Electronic Supplementary Information

Microcracking of Ni-rich Layered Oxide Does Not Occur at Single Crystal Primary Particles Even Abused at 4.7 V

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Experimental Section

The cathode slurry was prepared by using a vacuum mixer. SC-NMC or Poly-NMC, Polyvinylidene fluoride (PVDF), and carbon black super P were mixed in N-Methyl-2-pyrrolidone (NMP) solvent at a weight ratio of 0.952: 0.024: 0.024, respectively in a total mass of 3 kg. The slurry with a viscosity in the range of 6000-8500 centipoise (cPs) was coated on an aluminum foil current collector by the roll-to-roll coating semi-automatic machine and dried at 120°C to evaporate NMP solvent having a regerative system of NMP. Electrodes were cut into 65 cm*6.7 cm (reported in Area unit) and active mass loading c.a. 10.60 g and 13.66 for SC-NMC and Poly-NMC, respectively. On the other hand, the anode side was produced by following the previous report[1, 2]. The n/p ratio is fixed to be 1.1 according to the recommendation in the commercial LIBs.

The base electrolyte system was used in this study is 1.0 M $LiPF_6$ in Ethylene carbonate (EC)/Dimethyl carbonate (DMC), Ethyl methyl carbonate (EMC), and Fluoroethylene carbonate (FEC) solvents and used triple-layered PE/PP/PE with ceramic coating from Celgard as the polymer separator. Note, all commercial materials and chemicals were marketed from Gelon LIB Co.,LTD, Shandong, China.

SC-NMC and Poly-NMC were characterized using a field emission scanning electron microscope (FE-SEM, JEOL-JSM-7610F, JOEL Ltd.) with a backscattered electron detector at an accelerating voltage of 15kV. The powder of SC-NMC and Poly-NMC was placed on the carbon tape. The electrodes were cut into small square pieces and placed on the carbon tape. Chemical composition analysis was performed using inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer) and X-ray fluorescence spectroscopy (XRF). The result from ICP-OES was shown in Table 1S, the transition metal Nickel composition:

Manganese: Cobalt is 8:1:1 for SC-NMC and Poly-NMC. The crystallographic structure of the materials was studied by X-ray diffraction (XRD, Bruker) using Cu K-alpha radiation. For the *in situ* XRD, the XRD cell was coupled with Autolab (PGSTAT204). The XRD results were collected every 369 seconds in the range of 10-70^{o} charging-discharging at 0.1C at the same time. The Rietveld refinement analysis was carried out by Rietica software.

For electrochemical impedance spectroscopy (EIS), all samples were measured at room temperature (25 ± 1.0°C) using Autolab(PGSTAT204). Data were collected from 100kHz to 10 mHz with 5 mV signal amplitude and 50 number of frequencies.

Galvanostatic charge-discharge cycling was performed at room temperature by using battery tester (Gelon). Before cycling, all 18650 battery cells were wet at 1.5 V for 48 h and taken to the step formation process for one cycle. The rate capability test and stability were then performed in a range of 3.0-4.2 V at 1C (1,950 mA and 2,350 mA for SC-NMC Poly-NMC, respectively.). The battery cell formation process is an essential step for the battery cell performance. This work studied the three-difference upper cut-off voltages (UCV), including 4.0, 4.2, and 4.4 V, while the lower voltage shows no significant difference between 2.8 V and 3.0 V (no peak in dQ /dV in that range). Apart from different upper cut-off voltages, we also studied the constant current (CC) and constant current constant voltage (CCCV) discharging mode. An overall summary is shown in **Figure 6** which offers the six different methods for discharging steps. In contrast, on the charging step, we used multistep starting from OCV to 2.7 V (at C/40 rate), 2.7 to 3.0 V (at C/20 rate), 3.0 to 3.5 V (at C/15 rate), and 3.5 to upper voltage (at C/12.5 rate) and followed by long term cycles at 1C rate (C rate from capacity determination after formation process).

