Supporting information

Unveiling the impacts of charge/discharge rate on the cycling performance of Li-metal batteries

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EXPERIMENTAL METHODS

Electrochemical test. Cells for cycling tests under different charge/discharge rates were assembled in a dry room at SES. The dew point of the dry room is controlled at -50°C. The cells are in a 3/4-layer format, meaning 3 layers of cathodes and 4 layers of anodes. The anodes for full cells are Li/Cu composite foil with 20 um Li coating on each side of a Cu current collector. The anodes for anode free NMC||Cu cells are dried Cu foil with a thickness of 8 um. The cathodes are NMC 811 polycrystal particles coated on each side of an Al current collector. The areal loading of the cathode is 3 $mAh \cdot cm^{-2,}$ and the dimensions of the cathode are 4.5 cm * 3 cm. The separator is ceramic-coated PE film. Electrolyte is a non-aqueous, high concentration, organic electrolyte with a filling weight of 4 $g \cdot Ah^{-1}$ for cycling tests and post-cycling analysis or 2.5 $g \cdot Ah^{-1}$ for pulse discharge tests. The electrodes, separator, and electrolyte were sealed in a soft pouch and put in the constant pressure jigs at 0.8 MPa. The cells have an initial capacity of around 260 mAh. The cycling tests were done on Neware BTS4000 testers with different charge/discharge rate combinations at room temperature. The voltage window is 2.5 V- 4.3 V for all the cycles with 0.8 MPa pressure. After the cycling tests were done, the cells were charged/discharged to the wanted SOC and torn down in the dry room. The electrodes were saved under vacuum for further characterization. The leakage current tests were done on Arbin LBT with high precision. The cells were charged to 4.3 V and the leakage current was monitored and recorded.

Scanning electron microscopy. The SEM characterization at SES AI was done on a SNE-4500M benchtop SEM with an operating voltage of 10 kV. The Li anode cross-section was prepared on a Gatan Ilion II ion mill at a temperature of -160 ° in the dry room.

Transmission electron microscopy. The samples were transferred to a ThermoFisher Talos 200X TEM (operated at 200 kV) using an airtight method. The probe current for EDS maps on the TALOS was around 98 pA and used an acquisition time of 4 mins in total. EDS mapping was acquired from areas with low-dose technology to minimize possible electron beam irradiation effects. The EELS characterization of samples was performed using the Talos microscope equipped with a Gatan Continuum (1069) EELS spectrometer, and the probe current for EELS maps on the TALOS was around 98 pA based on low dose technology. The SAED (selected area electron diffraction) images are acquired with electron dose rate ~0.1 e $Å^{-2}$ s^{-1} for ~8s (FEI Ceta camera).

X-ray photoelectron spectroscopy. The XPS was conducted on a Kratos AXIS-Supra, using an Al target as the X-ray source and 10^{-9} Torr pressure. The cycled electrodes for XPS tests were transferred to a nitrogen-filled glovebox directly connected to the chamber without any air exposure. Survey scans were performed with a step size of 1.0 eV, followed by a fine scan with 0.1 eV resolution. The spectra were analyzed by CasaXPS software to identify different chemical species.

Active Li^0 quantification. The cycled sample was punched and immersed into 6wt% Bp/THF (Biphenyl/Tetrahydrofuran) solution for 48 hours to dissolve all the active Li^0 attached to the

current collector. The solution was further digested with 98% H_2SO_4 and 30% H_2O_2 solution for Inductively coupled plasma mass spectrometry measurements. The measurement was done by ICP-MS (iCAP RQ, Thermo Fisher Scientific). The digested sample was diluted with DI water. The ICP sample solution was prepared by mixing the diluted solution with 0.5% HCl + 0.5% HNO_3 solution.

Inactive Li^0 quantification. After dissolving the sample in Bp/THF solution, ethanol was injected into the vial to react with the inactive Li^0 isolated by the SEI. The generated H_2 gas was quantified by the Titration Gas Chromatography (TGC). The TGC experiments were performed using a Shimadzu GC-2010 Plus Tracera equipped with a barrier ionization discharge (BID) detector. The Split temperature was kept at 200°C with a split ratio of 2.5 (split vent flow: 20.58 $ml \cdot min^{-1}$, column gas flow: 8.22 $ml \cdot min^{-1}$, purge flow: 0.5 $ml \cdot min^{-1}$). Column temperature (RT-Msieve 5A, 0.53 mm) was kept at 40°C, and the BID detector was held at 235°C. Helium (99.9999%) was used as the carrier gas, and the BID detector gas flow rate was 50 $ml \cdot min^{-1}$. The electrode sample was put in a septum sealed glass vial, and after injecting 0.5 mL ethanol (200 proof anhydrous), the sample gases were injected into the machine via a 50 μL gastight Hamilton syringe.

