

Electronic supplementary information (ESI)

**Revealing Unprecedented Cathode Interface Behavior in All-Solid-State Batteries with
Oxychloride Solid Electrolytes**

Feipeng Zhao,^{a,†} Shumin Zhang,^{a,†} Shuo Wang,^c Carmen M. Andrei,^d Hui Yuan,^{d,e} Jigang Zhou,^f
Jian Wang,^f Zengqing Zhuo,^g Yu Zhong,^h Han Su,^h Jung Tae Kim,^a Ruizhi Yu,^a Yingjie Gao,^a
Jinghua Guo,^g Tsun-Kong Sham,ⁱ Yifei Mo,^c Xueliang Sun^{a,b*}

^a Department of Mechanical and Materials Engineering, Western University, London, ON, N6A
5B9, Canada

^b Eastern Institute for Advanced Study, Eastern Institute of Technology, Ningbo, Zhejiang
3150200, P.R. China

^c Department of Materials Science and Engineering, University of Maryland, College Park, MD
20742, USA

^d Canadian Centre for Electron Microscopy, McMaster University, Hamilton, ON, L8S 4M1,
Canada

^e Department of Materials Science and Engineering, McMaster University, Hamilton, ON, L8S
4L7, Canada

^f Canadian Light Source Inc., University of Saskatchewan, Saskatoon, SK, S7N 2V3, Canada

^g Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

^h State Key Laboratory of Silicon Materials, Key Laboratory of Advanced Materials and
Applications for Batteries of Zhejiang Province, School of Materials Science & Engineering,
Zhejiang University, Hangzhou 310027, China

ⁱ Department of Chemistry, Western University, London, ON, N6A 5B7, Canada

Corresponding E-mail address: xsun9@uwo.ca

Experimental section

All-solid-state battery assembly

Cathode composites were made by mixing CAMs (LCO, NCM523, or NCM83) and LTOC SEs in a mass ratio of 7:3. All CAMs were purchased without any further modifications. About 60 mg of the LTOC electrolyte powder was pressed at ~300 MPa to form a solid electrolyte layer (10 mm diameter). The cathode composites (~ 5 mg) were uniformly spread onto the surface of the one side of electrolyte layer and pressed with ~360 MPa for five minutes. Subsequently, a piece of In metal foil was placed on the other side of the electrolyte layer, followed by attaching a piece of 20 μm -thick Li metal foil (10 mm diameter). Then, the cell was pressed at ~120 MPa for three minutes. The obtained internal cell was sandwiched between two stainless-steel rods as current collectors and sealed in the customized mold cell for various electrochemical characterizations. To prevent the direct contact between LTOC and Li-In anode, 40 mg of interlayer electrolytes (lithium yttrium chloride (LYC) for RT and HT cells or LGPS for LT cells) were introduced at the anode side. The LTOC, LYC and LGPS were prepared according to the reports as elsewhere,¹⁻³ possessing ionic conductivities of $1.0 \times 10^{-2} \text{ S cm}^{-1}$ (**Figure S18** shows the ionic conductivity measurement for the prepared LTOC SEs), $9.0 \times 10^{-4} \text{ S cm}^{-1}$ and $6.2 \times 10^{-3} \text{ S cm}^{-1}$, respectively. All cell fabrication processes were carried out in an Ar-filled glove box ($\text{O}_2 < 0.1 \text{ ppm}$, $\text{H}_2\text{O} < 0.1 \text{ ppm}$). To ensure good physical contact between various solid components, a stack pressure of ~80 MPa was applied on the mold cell during testing.

Electrochemical characterizations

Galvanostatic charge/discharge measurements were conducted on the Neware battery test system under voltage profiles of 1.9 ~ 3.7 V (vs. Li-In) for NCM CAMs and 1.9 ~ 3.6 V for LCO. CV measurements were conducted on VMP3 at various scan rates from 0.05 to 0.3 mV s^{-1} . In-situ EIS

measurements (0.1 Hz to 7 MHz) were recorded using the VMP3 instrument during the first charge/discharge at 0.2 C. GITT measurements were carried out using Neware battery test system. The transient discharge voltage profiles were recorded by applying a current density of 0.1 C for 20 min followed by a 2 h relaxation until voltage reaches 3.7/1.9 V for charging/discharging processes. Freezers and ovens manufactured by Thermo Fisher Scientific were used to control the LT and HT conditions, respectively. The temperature-dependent ionic conductivities were obtained via the electrochemical impedance spectroscopy (EIS) measurements on a multichannel potentiostat 3/Z (German VMP3). The applied frequency range was 1 Hz to 7 MHz and the voltage amplitude was 20 mV. The test cell was fabricated by pressing ~100 mg of the electrolytes into a pellet (diameter 1 cm) under a pressure of ~300 MPa. Stainless-steel rods were employed as the current collector. The resultant internal cell was sealed in a customized mold cell with screws for EIS tests.

Interface Thermodynamic calculations

The pseudo-binary interface between the LTOC and cathodes materials is constructed to evaluate the interfacial stability, and the phase equilibria are calculated with minimum mutual reaction energy. The phase equilibria only include the materials that are experimentally existed, and exclude all compounds containing Cl with positive valence states. The energies of materials were obtained from MP database. More details can be found in previous studies.⁴⁻⁶

Other characterizations

SEM images for the CAM particles were obtained by using a Hitachi S-4800 field-emission SEM (FE-SEM, acceleration voltage 5 kV). Focused ion beam (FIB)-SEM was carried out on a Zeiss Sigma FESEM, which was connected with Thermo Scientific Helios G4 UXe Dual Beam Plasma FIB (PFIB) instrument. The analysis was carried out at a working distance of ca. 4 ~ 5 mm and

using accelerating voltages in the range of 10 ~ 20 kV and a beam current of 3.2 nA. TEM characterizations were performed in a Talos 200X (Thermo Fisher Scientific) operated at 200 kV. HAADF was performed with a spot size less than 1 nm, convergence semi-angle 10.5 mrad. EELS experiments were performed using a Gatan Continuum S spectrometer with a CMOS detector at a dispersion of 0.75 eV. The collection semi-angle was 30 mrad. All the data was acquired and processed using Digital Micrograph from Gatan. The presented EELS signal was background subtracted. XPS spectra were obtain by using Krotos AXIS Ultra Spectrometer system using a monochromatic Al K(alpha) source (25 mA, 15 kV). STXM was carried out on the Soft X-ray Spectromicroscopy (SM, 130 ~ 2700 eV) beamline at CLS. STXM data was analyzed using the aXis2000 software. XAS of O K-edge were measured using bending magnet beamline at BL7.3.1 endstation of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory.