Electrochemical protocols for battery testing, for the current density of each battery testing, relied on the cathode active materials (Poly-NMC/SC-NMC) for which the practical capacity of 180 mAh/g, N/P ratio of the battery was matched with graphite anode in the range of 1.1to prevent the Li-dendrite during the cycling. The electrochemical testing includes long-term stability at 1C current density, rate capability (from 0.1C to 2C), and long-term stability at 1C with a slow current density of 0.1C during the cycling for dQ/dV observation. The charging step is performed by CCCV charging with stop current C/20, and the discharging step is performed by CC charging.

Supporting results

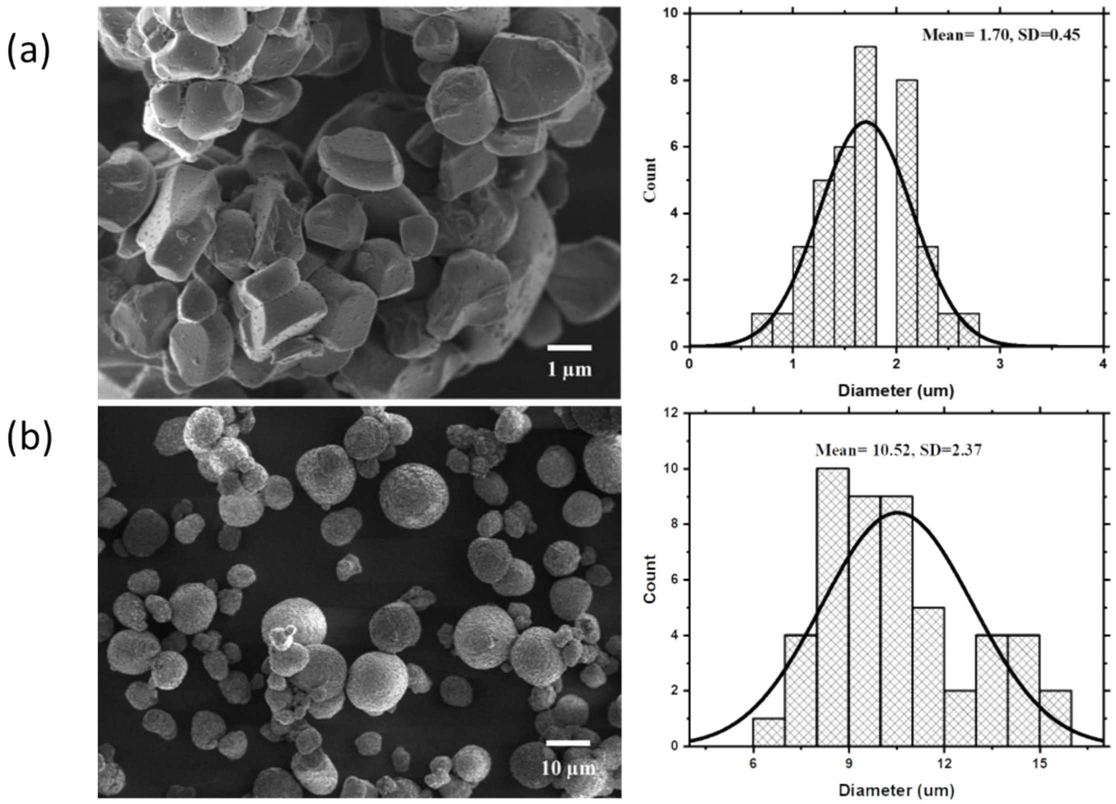

Figure S1. FESEM images of (a) single-crystal NMC811 (SC-NMC) powder and (b) polycrystal NMC811 (Poly-NMC) powder. Note, the average particle sizes calculated by ImageJ (Version 1.53t) are 1.70 ±0.45 µm and 10.52 ± 2.37 µm of SC-NMC and Poly-NMC, respectively.