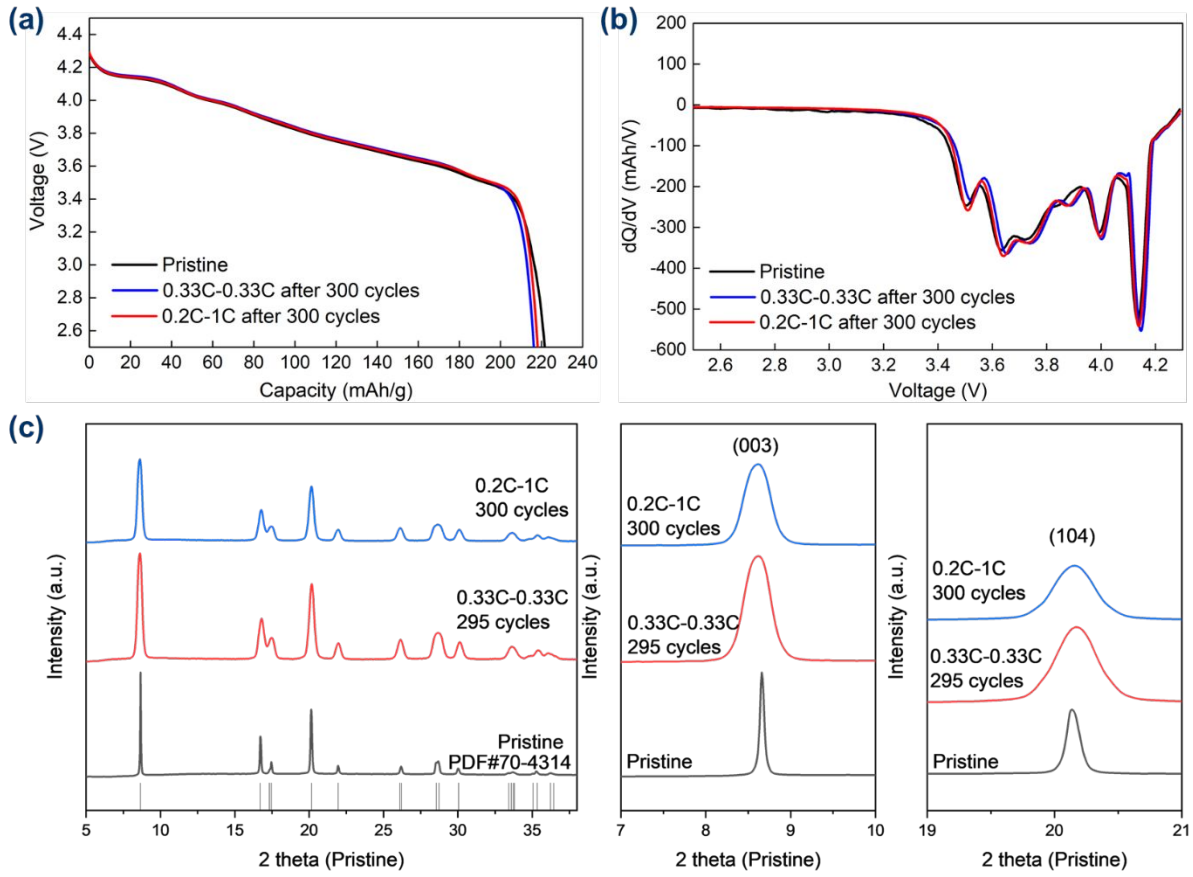

Figure S 1 Post-analysis of cathodes cycled under 0.2C-1C and 0.33C-0.33C after 300 cycles: (a) XRD spectra of cycled cathode (b) discharge curve. (c) dQ/dV plot. The cathodes cycled under 0.33C-0.33C and 0.2C-1C conditions for 300 cycles were removed, rinsed, and reassembled in coin cells with fresh Li. These coin cells were charged to 4.3 V and discharged to 2.5 V at 0.1C to evaluate any irreversible capacity loss from the cathode.

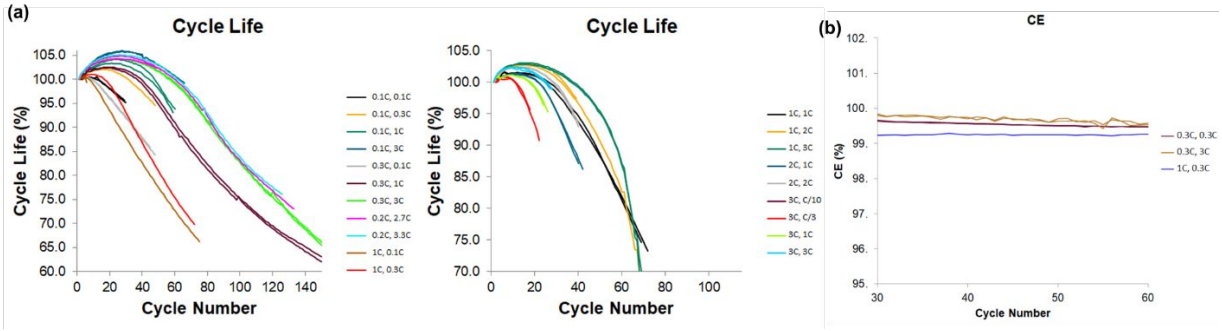

Figure S 2 NMC||Cu pouch cell tests under different charge/discharge rates. The CE results were used to generate the color map in Figure 1b. (a) Cycling results. (b) CE of 0.3C-0.3C, 0.3C-3C, and 1C-0.3C from 30 to 60 cycles.