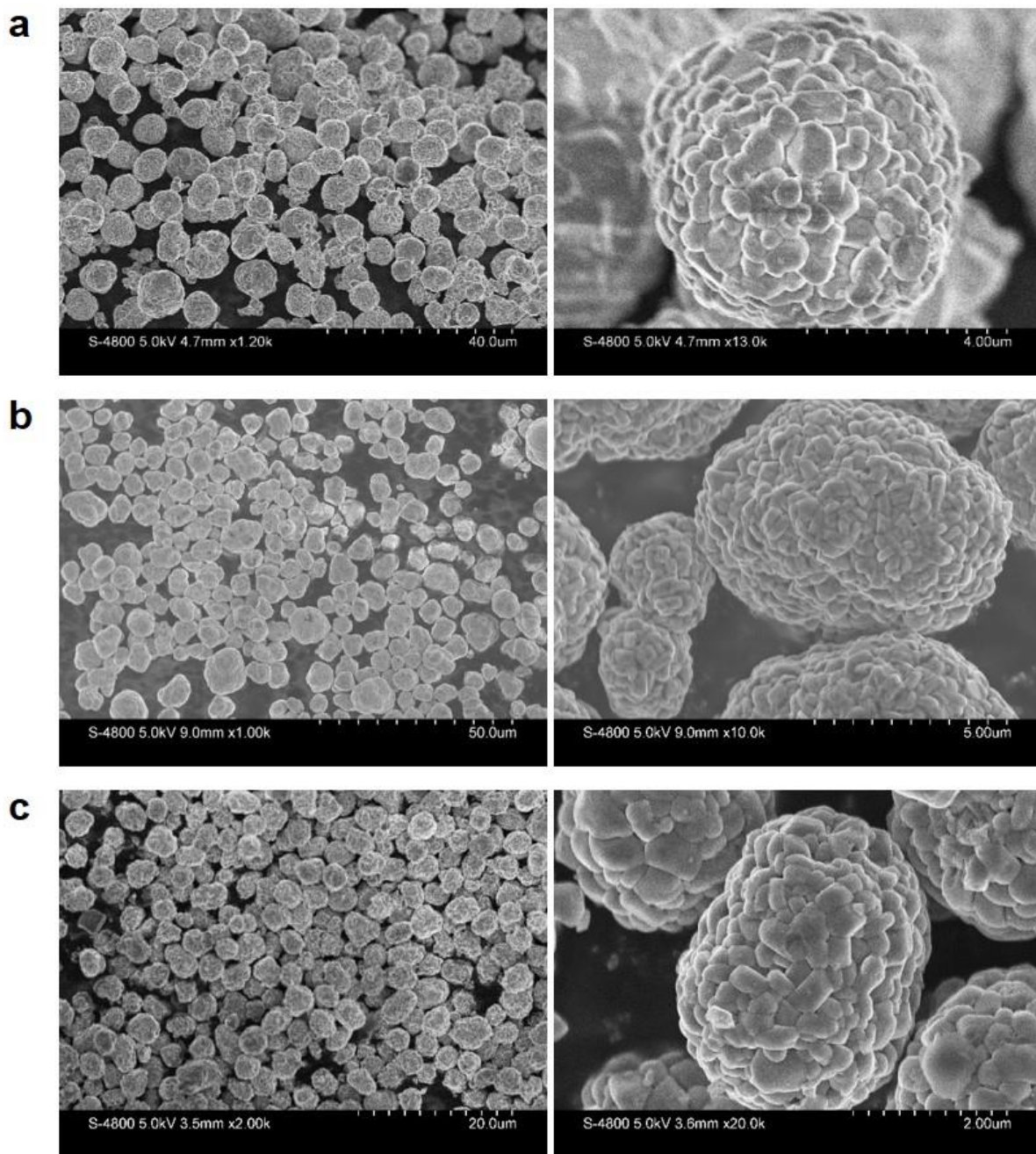


Figure S1. Morphologies of three CAMs used in this work. (a) SEM images of LCO. (b) SEM images of NCM523. (c) SEM images of NCM83. All CAMs are polycrystalline with similar secondary particle size.

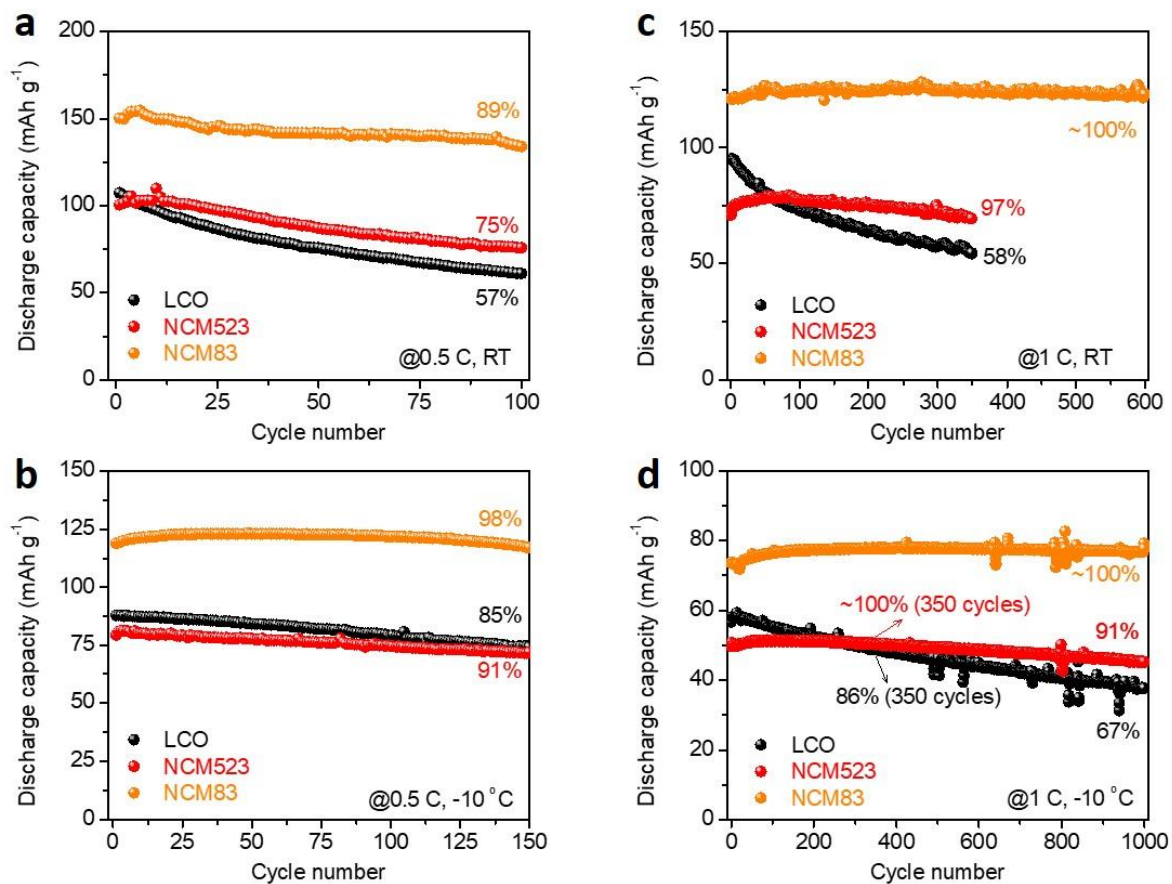


Figure S2. (a-b) Cycling performance of three kinds of cathode materials tested at 0.5C and RT or -10 °C. (c-d) Cycling performance of three kinds of cathode materials tested at 1C and RT or -10 °C.

