

Supporting Information

Dendrite-Free Lithium Deposition with Self-Aligned Columnar Structure in a Carbonate-Ether Mixed Electrolyte

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EXPERIMENTAL

Materials

Lithium hexafluorophosphate (LiPF_6 , 99.99% purity), 1,2-dimethoxyethane (DME, 99.5% purity, inhibitor-free), Dimethyl carbonate (DMC, 99.9% purity) and ethylene carbonate (EC, 99.9% purity) were obtained from Sigma-Aldrich Corporation. The electrolytes were prepared by dissolving the desired amount of salt into the solvent, all operation in a glove box with Ar atmosphere (< 1 p.p.m. O_2 and < 1 p.p.m. H_2O).

Electrolyte

Four electrolytes have prepared by dissolving 1 M LiPF_6 in solution of EC:DMC (1:1, D/E-0), EC:DMC:DME (4.5:4.5:1, D/E-10), EC:DMC:DME (4:4:2, D/E-20) and EC:DMC:DME (3.5:3.5:3, D/E-30), respectively, based on volume ratio. Carbonate-ether mixed electrolytes with 40%, 50%, 60%, 70%, 80% and 90% of DME content were also prepared similar to above electrolytes. A 1 M LiPF_6 DME was prepared as same as above electrolyte as control electrolyte to studied the electrochemistry stability of DME solvent. All the electrolytes have been further dehydration by molecular sieve to reducing trace water in electrolytes. Only the D/E-30 electrolyte shows the best morphology of Li deposits.

Characterization

After the repeated cycling of Li deposition/dissolution the batteries were hold for 48 h and disassemble for characterization. The Li electrodes were thoroughly washed with anhydrous DMC to remove the residual electrolytes and dried in a glove box antechamber under vacuum prior to characterization and analyses. The Li electrodes were transferred in a Sample-Saver Storage Container filled with purified argon and loaded into the SEM machine in a glove bag purged with purified argon to avoid air

contamination. Li morphology was characterized by a scanning electron microscope [HITACHI SU-4800]. XPS depth profiling data were collected at room temperature with a XPS spectrometer (Thermo Scientific ESCALAB 250Xi). The Li electrodes were also transferred in a Sample-Saver Storage Container into the XPS machine to avoid air contamination. All spectra were calibrated with the C 1s photoemission peak at 284.8 eV to correct for the charging effect. Sputtering was performed with an argon ion beam gun operating at 2 keV with a spot size of $1 \times 1 \text{ mm}^2$.

Electrochemical Measurements

Coin cells of CR2032 type were used to prepare batteries for morphology and cycling-property study of Li electrodes with different electrolytes. The LiFePO_4 (LFP) electrode was prepared by coating a slurry of LFP, Super P conductive carbon, and sodium carboxymethyl cellulose (8:1:1 by weight) in deionized water onto an alumina foil, evaporating the deionized water solvent, and drying at about 120°C under vacuum overnight. The average capacity of LFP was 1.0 mAh/cm^2 . The glove box was filled with purified argon in which the oxygen and moisture contents were less than 0.5 ppm and 0.5 ppm, respectively. The electrolyte addition for each coin cell is $150 \mu\text{L}$. The Li metal foil (1 mm thick with 99.9% purity) was cut into 15 mm diameter disks as Li electrodes, and surface passivation layer was removed by ceramic tip. The scan rate of CV test was at 0.1 mV/s , the voltage range was 2.8–3.8 V.