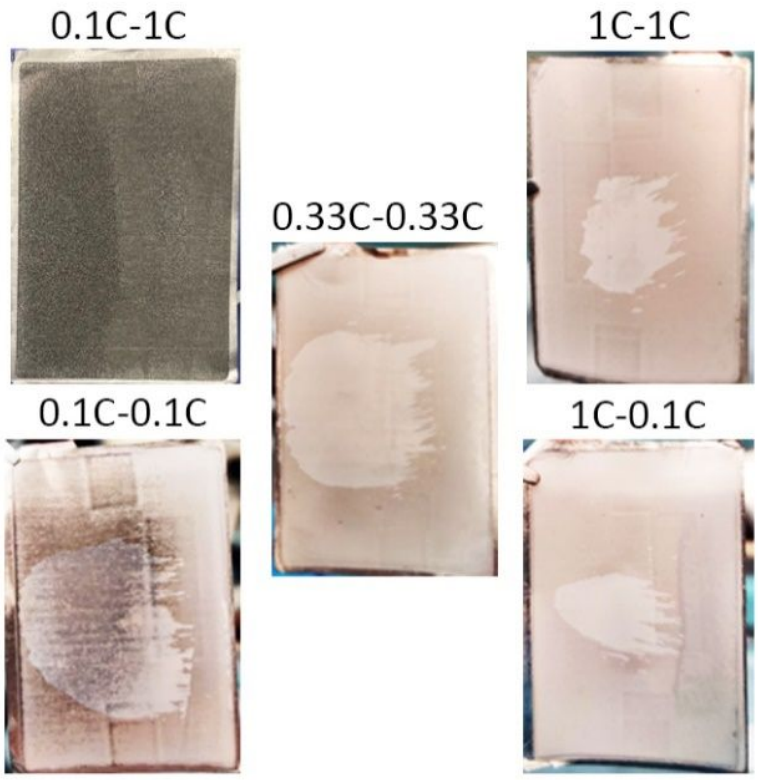

Figure S 3 Photos of 100% SOC Li anodes after teardown.