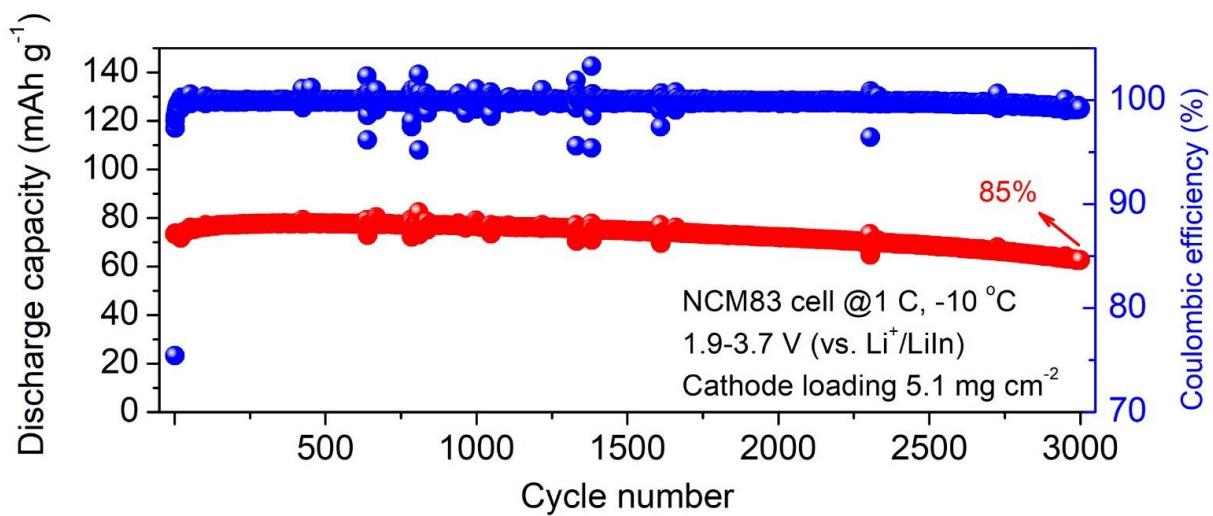


Figure S3. Long-term cycling performance of the NCM83 cell at a high rate of 1 C and $-10\text{ }^{\circ}\text{C}$.

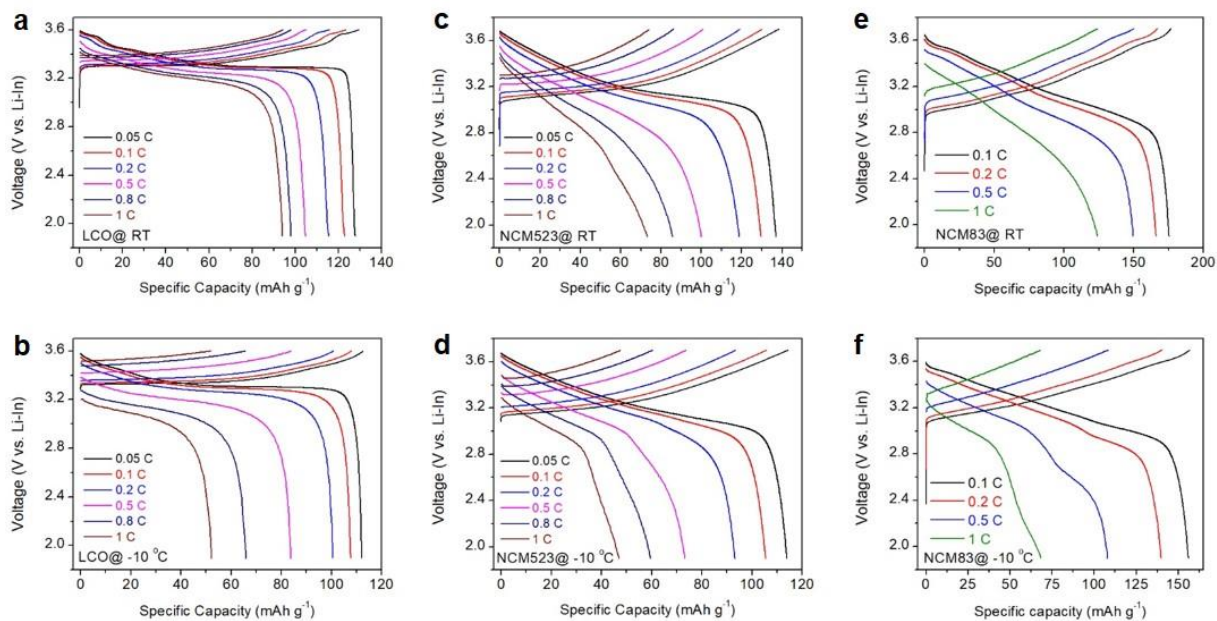


Figure S4. (a, b) Charging and discharging curves of the LCO cells measured at RT and -10 °C, respectively. (c, d) Charging and discharging curves of the NCM523 cells measured at RT and -10 °C, respectively. (e, f) Charging and discharging curves of the NCM83 cells measured at RT and -10 °C, respectively.

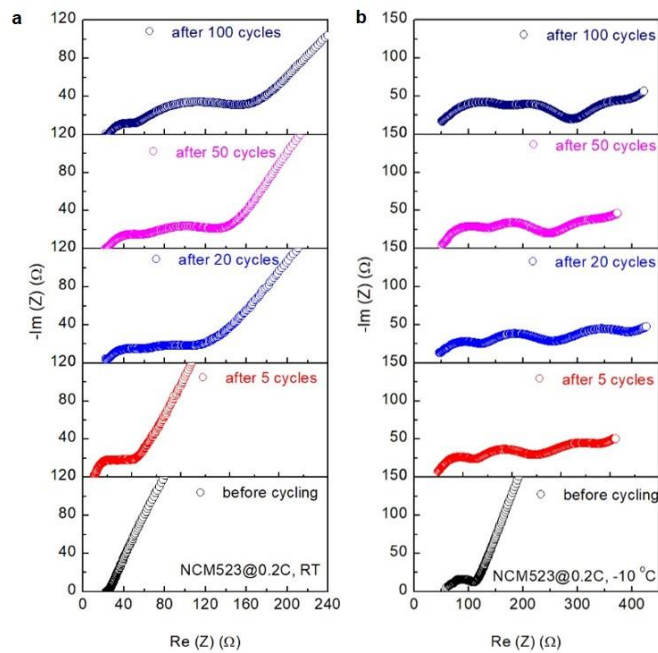


Figure S5. Cycle number-resolved EIS plots of the NCM523 cell cycled at a low rate of 0.2 C at RT (a) and -10 °C (b), respectively.