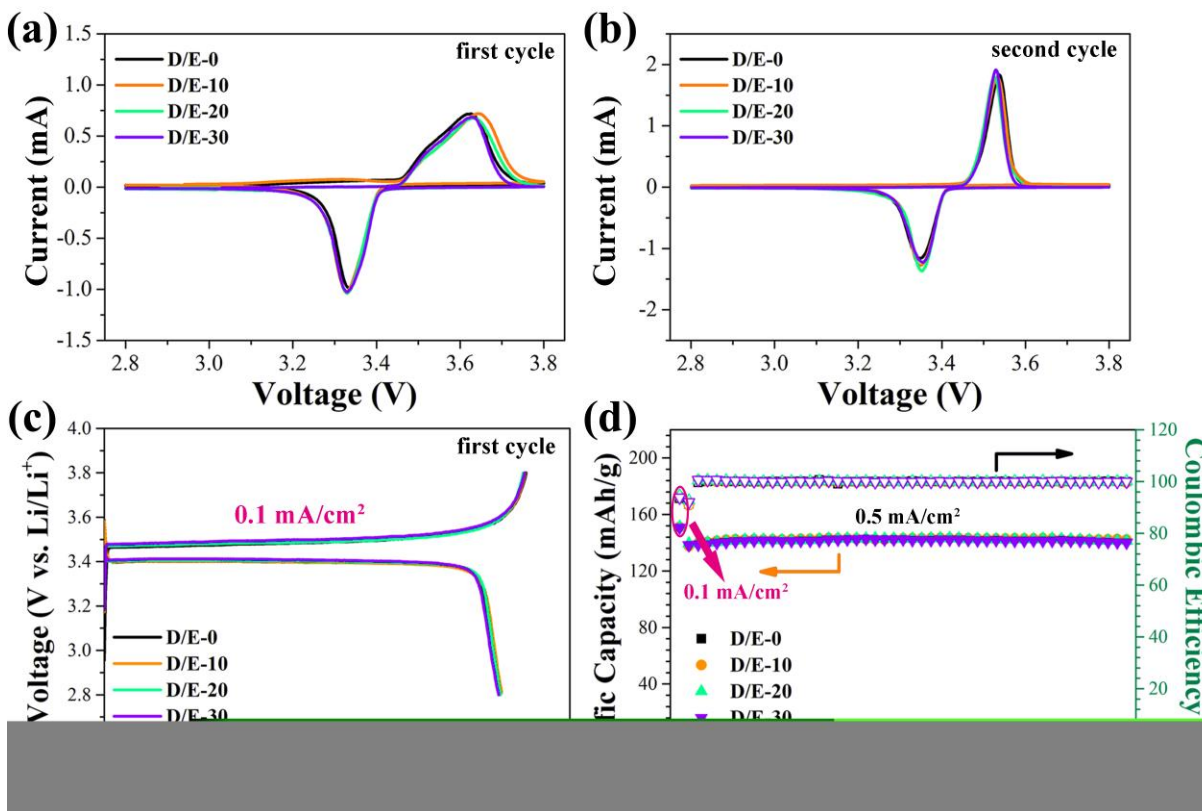


Figure S1. CV and galvanostatic charge/discharge profiles of LFP | Li batteries with various carbonate-ethers mixed electrolytes. (a-b) CV curves in the first and second cycles; (c) voltage-capacity profiles in the first cycle at 0.1 mA/cm²; (d) capacity retention and Coulombic efficiency at 0.5 mA/cm² (0.1 mA/cm² in the first cycle)

Figure S1a shows CV curves in the first cycle for four different carbonate-ether mixed electrolytes. All CV curves are identical, regardless of the electrolyte. There are no new oxidation and reduction peaks observed. The same result is found for the second CV cycle of batteries, Figure S1b. The CV results suggest that carbonate-ether mixed electrolyte can work stably among 2.8–3.8 V (v.s. Li/Li⁺). Figure 1c shows the voltage-capacity profiles of batteries in the first cycle (0.1 mA/cm²). All batteries show almost the same charge and discharge specific capacities of 163 and 152 mAh/g, respectively. Figure S1d shows capacity retention and Coulombic efficiency of batteries cycled at 0.5 mA/cm² (the first cycle is 0.1 mA/cm²). There is no significant difference for the four electrolytes. The above results demonstrate that the carbonate-ethers mixed electrolyte shows great stability under 3.8 V and no significant side reaction between anode and cathode.