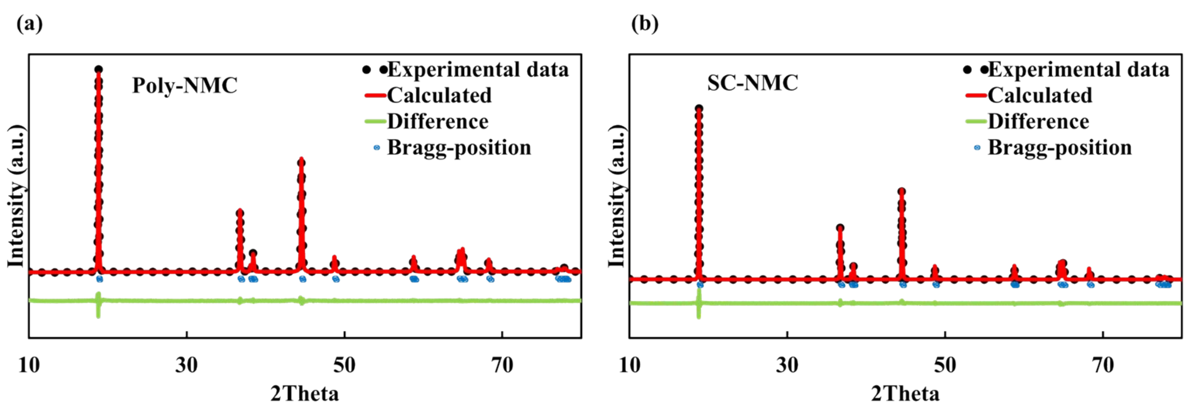

Figure S2. XRD pattern from the Rietveld refinement of (a) Poly-NMC and (b) SC-NMC.

Table S1 Rietveld refinement parameters of SC-NMC and Poly-NMC.

Sample	A (Å)	C(Å)	c/a	V (Å³)	Bragg - R-factor	Ni/Li(%)
SC-NMC	2.8721(1)	14.1894(0)	4.940	101.3670(5)	1.995	2.6
Poly-NMC	2.8737(9)	14.2022(3)	4.942	101.5631(3)	2.262	1.6