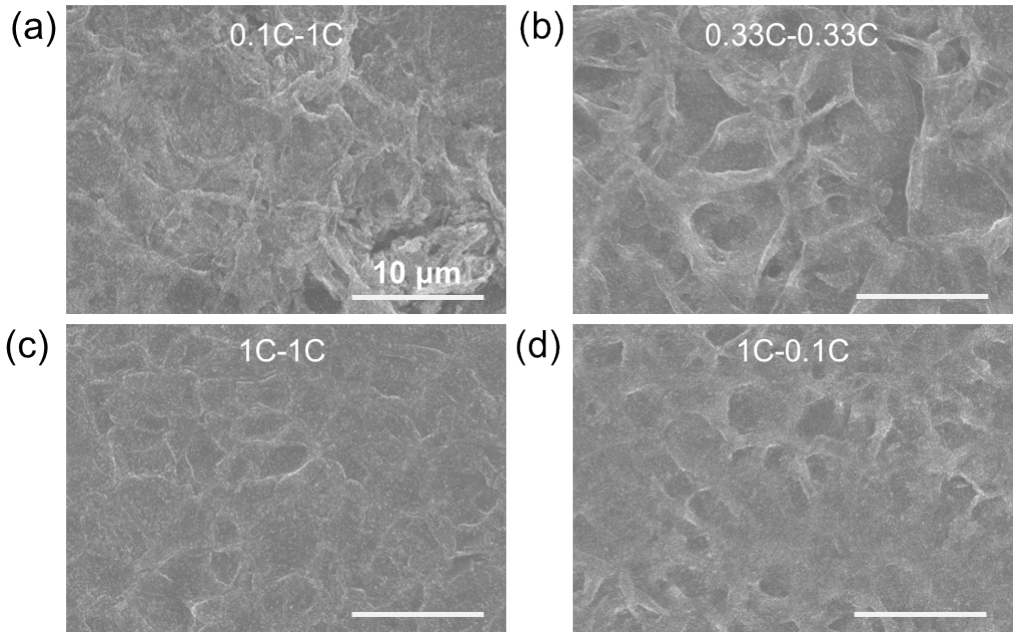

Figure S 4 0% SOC top-view SEM images

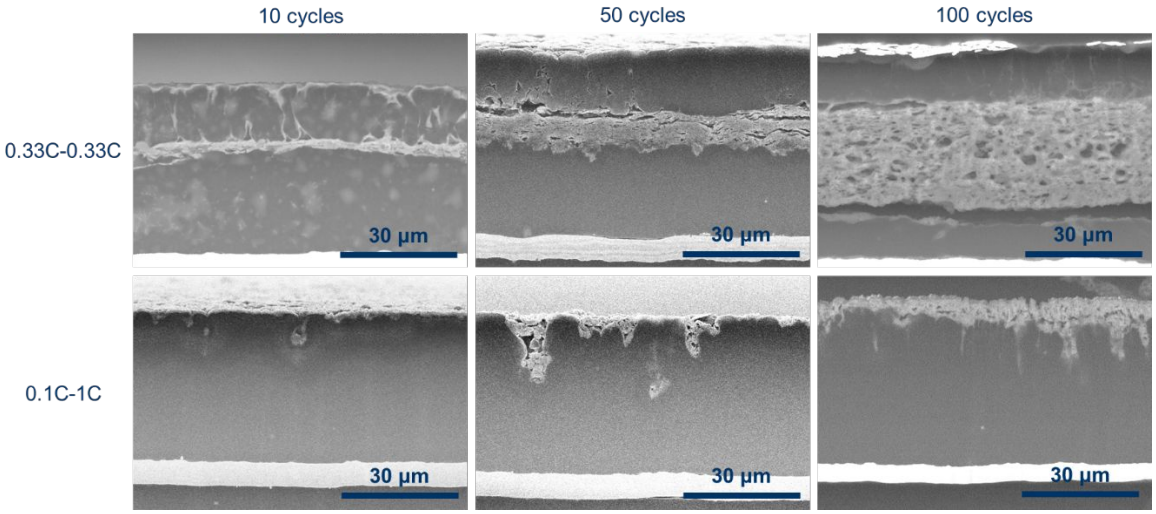

Figure S 5. Cross sections of Li anodes under 100 % SOC after different cycles.

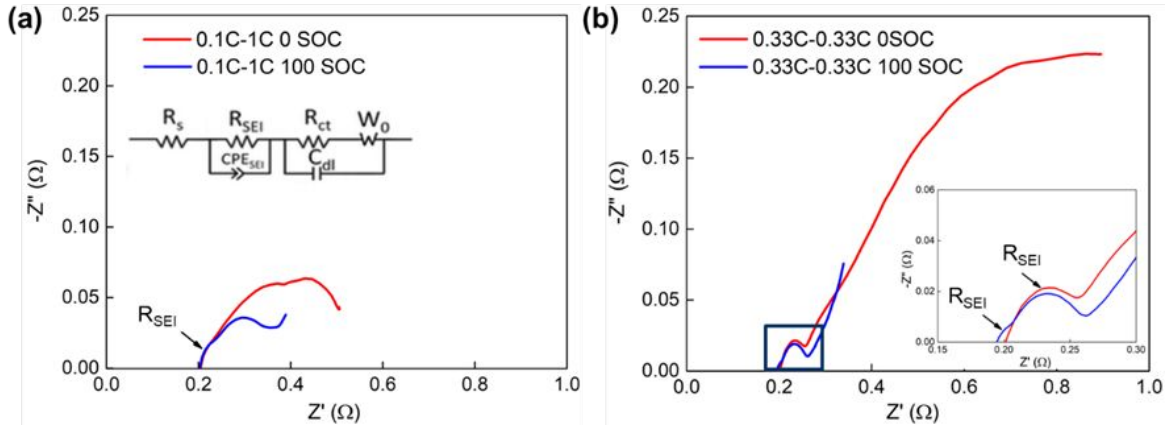

Figure S 6. EIS plots of a 0.1C-1C cell and 0.33C-0.33C cell after 50 cycles under 0% SOC and 100% SOC with arrows pointing to the R_{SEI}. (a) 0.1C-1C cell. (b) 0.33C-0.33C cell.