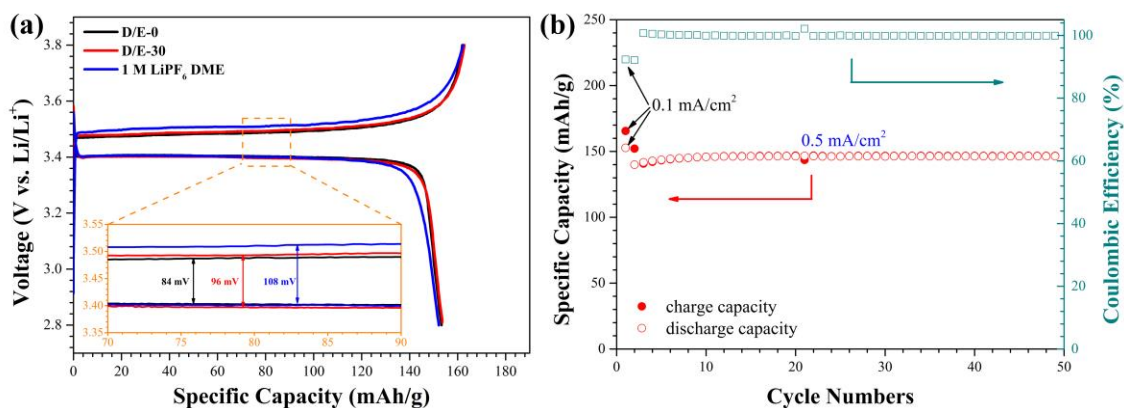


Figure S2. Galvanostatic charge/discharge profiles of LFP | Li batteries. (a) voltage-capacity profiles in the first cycle at 0.1 mA/cm² with 1 M LiPF₆ DME, D/E-0 and D/E-30 electrolytes, respectively (b) capacity retention and Coulombic efficiency at 0.5 mA/cm² with 1 M DME electrolyte. The inset picture in (a) is the magnification of the orange area.

The voltage–capacity profile of a battery with 1 M LiPF₆ DME in the first cycle shows curves similar to that of batteries in mixed carbonate-ethers electrolyte and there is only a slight increase in polarization for this electrolyte, Figure S2a. The battery also shows a stable cycling performance, Figure S2b.

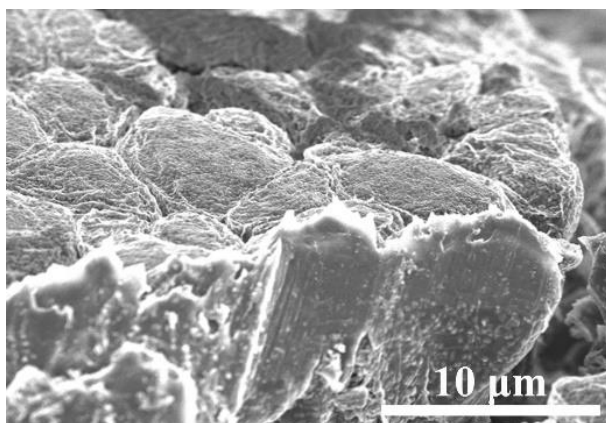


Figure S3. SEM Cross-sectional image of Li deposits after the 50th cycle under 0.5 mA/cm² in D/E-30 electrolyte.