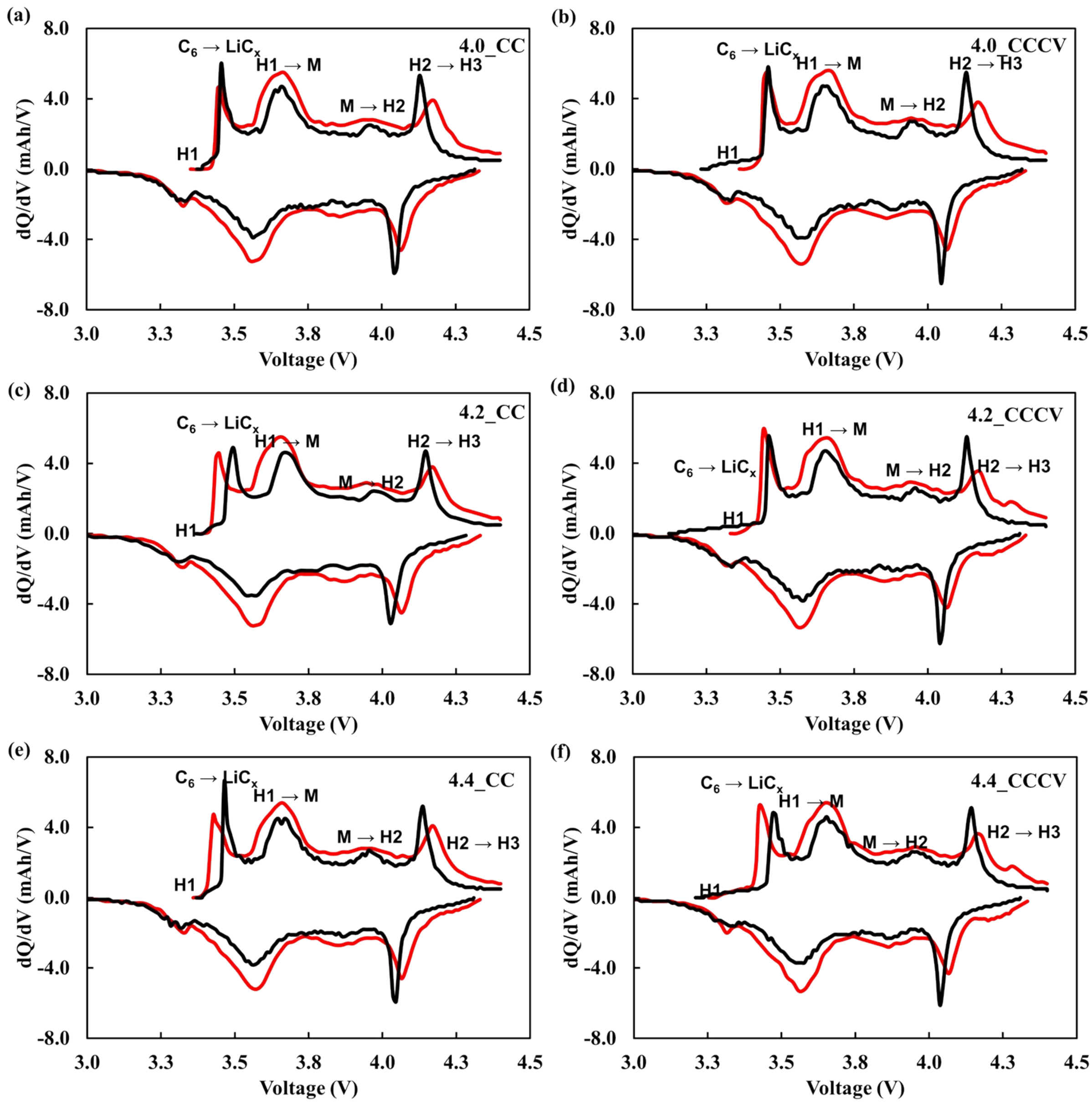

Figure S3. Differential capacity as a function of voltage (dQ/dV) of SC-NMC and Poly-NMC after the formation process (a) 3.0-4.0 V_CC (b) 3.0-4.0 V_CCCV (c) 2.8-4.2 V_CC (d) 2.8-4.2 V_CCCV (e) 2.8-4.4 V_CC and (f) 3.0-4.0 V_CCCV.