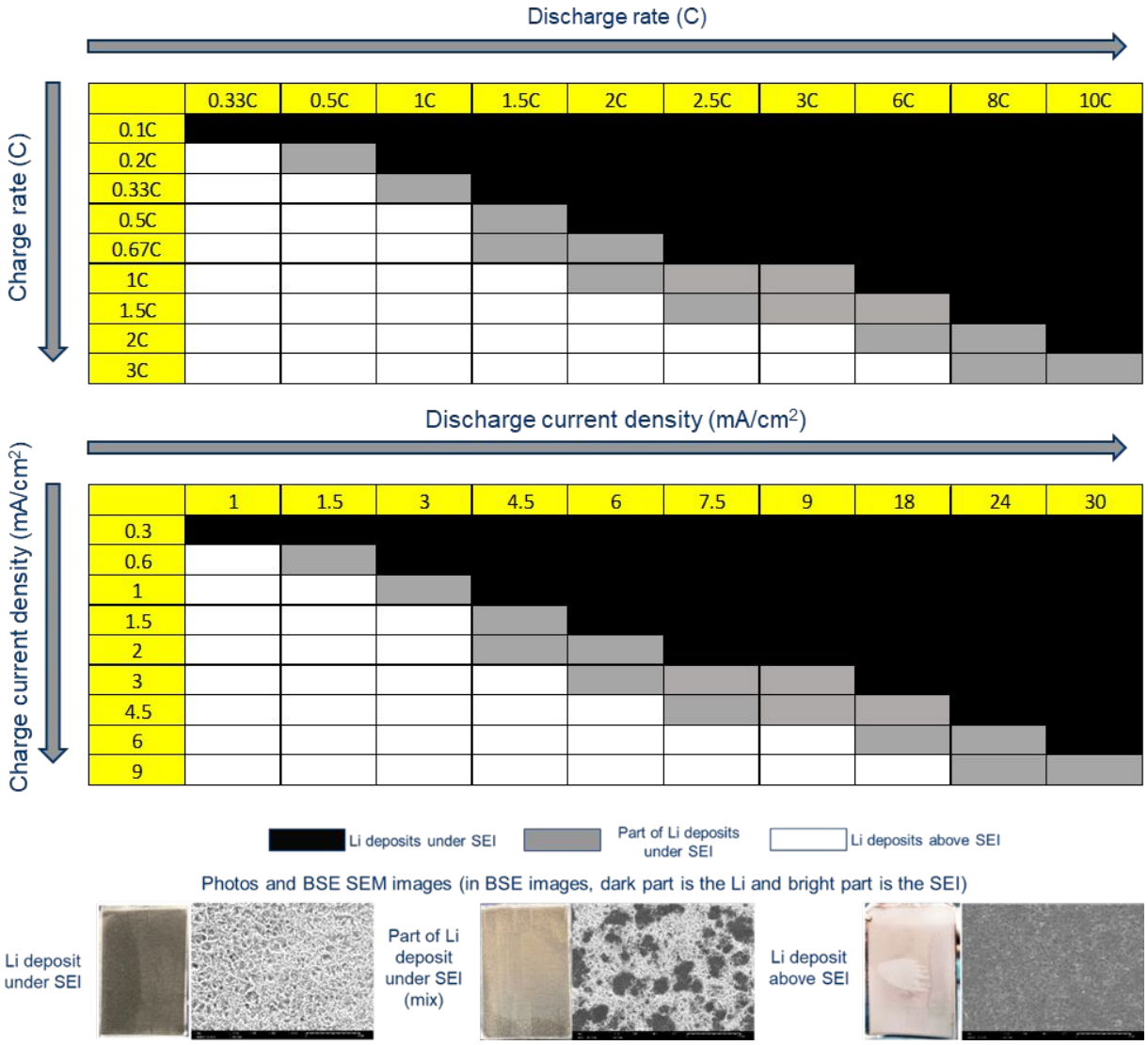

Figure S 7 Charge/discharge rate and corresponding current density maps

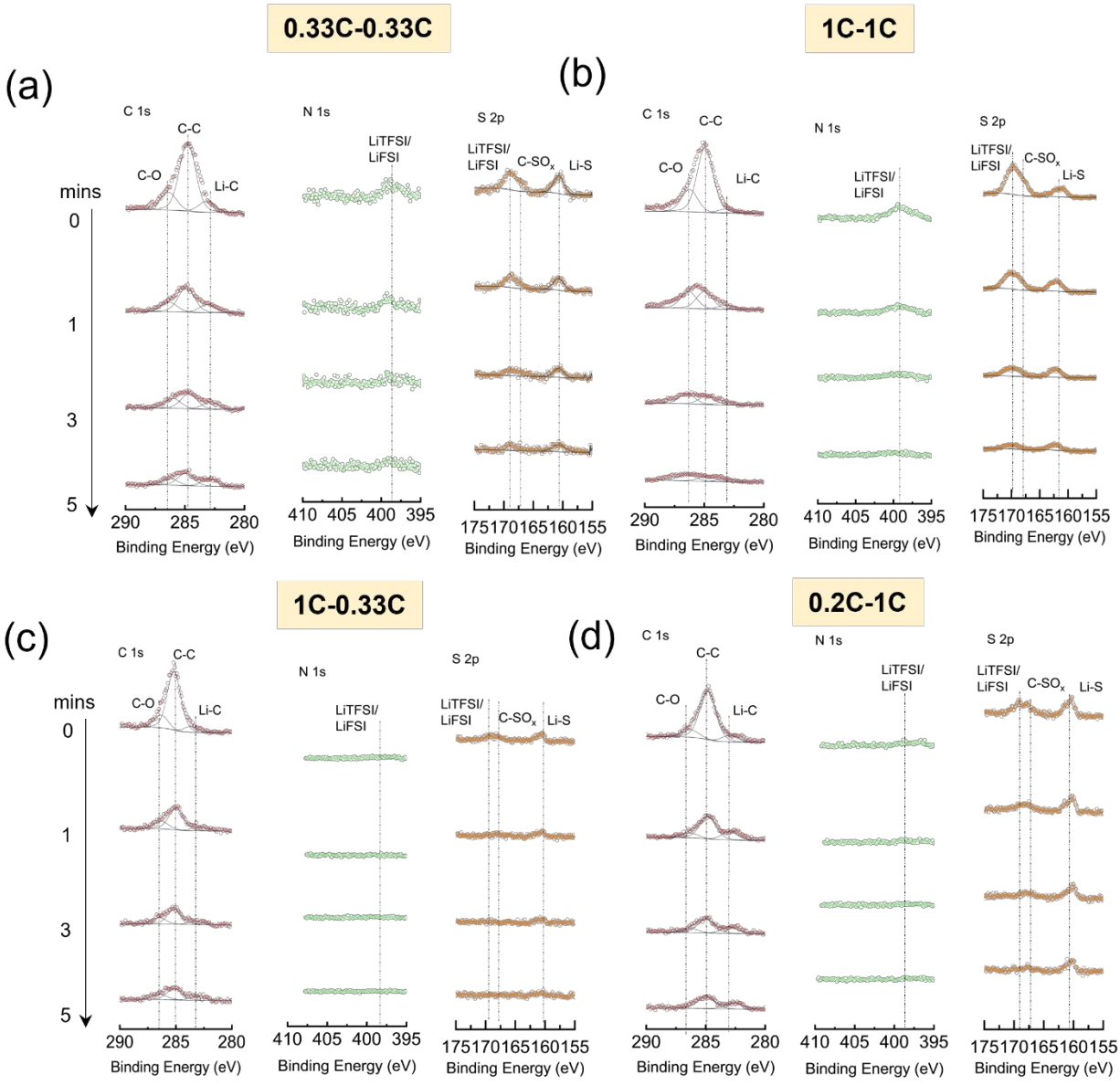

Figure S 8 XPS spectra of Li anode after cycling at (a) 