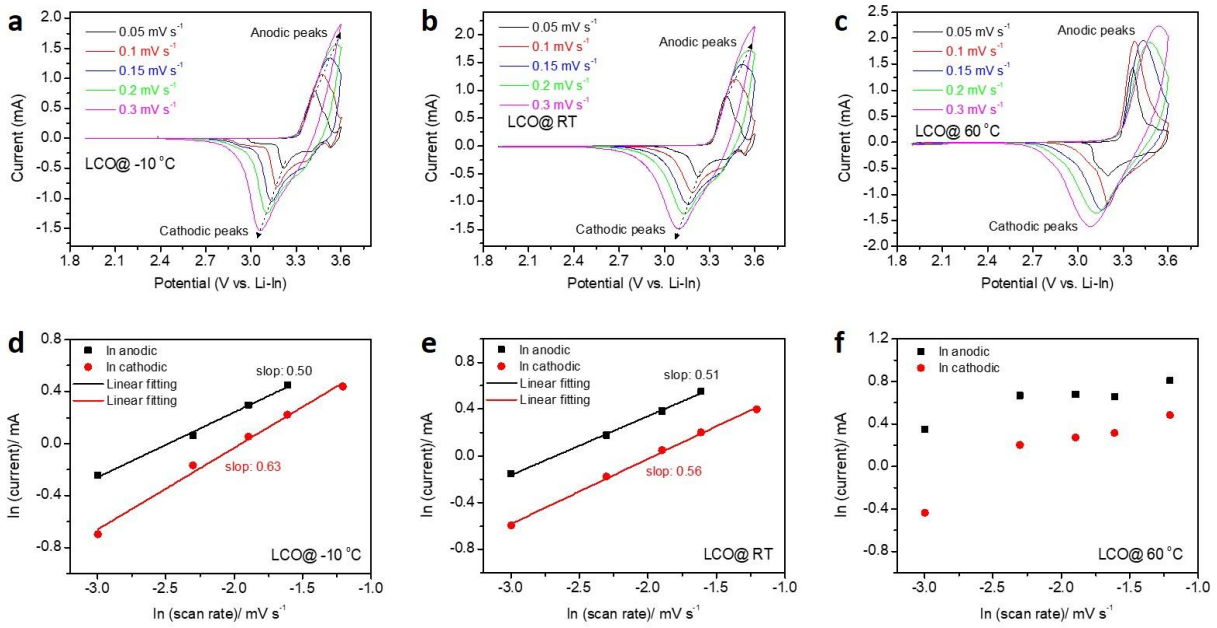


Figure S6. (a-c) CV curves of the LCO cells measured at various scan rates at -10 °C (LT), RT, and 60 °C (HT), respectively. (d-f) The linear fittings for the scanning rate-dependent cathodic and anodic peak currents from (a-c).

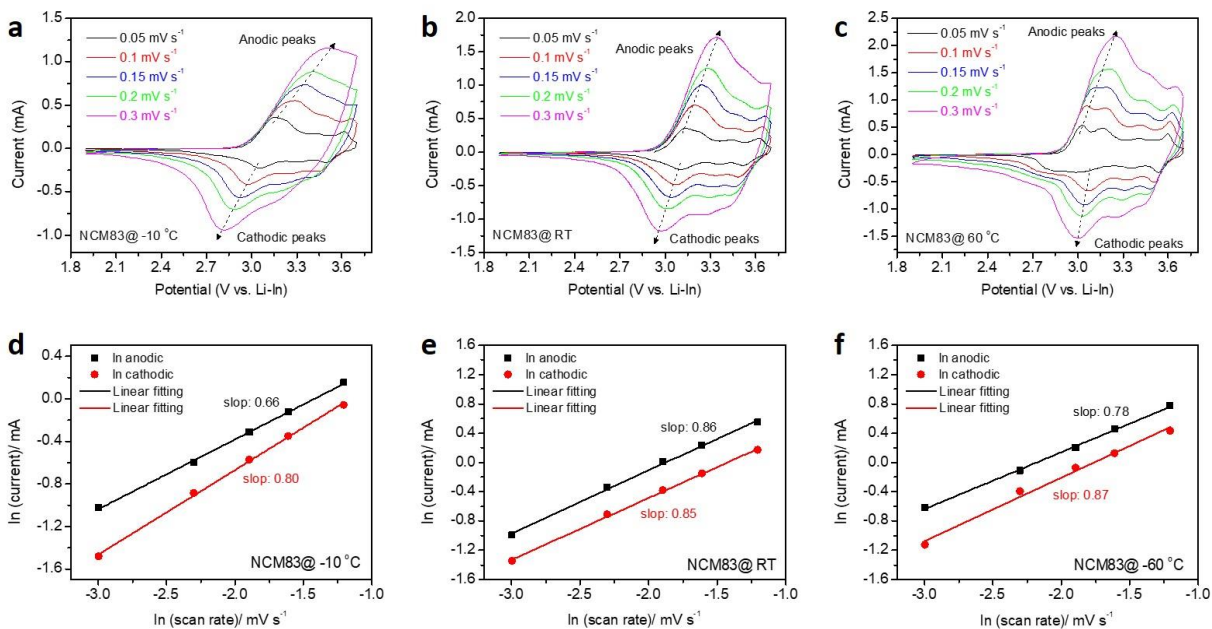


Figure S7. (a-c) CV curves of the NCM83 cells measured at various scan rates at -10 °C (LT), RT, and 60 °C (HT), respectively. (d-f) The linear fittings for the scanning rate-dependent cathodic and anodic peak currents from (a-c).

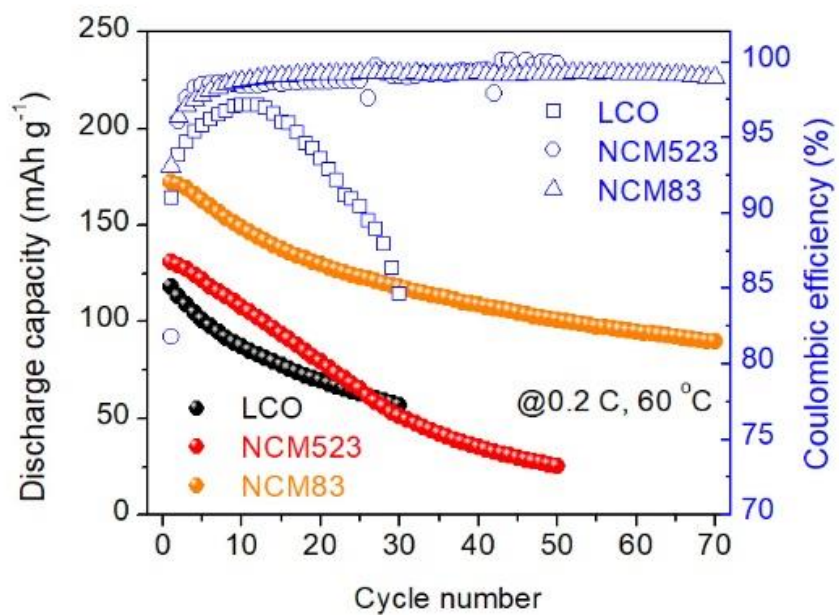


Figure S8. Cycling stability of the LTOC-based solid cells using three CAMs (LCO, NCM523, and NCM83) measured under 60 °C (HT).