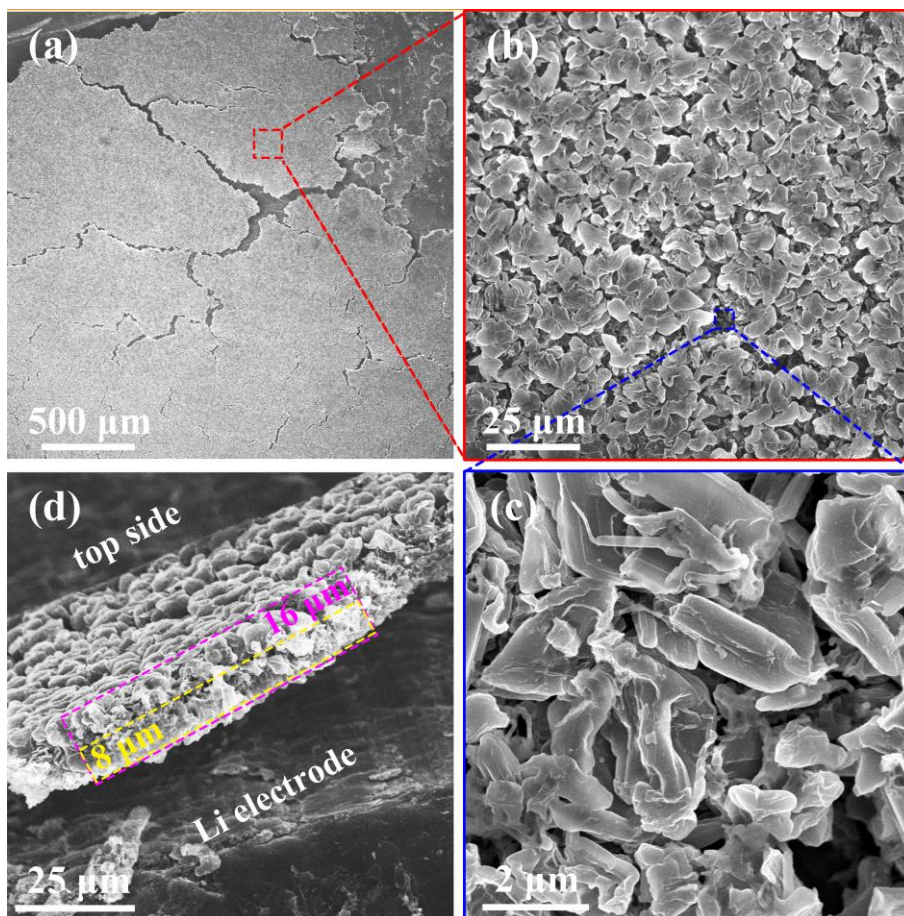


Figure S4. Top-view and cross-sectional SEM images of Li deposits after the 50th cycle with 1 M LiPF_6 DME electrolytes at 0.5 mA/cm^2 . (a) low-magnification top-view SEM image. (b) high-magnification top-view image of the red area marked on (a). (c) high-magnifications image of the blue area marked on (b) showing the bottom layer of Li deposits. (d) Cross-sectional image of Li electrode and Li deposits.

SEM images of a Li electrode after the 50th cycle with 1 M LiPF_6 DME, Figure S4, show that the Li deposits can be divided into two layers. The top layer shows loose bulk-like Li deposits with an average size of $\sim 10 \text{ μm}$ while the bottom layer shows Li dendrites with random sizes ($< 3 \text{ μm}$). Due to this structure, the Li deposits may not get enough electronic conduction from Li electrode, resulting in more “dead Li”.

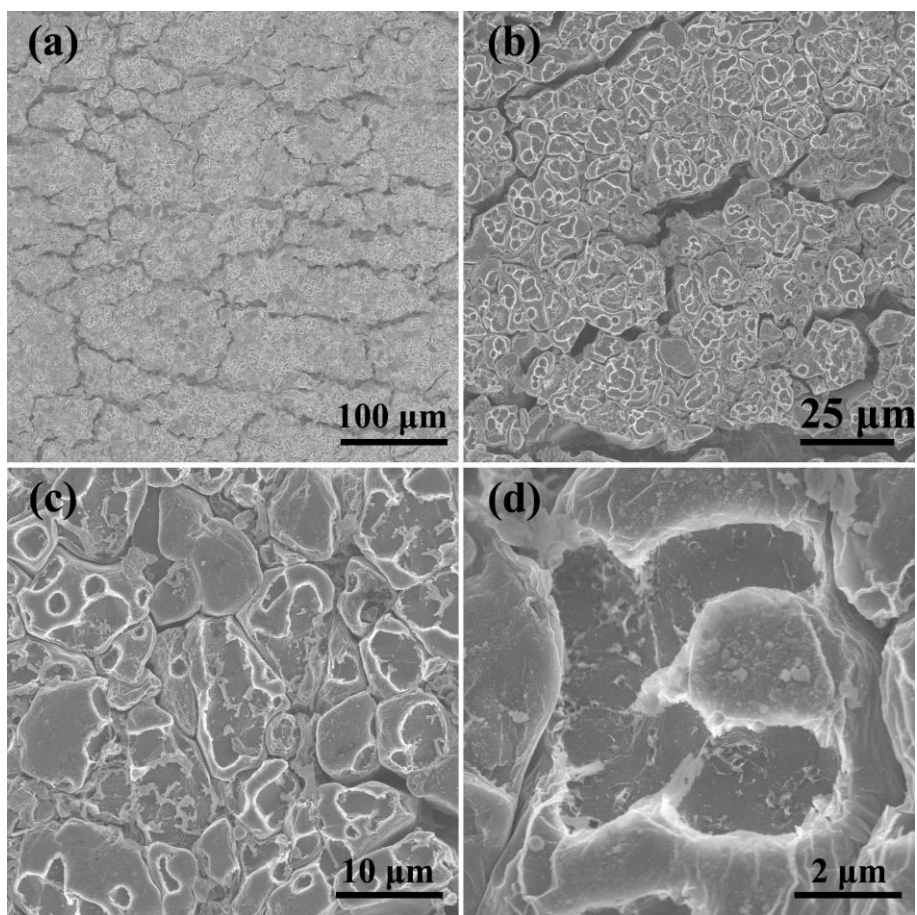


Figure S5. Various magnifications of top-view SEM images of the Li electrode after the 30th cycles with D/E-30 electrolyte at 0.5 mA/cm² (20% depth of discharge).