0.33C-0.33C; (b) 1C-1C; (c) 1C-0.33C and (d) 0.2C-1C after 50 cycles.

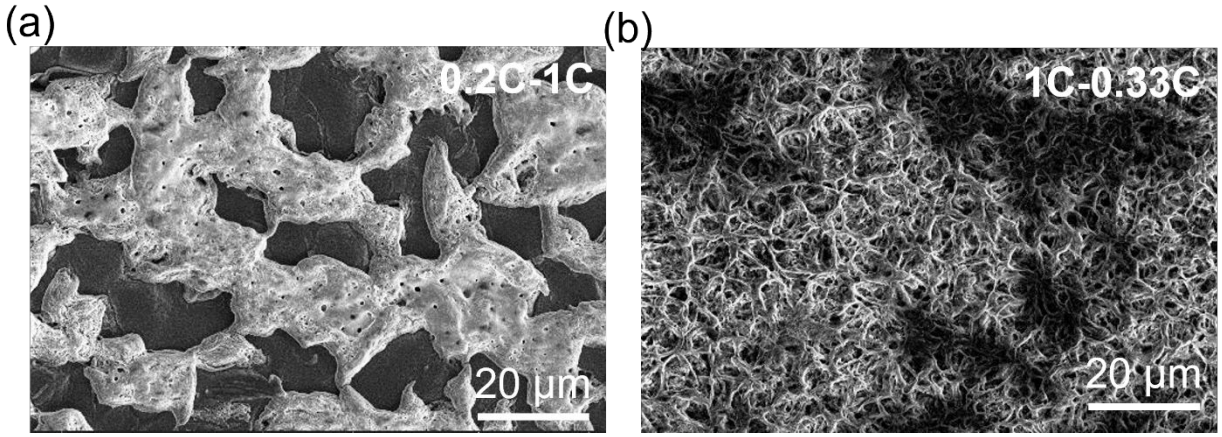

Figure S 9 SEM image of cycled Li anode after cycling at (a) 0.2-1C; (b) 1C-0.33C after 50 cycles.