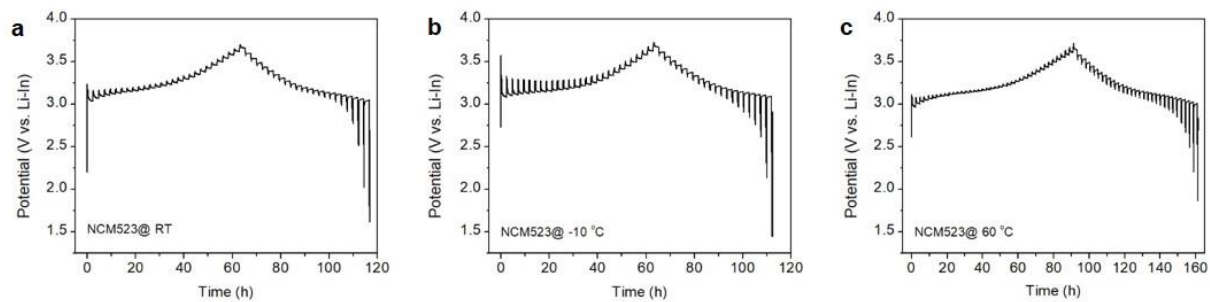


Figure S9. The GITT curves of the NCM523 cells performed at 0.1 C under (a) RT, (b) -10 °C , and (c) 60 °C.

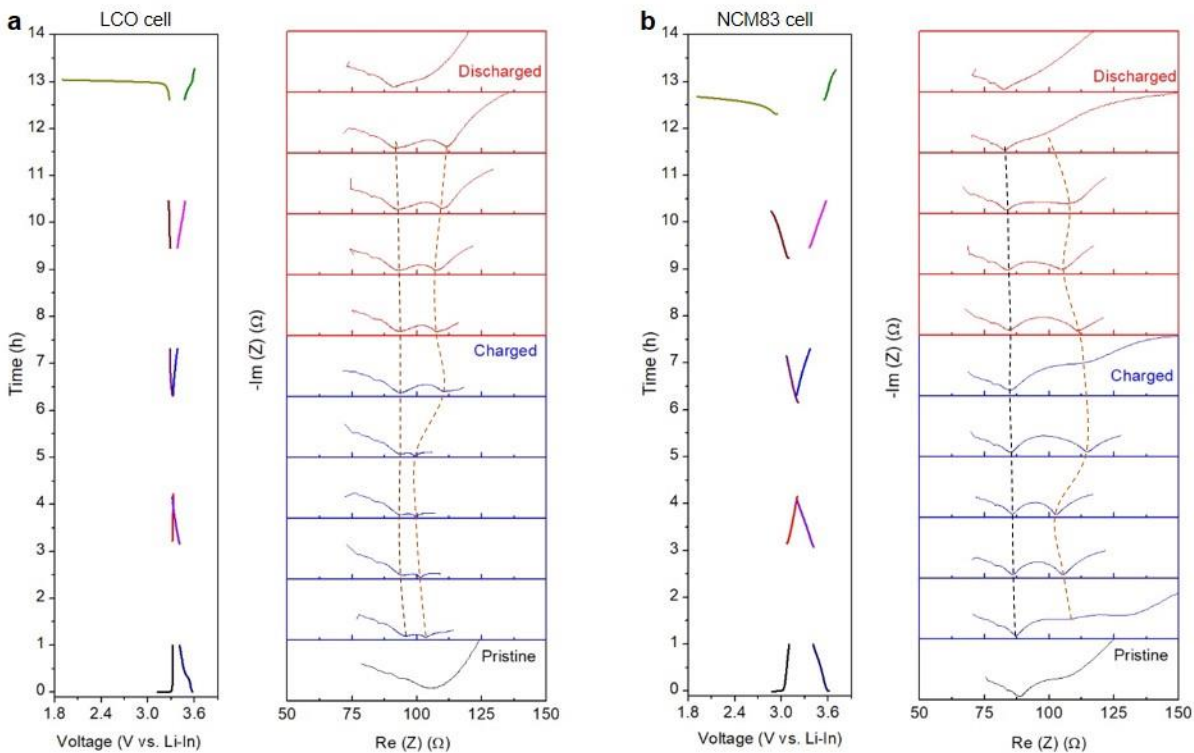


Figure S10. Interphase formation between LTOC SEs and CAMs (LCO and NCM83). (a, b) The first-cycle charge/discharge profiles during the in-situ EIS measurements for the LCO cell and NCM83 cell respectively cycled at 0.2 C and RT. The intermediate space is the rest time applied for achieving equilibrium state before collecting each EIS plot at different charging and discharging states. The contribution within the region marked by dash lines was mainly made by the LTOC/CAM interface, on the premise of that anode interface is stabilized during testing.