To prove the micron-scale columnlike Li deposits have electrochemical activity and can provide reversible capacity, an additional battery after the 30th cycle with D/E-30 was discharged at 0.1 mA/cm² to 20% depth of discharge for SEM, Figure S5. The results show that the gaps between each column-like Li deposits are slightly increased, suggesting that electrochemical delithiation process is indeed involved with the Li deposits. Furthermore, many pits are located on top surface of the Li deposits, indicating that Li on the surface also participate in the electrochemical delithiation.

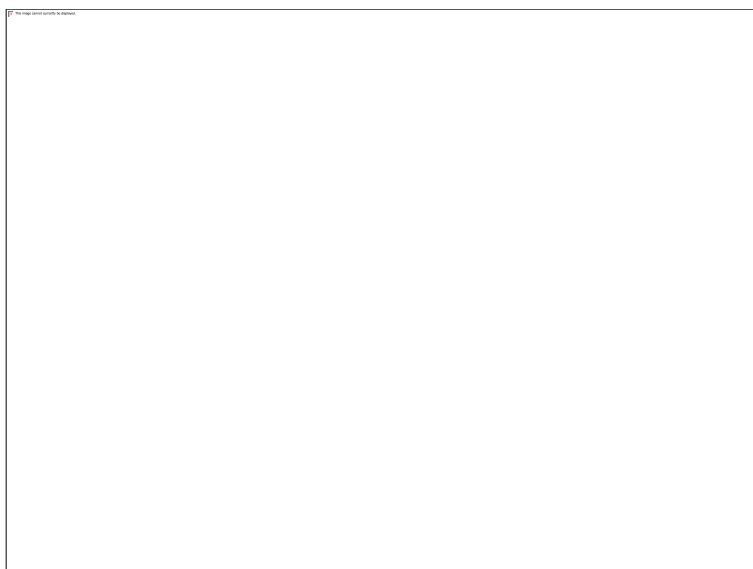


Figure S6. Charge-discharge profiles of the 2nd and 200th cycle of LFP | Li battery with D/E-30 electrolyte, which shows a slight increase of overpotential.

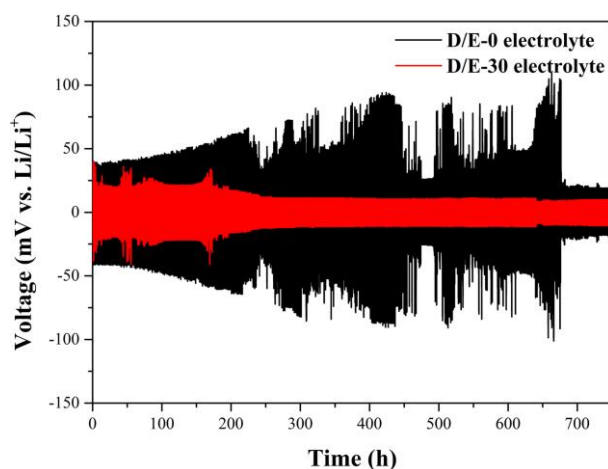


Figure S7. Voltage profiles for Li plating-stripping as a function of time in symmetric cells using carbonate electrolyte (D/E-0, black) and mixed carbonate-ethers electrolyte (D/E-30, red) with current density of 1 mA/cm^2 for 1 mAh/cm^2 . The battery without DME displays an increased voltage polarization and random voltage oscillation during cycling, suggesting that rapid loss of Li may occur in the repeated reconstruction of the SEI and/or a growth of SEI into a thick layer leading to increased impedance.