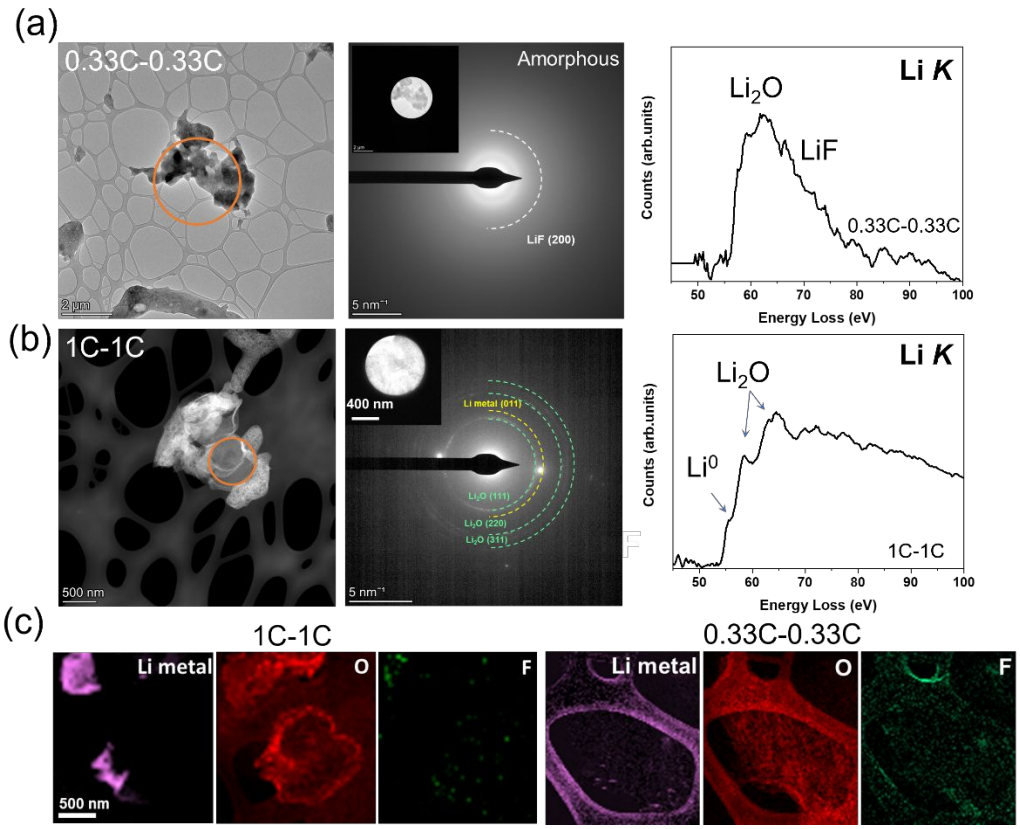

Figure S 10 TEM and SEAD pattern of cycled Li anode after cycling at (a) 0.33C-0.33C; (b) 1C-1C. (c) EELS mapping and spectra of the sample cycling at 1C-1C.

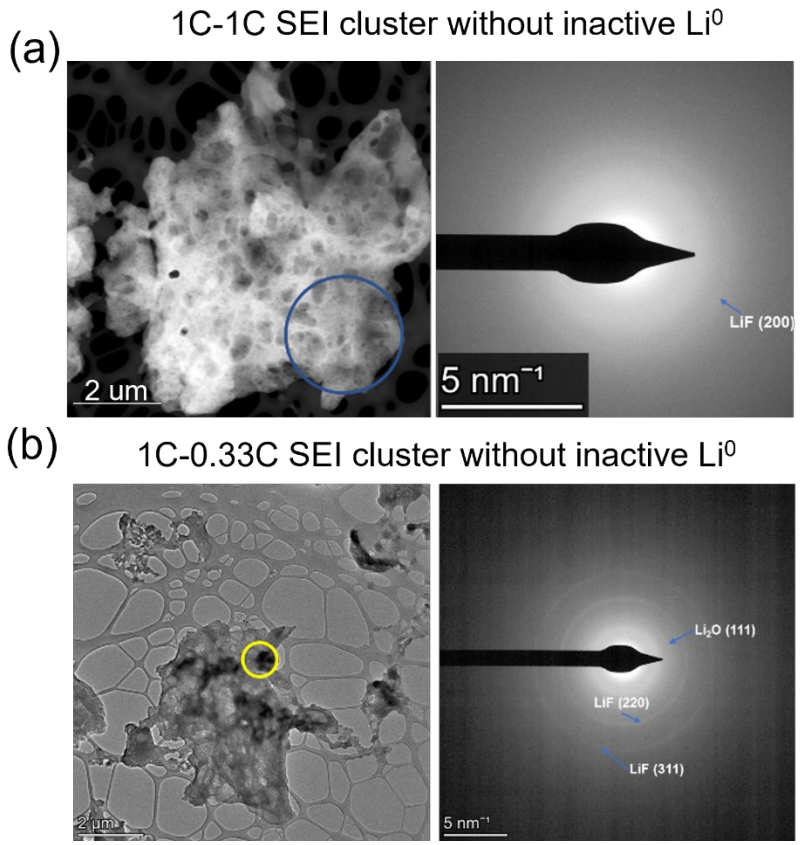

Figure S 11 TEM and SEAD pattern of cycled Li anode after cycling at (a) 1C-1C; (b) 1C-0.33C.