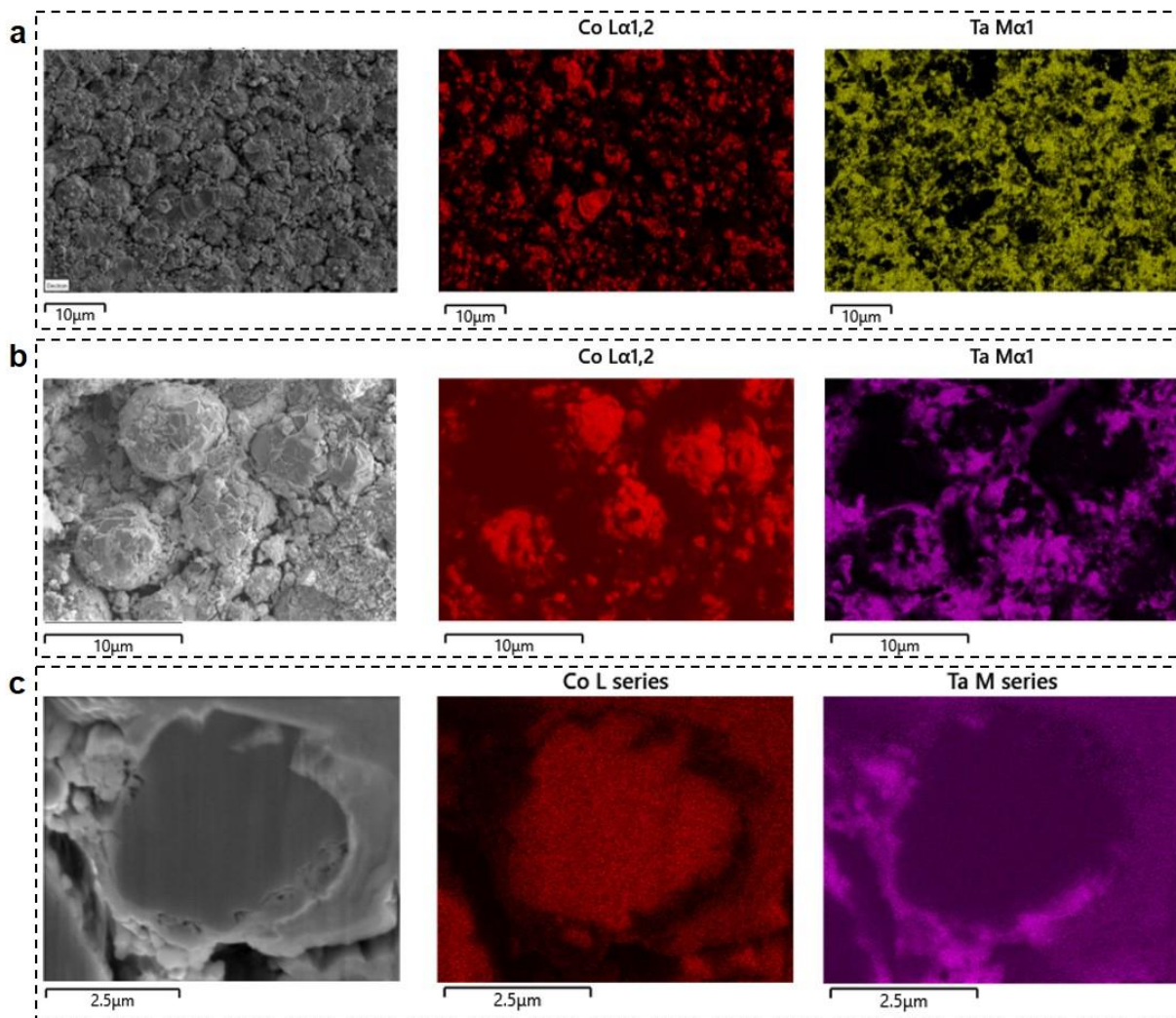


Figure S11. Morphologies of the LCO/LTOC cathode composite after cycling at RT. (a-b) SEM images and EDS element mapping for the surface of the LCO/LTOC electrode at different scales. (c) One SEM image and EDS element mapping for the PFIB-cut LCO/LTOC composite particle.

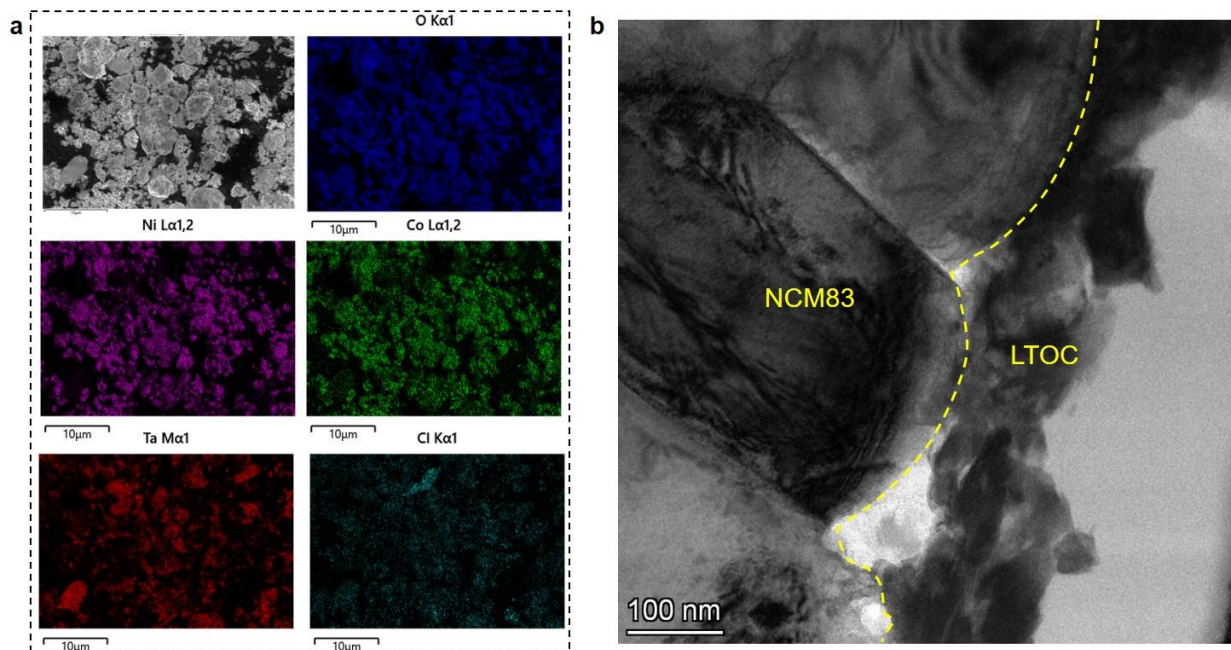


Figure S12. Morphologies of the NCM83/LTOC cathode composite after cycling at RT. (a)

One SEM image of the NCM83/LTOC powder and EDS element mapping for this whole area.

(b) One TEM image of the PFIB-cut NCM83/LTOC composite particle.

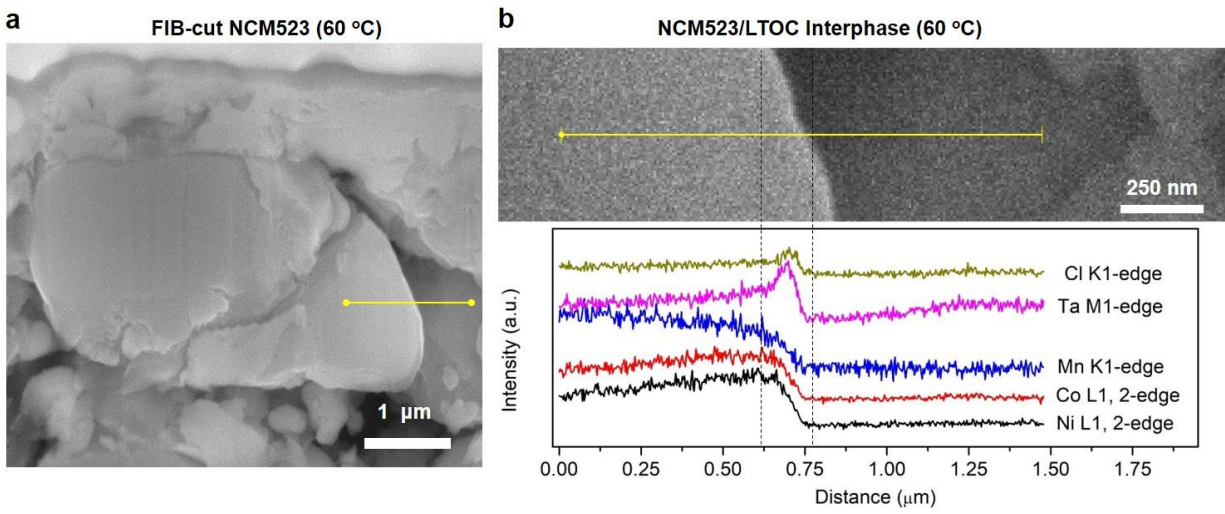


Figure S13. (a) SEM image of a FIB-cut NCM523 particle. (b) EDS Line scan (marked with yellow line) across the surface of the FIB-cut NCM523 particle.

