Supporting Information

for

Multiscale Correlative Imaging Reveals Sequential and Heterogeneous Degradations in Fast-

Charging Batteries

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Supplementary Methods

Electrochemistry tests:

2 Ah cylindrical 18650-type cells were prepared and provided by a reputable battery manufacturer (Eve Energy Co., Ltd, China). The fast charging (2 C) rate and slow charging rate (0.5 C) were selected for comparison during the electrochemical experiments. The voltage range is between 2.5 and 4.2 V. These batteries were charged using a CC-CV protocol. For the fast-charging cells, they were charged to 4.2 V at 2 C and then held at 4.2 V until the charging current dropped to 0.05 C. For the slow-charging cells, they were charged to 4.2 V at 0.5 C and then held at 4.2 V until the charging current dropped to 0.05 C. For the slow-charging cells, they were fully charged, they were allowed to rest for 15 min to reduce the heat effect and then discharged to 2.5 V at the respective C-rate used in their charging process. These charging and discharging steps were repeated. A Neware 5 V/6 A Battery Test System was used in our tests. The dQ/dV curves and DC resistance are directly exported from the raw data using the Neware software. The Coulombic efficiency is calculated as the ratio of the discharge capacity to the charge capacity.

Micro-CT characterizations:

Three fast-charging batteries at different cycles (200th, 400th, and 500th) were chosen for the Micro-CT tests. These batteries were stopped at the discharged state at 2.5 V. The 3D Micro-CT tomography profiling was performed on a lab-based system (Zeiss Xradia 520, Carl Zeiss). The X-ray beam parameters comprised an emission energy set at 140 keV and a power of 10 mW. Subsequently, fine-tuning was carried out, which involved manipulating the distance between the emission source, detector, and the battery to obtain a voxel resolution of 20 μ m and a field of view of 2 mm × 2 mm. A total of 3601 consecutive slices were acquired over 180° rotations, with each slice exposed to the X-ray beam for 1.5 s. Different components in the slice were recognized using Matlab (codes available upon reasonable request) based on the X-ray intensity. The electrode center for each circle was exported by fitting the electrode curve via Gaussian function, then the layer spacing between electrode was calculated. The curvature of

cathodes was measured using the curvature analysis function in ImageJ.

Disassembly and SEM-EDX characterization:

After the micro-CT tests, the cathode, anode, and separator of each cycled battery were obtained by disassembling in an Ar-filled glovebox ($H_2O < 0.1$ ppm; $O_2 < 0.1$ ppm). Optical photos of the three key components were taken immediately. Some region of interest from the anode was cut off using scissors and washed carefully by dimethyl carbonate (DMC) to remove the electrolyte and LiPF₆. The circular NCM cathode pieces were punched from the same area of inside region of the cycled cathode sheets using a hollow punch (12 mm in diameter). These circular discs were weighed inside the glovebox to get the unwashed mass with the remaining liquid electrolyte. Subsequently, these samples are soaked in DMC solvent for 24 h. Then, the washed pieces were taken out and heated at 90 °C for 12h to remove the DMC solvent inside the glovebox. They were weighed again to get the NCM cathode mass without electrolyte. The electrolyte mass of the NCM electrode is obtained by subtracting the weight of the unwashed electrode from the washing.

The surface composition analysis of the NCM cathode were conducted on a field-emission SEM (RISE MAGNA, Tescan). The methods and procedures for the SEM-EDX characterizations are as follows. First, the unwashed NCM cathodes were recovered after the cylinder cells were disassembled inside the argon-filled glovebox. Then, they were punched into circular discs with a diameter of 12 mm using a hollow punch. The cathode discs were then allowed to dry inside the argon-filled glovebox for 24 h to remove the solvent in the electrolyte and to keep the LiPF₆ salt left at the cathode surface. The depletion and decomposition of the liquid electrolyte would reduce the amount of LiPF₆ left at the cathode surface. After drying, the cathode discs were transferred into the SEM chamber using a vacuum-transfer holder to avoid the impact of air and moisture. The regions for the SEM-EDX analysis were chosen under the SEM mode, which operated at 5 kV and a current of 1 nA. The SEM-EDX characterizations were conducted at 20 kV and a current of 1 nA. The elemental ratios of P/Mn and F/Mn were used to estimate the relative amount of the electrolyte. We note that signals of P and F elements are from LiPF₆ left and the NCM cathode surface whereas the signal of Mn comes from the NCM.