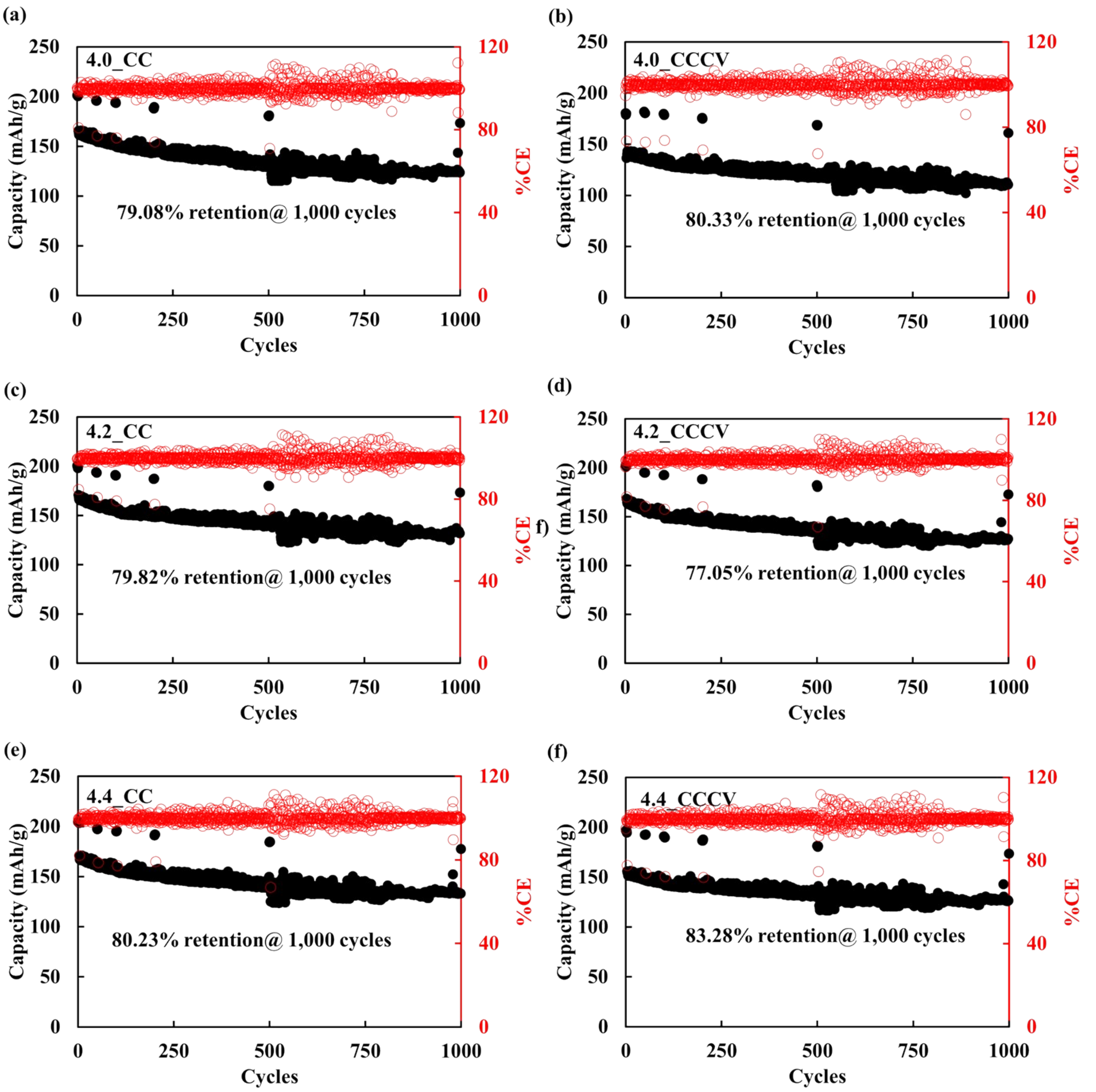

Figure S4. Electrochemical performance of SC-NMC of different formation condition including (a) 3.0-4.0 V CC (b) 3.0-4.0 CCCV (c) 2.8-4.2 V CC (d) 2.8-4.2 V CCCV (e)2.8-4.4 V CC and (f) 2.8-4.4 V CCCV at 1C-rate and 0.1C (Check-up cycle) in the window volage 3.0-4.2V