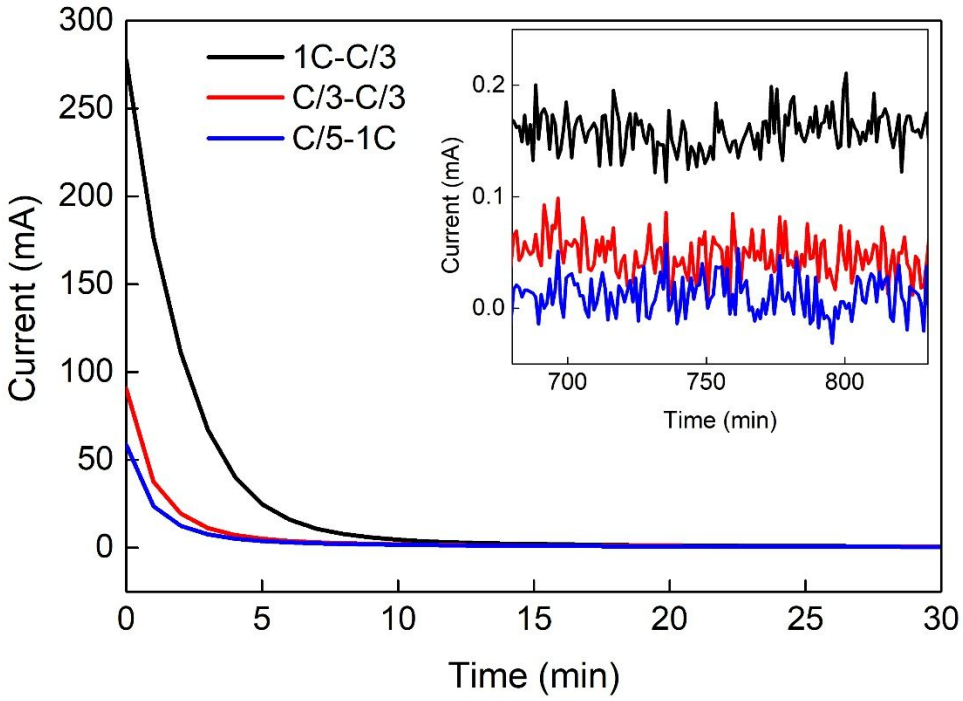

Figure S 12 Leakage current under different charge/discharge rates

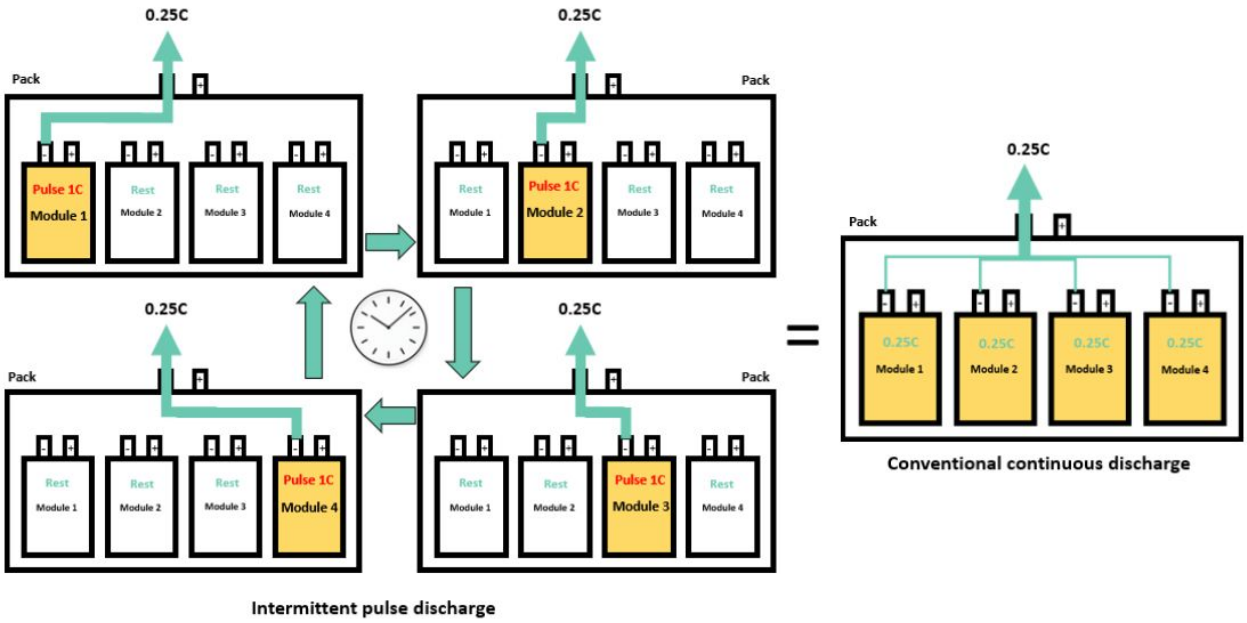

Figure S 13 Diagram shows possible way to use the pulse discharge protocol in EVs