Cross-sectional multimodal characterizations:

All NCM cathode samples were washed several times by DMC in argon-filled glovebox. Then the samples were polished by three Ar⁺ ion beams on the EM TIC 3X (Leica) ion-milling instrument to get the smooth and flat cross-sections. The multi-modal studies were conducted on Tescan SEMs (RISE MAGNA and GAIA instruments), in order to gain the particle tomography, crystal structure, and Li element concentration for the same region of interest. Firstly, a SEM image of 8 k resolution was captured on RISE MAGNA, using 5 kV electron accelerating voltage and under In-Chamber BSE imaging mode. Then, the same sample was moved coaxially under the Raman 100X objective lens, keeping the same interested area directly shown as optical image. Optimized test conditions were selected to conduct single point Raman scanning for cross-sectional particle, with the parameters of 532 nm laser, 1.25 mW laser power, total 60 s integration time, 600 g/mm grating, which ensured that the particles were un-damaged and high-quality Raman spectra. Typically, approximate 100 particles were chosen to do single point scanning for each

cross-section. Statistical analysis of the multi-particles was done after background removal, datasmoothing, and normalization. The distance of particle to electrode surface were measured using the line profile function in ImageJ. Another FIB-SEM-ToF/SIMS (TESCAN GAIA) was used to acquire the relative lithium concentration from the cross-sections of the particles from the same region of interest. Focused Ga⁺ was used as sputtering ion beam to sputter the sample and to produce the secondary Li⁺ ions. The same cross-sectional interested area was located under the SEM mode and then tilted 45°perpendicular to the ion beam to perform the ToF/SIMS mapping experiments. To obtain data that can be analyzed statistically, consistent and rigorous testing parameters and operations were followed. After the optimization, the parameters were as follows: positive test mode was chosen to detect the secondary Li⁺ ion, 30 kV-500 pA ion beam was adjusted to gain high yield of secondary Li⁺ ion at 70 nm spatial resolution. A typical scanning area of $100 \times 100 \ \mu m^2$ was set to reduce shadow effect and to obtain 50-100 particles Li distribution for statistical analysis. 20 sputtering frames was controlled to get stable secondary Li⁺ ion yield. For further statistical analysis of the data, Matlab codes (available upon request) were written to remove background and signal noise caused by the edge effect, and extract lithium concentration from the region of interest.

Surface characterizations:

Time-of-flight secondary-ion mass spectrometry (ToF-SIMS) depth-profiling was performed on ToF-SIMS 5-100 spectrometer (ION-TOF GmbH, Germany), utilizing Bi^{3+} analysis ion-beam, and Cs^+ sputtering ion beam as detection enhancement for negative or positive secondary-ion fragments. All samples were washed multiple times using DMC to remove electrolytes and surface impurities. Then, the samples were dried at 80°C for 12 h under argon, and subsequently moved to the ToF-SIMS chamber via a transfer holder. The ToF-SIMS depth profiling experiments were conducted in an ultra-high vacuum environment with a pressure of 2 × 10⁻⁹ mbar, in order to acquire data suitable for semi-quantitative analysis. Negative mode was selected, with a typical scanning area of 100 × 100 μ m² using a 30 keV Bi³⁺ ion beam at a 45° injection angle, and the sputtered area was 300 × 300 μ m² using a 2 keV Cs⁺ ion beam injected at the 45° direction. The integrated yields of secondary-ion fragments of interest were determined by calculating the full-width-half-maximum (FWHM) area under the depth curve of the fragment profiles.

Thermal run-away tests:

The thermal-safety behaviors of the cycled batteries were characterized by an ARC (Extended Volume Plus Accelerating Rate Calorimetry, Thermal Hazard Technology). The cycled batteries were charged to 4.2 V before the ARC tests. The thermocouple was placed on the battery to obtain an accurate temperature. The curves of heat rate were examined by the ARC in the exothermal mode. The thermal runaway tests were proceeded in heating (with the heating step of 5 °C, waiting and seeking mode to search the specific temperature of self-heating). Once the heat rate of the cells increased to 0.02 °C·min⁻¹, the apparatus switched to the adiabatic mode.

Supplementary Figures



Figure S1. The direct current internal resistance (DCIR) as a function of cycle number between the fast-charging (2 C) and the slow-charging (0.5 C) cells.



Figure S2. Cathode-layer spacing distances in directions vertical to (**a**) and in parallel with (**b**) the aluminum tab for the 200th and 400th cycled batteries. (**c**), (**d**) and (**e**) are xy-slice X-ray CT images at different cycles, L1 and L2 are the two directions we calculated the cathode-layer spacing distance and local curvature. (**f**) and (**g**) are xz-slice X-ray CT images at 200th and 400th cycles.