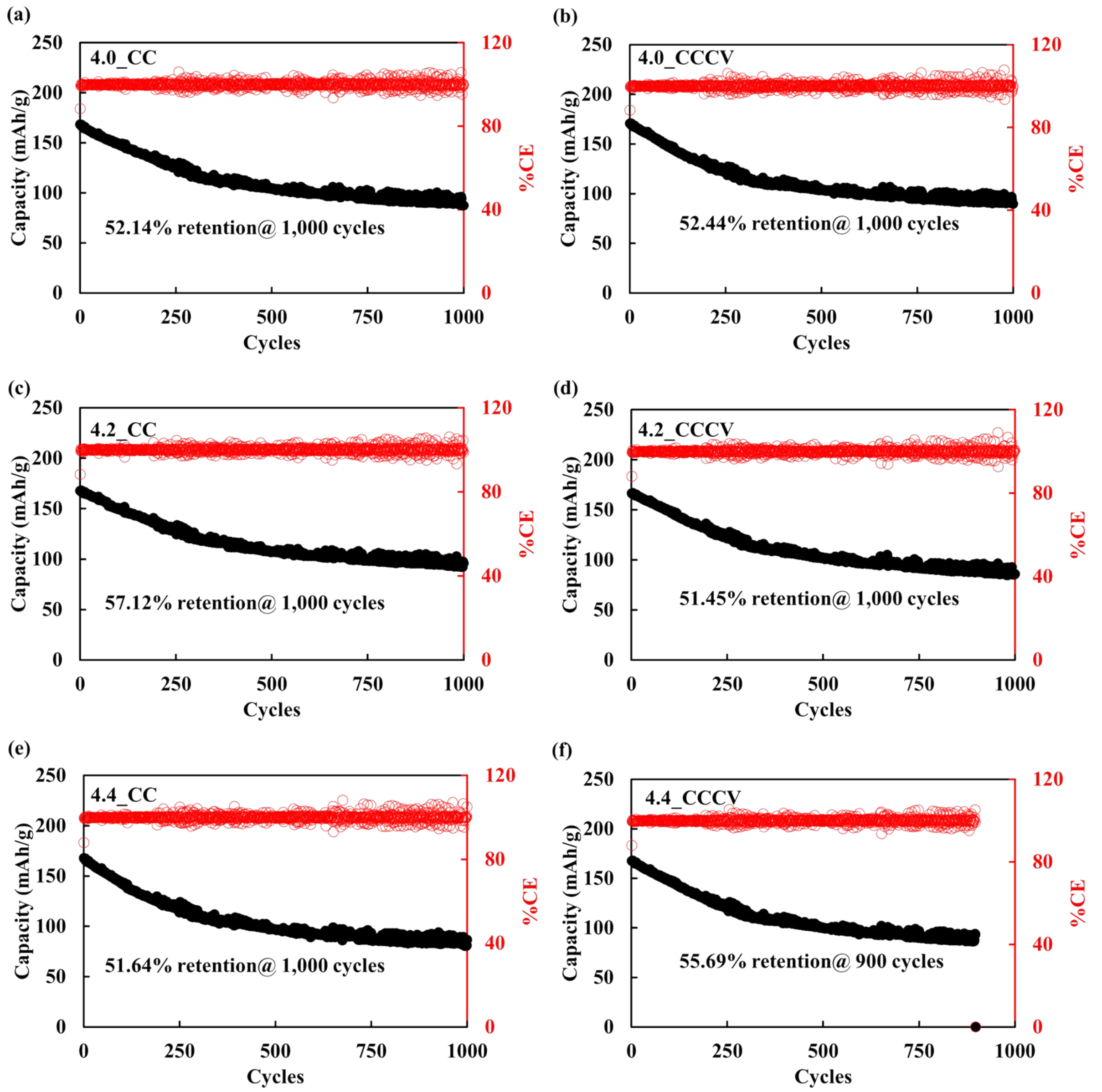

Figure S5. Electrochemical performance of Poly-NMC with different formation conditions including (a) 3.0-4.0 V CC (b) 3.0-4.0 CCCV (c) 2.8-4.2 V CC (d) 2.8-4.2 V CCCV (e)2.8-4.4 V CC and (f) 2.8-4.4 V CCCV at 1C-rate in the window volage 3.0-4.2V.

Mechanical strength of SC-NMC

We have found that the mechanical strength of SC-NMC is outstanding according to following experiment:

1. The mechanofusion process, which generally applies high mechanical energy or shear force at the surface of core materials. This can break or crack the materials e.g., the surface of Poly-NMC transformed into a smooth surface and smaller sizes, but SC-NMC remains the same morphology after the mechanofusion.
2. The mortar and pestle did not affect the SC-NMC particle, showing no crack in the primary particle.
3. Even at the high voltage/long-term testing, the electrochemical process also did not destroy the structure of SC-NMC.

These results should be the reason behind the high stability of SC-NMC in LIBs indicating that there is no particle cracks at the single crystalline primary particles of NMC811.