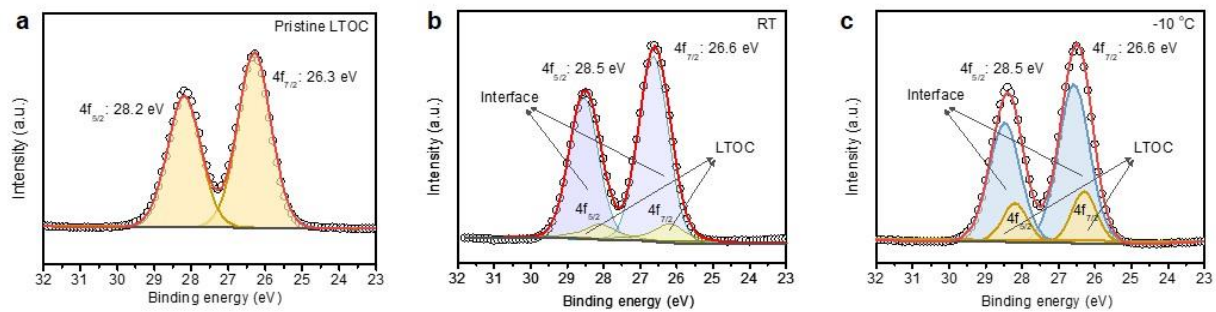


Figure S14. Ta 4f XPS spectra of (a) bare LTOC SSEs, (b) cycled NCM83/LTOC cathode composites at RT, and (c) cycled NCM83/LTOC cathode composites at -10 °C.

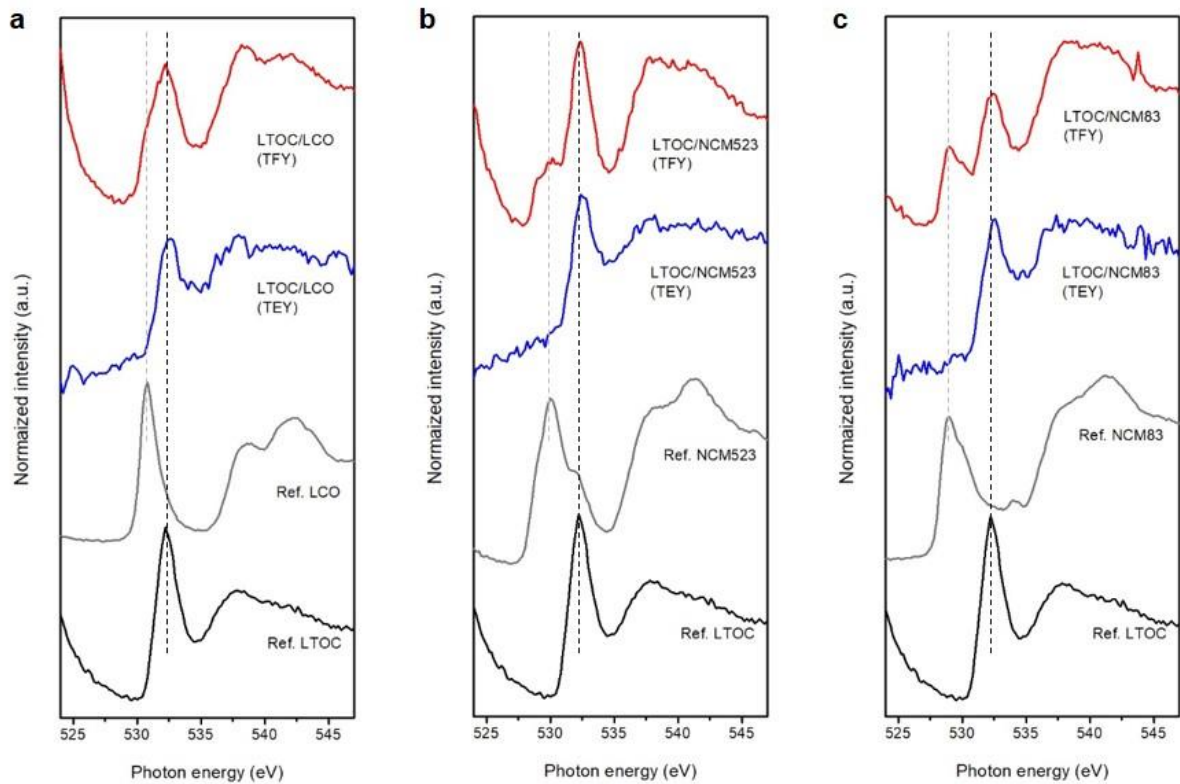


Figure S15. O K-edge XAS spectra of three LTOC/CAM composites after cycling (20 cycles, 0.1 C and RT). (a) LTOC/LCO. (b) LTOC/NCM523. (c) LTOC/NCM83. The O K-edge spectra of LTOC/CAMs composites were collected in two modes: surface-sensitive total electron yield (TEY) mode and bulk-sensitive total fluorescence yield (TFY) mode.