Figure S3. Morphological and chemical characterizations of the anode surface. SEM images showing graphite exfoliation (a), mossy-like lithium (b), dendritic lithium (c), and transition-metal deposition (d). (e) and (f) are the corresponding EDX elemental maps of panel (d).



Figure S4. SEM image of non-metal compounds depositions on the surface of graphite anode.



Figure S5. SEM and EDX characterizations of the unwashed NCM cathode surface at the 1st , 200th, 400th, and 500th cycles. (a) SEM images. (b) to (g) are the corresponding EDX elemental maps of panel (a). These cathodes were recovered from the fast-charging cells.



Figure S6. SEM and EDX characterizations of the unwashed NCM cathode surface at the 1st, 340^h, and 600th cycles. (a) SEM images. (b) to (g) are the corresponding EDX elemental maps of panel (a). These cathodes were recovered from the slow-charging cells.



Figure S7. **Electrolyte depletion during slow-charging at the cathode**. **a** and **b** are the element content ratios of F and P to element Mn respectively for the unwashed NCM cathode samples recovered from the slow-charging cells. The capacity retention was 94% and 90% for the cells stopped at the 340th and the 600th cycles. The SEM-EDX data was shown in **Figure S6** above. **c** depicts the weight of the unwashed NCM cathodes (red columns) and the washed and dried ones (green columns). These samples are circular discs with a diameter of 12 mm cut from the inside region of the NCM cathode sheets. **d** is the estimated weight of electrolyte in the NCM cathode samples (left side, determined based on results from Panel (**c**) and the electrolyte depletion ratio (right side).



Figure S8. (a) Cross-sectional SEM morphologies of the NCM cathodes. (b) NanoSIMs images of Li distribution of the same area in (a). (c) Raman spectra along the depth direction, which were obtained from the same area in (a). (d) Cross-sectional SEM images of typical NCM particles for the 200th, 400th, and 500th cathodes. (e) Li distribution maps of typical NCM particles. (f) NCM particle crack ratio as a

function of cycle number, using the three particles in panel (d) as explanatory examples. (g) The distribution of lithium concentrations in the three NCM particles shown in panel (e). (h) Raman spectra collected from the region shown in panel (d), marked by the white circles.



Figure S9. Additional thermal safety test results. a, ARC test results from the normal cell (green curve) and the cell with a slight excess of liquid electrolyte (red curve). The ARC tests were done at the charged states (charged to 4.2 V). **b**, Three characteristic temperatures (T1, T2, and T3) for two type of batteries. T1 is the onset temperature for the detectable self-heat generation. T2 is the trigger temperature for thermal-runaway ($dT/dt > 1^{\circ}C \min^{-1}$). T3 is the maximum temperature that the battery can reach during a thermal-runaway. **c**, Temperature increasing rate versus battery temperature during the ARC tests.

Supplementary Tables

No.	Items	Specification
		2000mAh
1	Nominal Discharge Capacity	Charge: 1A, 4.20V, CCCV 100mA cut-off
		Discharge: 0.4A, 2.50V DC cut-off
2	Nominal Voltage	3.60V
3	Standard Charge	CCCV, 1A, 4.20±0.05V, 100mA cut-off
4	Rapid Charge	CCCV, 4A, 4.20±0.05V, 100mA cut-off
5	Standard Discharge	DC, 0.4A, 2.50V cut-off
6	Max. Continuous Discharge	DC, 30A, 2.50V cut-off (cut-off temperature 80°C)
7	Charge/Discharge Voltage Range	4.20~2.50V
8	Initial Internal Impedance	$\leq 18 \mathrm{m}\Omega$
9	Cell Weight	45.0g Max (~42-43 g)
10	Cell Dimension	Height: 65.00±0.15mm
		Diameter: 18.35±0.10mm
		Ambient Temperature:
11	Operation Temperature	Charge: 0 to 45°C
		Discharge: -20 to 60°C

Table S1. The specifications of the 18650-type batteries used in this study.

Table S2. Comparison of key parameters of the normal cell and the cell with additional electrolyte. The cells with additional electrolytes were made with the help of the battery manufacturer.

No.	Items	Normal Cells	Cells with additional electrolyte
1	total mass/g	42.59	43.08
2	cathode mass/g	15.86	15.83
3	anode mass/g	13.08	13.10
4	electrolyte mass/g	3.90	4.72
5	cathode thickness/µm	107	100
6	anode thickness/µm	108	110