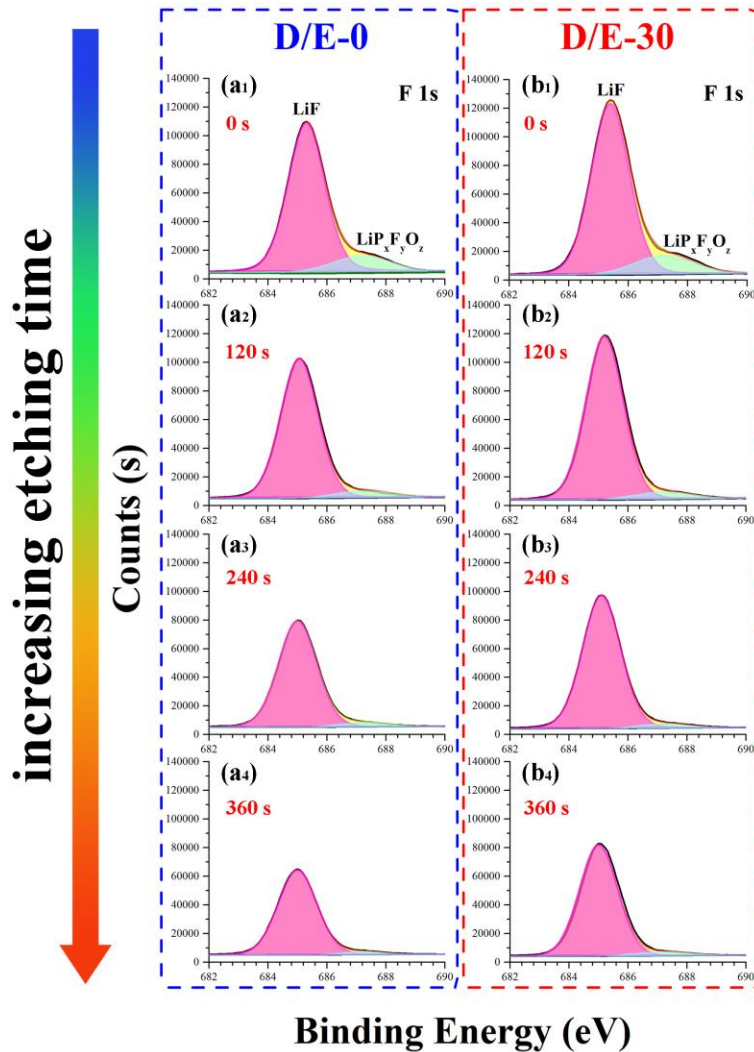


Figure S8. XPS depth profile analysis of F element on the surface of Li electrode after the 50th at 0.5 mA/cm² current density with carbonate (D/E-0) (a₁-a₄) and mixed carbonate–ethers (D/E-30) electrolytes (b₁-b₄).

The fitted XPS spectra of elemental F, as shown in Figure S8, show that the majority of elemental F is associated with LiF in both electrodes. A small amount of LiP_xF_yO_z is also detected even after long-time ion beam etching, which may be ascribed to decomposed products of LiPF₆ or LiPF₆ residual in gaps of columnlike deposited Li arrays.

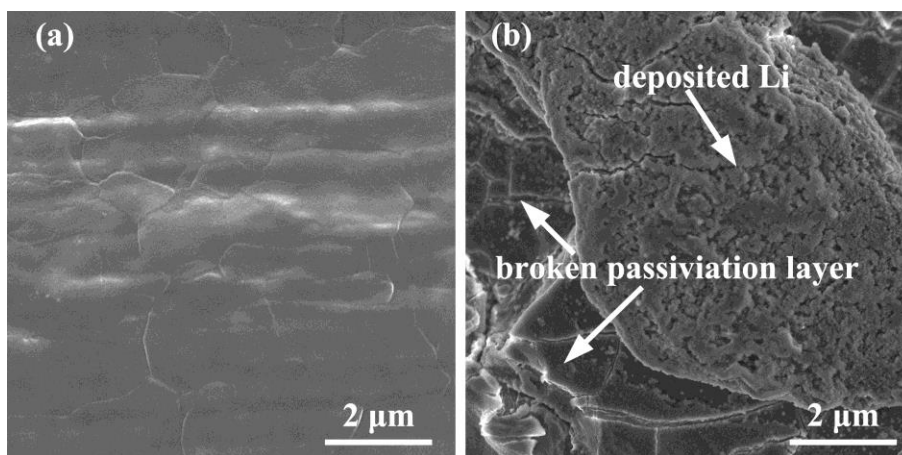


Figure S9. High magnification top-view SEM images of Li electrode before (a) and after (b) the 1st cycle at 0.1 mA/cm^2 . Two types of surface are observed after the 1st cycle: a smooth surface with cracks and a rough surface with Li deposits

Top-view SEM images of Li electrodes before and after the 1st cycle at 0.1 mA/cm^2 show that the passivation layer formed on the Li electrode in the 1st cycle starts to break, which may be caused by the nonuniform Li deposition.