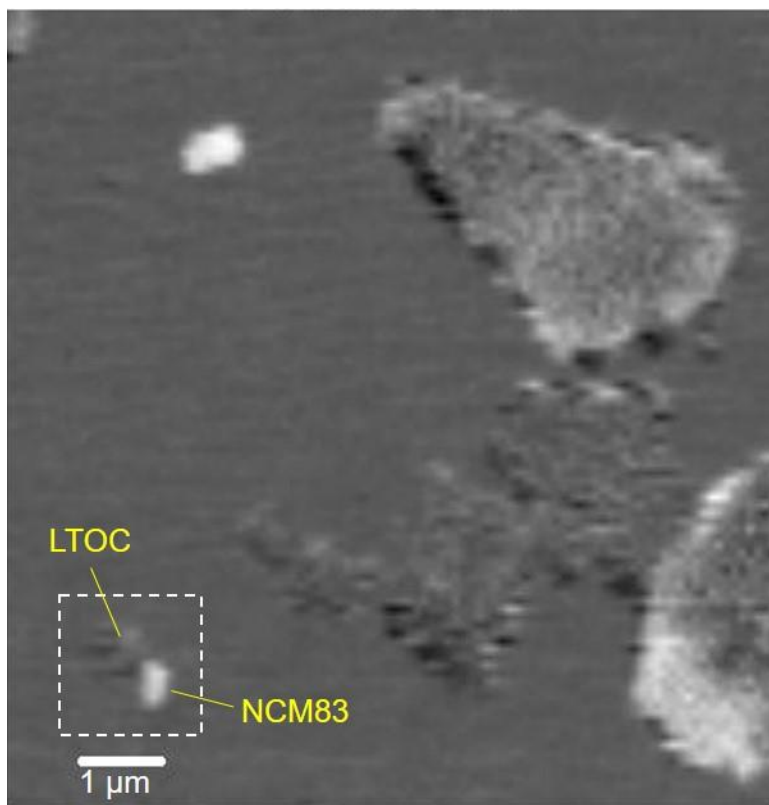


Figure S16. A subtracting mapping image of two images obtained under two transmission energies. In conventional STXM measurement, using two-energy image mapping: one is on the absorption energy of Co K-edge (780 eV); the other one is before the absorption edge (775 eV) to distinguish the LCO particle (bright area) from the LOC/LTOC cathode composites (RT). There is no absorption for the LTOC portion under neither energies, so LTOC area suggests relatively dark compared with the LCO particle. The rectangle area was picked to do the further analysis as indicated “LCO-RT” in **Figure 4a**. The similar procedure was performed to locate cathode particle in each sample.

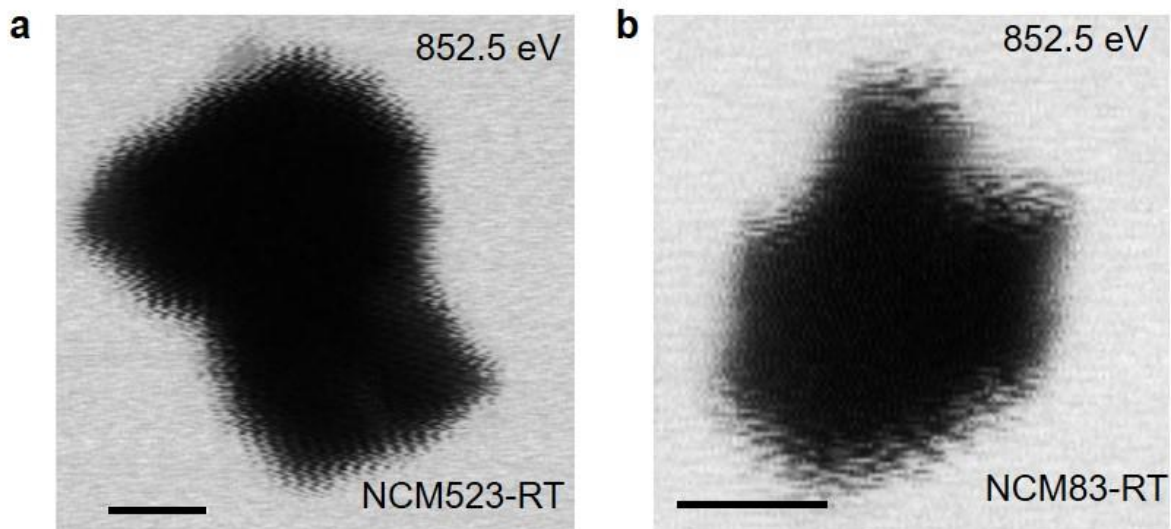


Figure S17. STXM images of the NCM particles after cycling against the LTOC SE at RT.

(a) One NCM523 particle. (b) One NCM83 particle. The images were taken in the conventional STXM at the energy of Ni L-edge (852.5 eV). Scale bar: 500 nm.

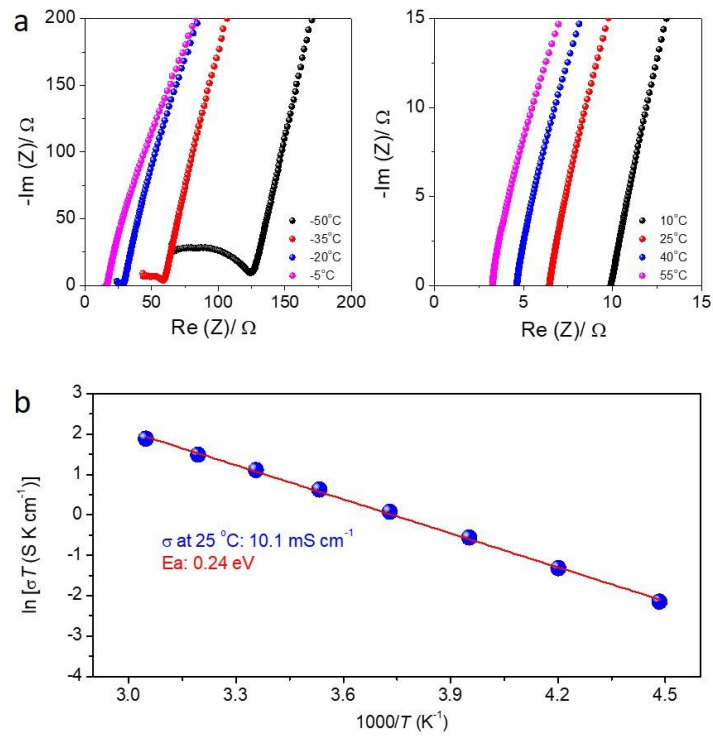


Figure S18. (a) Temperature-dependent EIS plots in measuring the ionic conductivity of the prepared LTOC solid electrolyte. (b) Arrhenius plot of the LTOC solid electrolyte.

References

1. Y. Tanaka, K. Ueno, K. Mizuno, K. Takeuchi, T. Asano and A. Sakai, *Angew. Chem. Int. Ed.*, 2023, **62**, e202217581.
2. T. Asano, A. Sakai, S. Ouchi, M. Sakaida, A. Miyazaki and S. Hasegawa, *Adv. Mater.*, 2018, **30**, 1803075.
3. J. Liang, N. Chen, X. Li, X. Li, K. R. Adair, J. Li, C. Wang, C. Yu, M. Norouzi Banis, L. Zhang, S. Zhao, S. Lu, H. Huang, R. Li, Y. Huang and X. Sun, *Chem Mater*, 2020, **32**, 2664-2672.
4. Y. Zhu, X. He and Y. Mo, *ACS Appl. Mater. Interfaces*, 2015, **7**, 23685-23693.
5. Y. Z. Zhu, X. F. He and Y. F. Mo, *Adv. Sci.*, 2017, **4**, 1600517.
6. Y. Z. Zhu, X. F. He and Y. F. Mo, *J. Mater. Chem. A*, 2016, **4**, 3253-3266.