated NMC622 with separator and LHCE and (b) plated Li, delithiated coated NMC622 with separator and LHCE. All cells are cycled at C/20 with corresponding electrolyte.