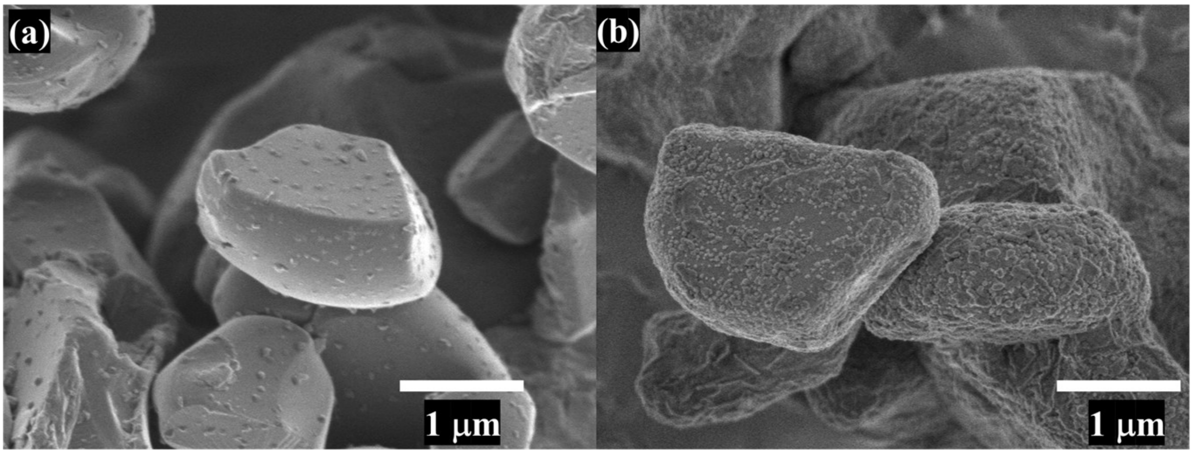

Figure S6. FESEM images of the NMC811 particle a) before and b) after the mechanofusion process of SC-NMC. (Note that the small particles at the surface of the SC-NMC after mechano-fusion is the impurity from humidity)

Safety test

Apart from the characterization and the battery performance, we also evaluated the safety test, including the impact test, altitude simulation test, shock test, and internal short circuit test, which followed the UN38.3 standard but more severe condition. SC-NMC and Poly-NMC battery cells, after the capacity determination, were charged to fully charged stage 4.2 V with a current density of 1C (while the protocols of UN38.3 is charged to 50%SOC). The Impact test was examined with a 5.5 kg metal object and a 61 cm height drop toward the battery cell; all batteries did not explode after the test. Altitude test, the cells were charged to 4.2 V and stored in the chamber at the altitude level of 15,000 meters (pressure around 11.6 kPa) for 6 h. The result reveals that the battery did not show any leaking or rupture. The shock test was set as 650-m height and repeating count 12 times, and the last method, the internal short circuit, was passed as well.

Figure S7. The impact test of the Li-ion batteries of (a) Graphite//SC-NMC and (b) Graphite//Poly-NMC. The inset photos showed the battery cells before and after tested.

Table S2. Safety test summary report along with the UN38.3 protocol.

Safety test summary report: UN38.3		
Specification	Cathode	SC-NMC
	Anode	Graphite
	Maximum capacity	2.0 Ah (2000 mAh)
	Testing voltage	Fully charged stage (4.2V)
	Approx. Mat. Loading	~11.5 g
	Nominal voltage	3.6-3.7 V
	Cell weight	~40 g
	Energy density	160 Wh/kg
Safety test		
Attitude simulation Pressure 11.6 kPa Hold time 6 hrs. Altitude 15,000 m		passed
Shock test Hight 650 m Repeating 12 times		Passed
External short circuit Internal resistance of the system: 80±20 mOhm Temperature of the test is 55±5 C		Passed
Impact test Weight 5.5 kg Distance 610 cm.		Passed No explosion
Test Reference: UN Manual of Tests and Criteria, sub-section 38.3, the fifth revised edition.		

Links to VDOs

1. Gas evolution of SC-NMC with different upper cell voltages
   https://www.dropbox.com/s/333m9hlsiklgbee/SC-NMC-jelly-rolls.mp4?dl=0
2. Gas evolution of Poly-NMC with different upper cell voltages
   https://www.dropbox.com/s/s7c3y85muj7ddpi/Poly-NMC-jelly-rolls%20.mp4?dl=0

Supporting references

1. N. Phattharasupakun, J. Wutthiprom, S. Duangdangchote, S. Sarawutanukul, C. Tomon, F. Duriyasart, S. Tubtimkuna, C. Aphirakaramwong and M. Sawangphruk, *Energy Storage Materials*, 2021, **36**, 485-495.
2. S. Tubtimkuna, N. Phattharasupakun, P. Bunyanidhi and M. Sawangphruk, *Advanced Materials Technologies*, 2022, **n/a**, 2200436.