Supplementary Information

Boosting Lithium Compatibility and Air Stability of Halide Electrolytes through Cyanamide Substitution

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Experimental

Synthesis of Li_2NCN

All preparations and sample treatments were conducted in an argon-filled glove box (O_2 and H_2O < 0.1 ppm) to protect the precursor from oxygen and moisture. Li_2NCN was synthesized via a solid-state method. Typically, the powdered raw materials were weighed according to the stoichiometric ratio of $LiNH_2 : C_3H_6N_6 = 6:1$, then ground in a mortar for 20 minutes to ensure uniform mixing. The ground powder was then placed in an alumina boat and quickly transferred to a tube furnace under an Ar atmosphere.

The heating program was set as follows: first, the temperature was increased to 270°C at a rate of 10°C/min within 27 minutes and held for 10 minutes. Then, it was further raised to 330°C at 1°C/min over 60 minutes. Next, the temperature was rapidly increased to 600°C at 10°C/min within 27 minutes, with no holding time. Finally, the sample was cooled to room temperature at a rate of 5°C/min, yielding the target product, Li_2NCN.

After cooling, the product was quickly transferred to a glove box to prevent moisture absorption and oxidation. The sample was then reserved for future use.

Synthesis of Li_2ZrCl_6 and $Li_2ZrCl_4CN_2$ solid electrolyte

All operations in this section were carried out in an argon-filled glove box (O_2 and $H_2O < 0.1$ ppm).

Synthesis of Li_2ZrCl_6:

The powdered raw materials were weighed according to the stoichiometric ratio of $LiCl:ZrCl_4 = 2:1$ and pre-mixed by grinding in a mortar for 3 minutes. Then, the mixed powder was transferred to a zirconia ball milling jar. The jar was then sealed under Ar protection and transferred to a high-energy ball-milling.

The milling process was carried out in two stages. First, pre-milling was performed at 100 rpm for 1 hour. Then, the rotation speed was increased to 600 rpm, and milling continued for 12 hours. After the milling ,the jar was transferred to glove box to collect the product.

Synthesis of $Li_2ZrCl_4CN_2$:

The powdered raw materials were weighed according to the stoichiometric ratio of $Li_2NCN:ZrCl_4 = 1:1$ and pre-mixed by grinding in a mortar for 3 minutes. Then, the mixed powder was transferred to a zirconia ball milling jar. The jar was then sealed under Ar protection and transferred to a high-energy ball-milling.

The milling process was carried out in two stages. First, pre-milling was performed at 100 rpm for 1 hour. Then, the rotation speed was increased to 600 rpm, and milling time was set for 12, 18 and 24 hours to study the impact of milling durations. After the milling ,the jar was transferred to glove box to collect the product.

Characterization

The X-ray diffraction (XRD) characterization was carried out on a Bruker D8 Advance diffractometer operating with a Cu Kα radiation ($\lambda = 1.5406$ Å). Scanning electron microscopy (SEM) images were obtained by a JEOL (JSM6510) scanning electron microscope. Transmission electron microscopy (TEM) observations were carried out on a JEOL (JEM-2100F) transmission electron microscope. Raman spectroscopy was conducted on a Jobin-Yvon LabRAM HR-800 spectrometer with a laser excitation wavelength of 532 nm. FT-IR was conducted using a Nicolet 6700 instrument with a resolution of 4 cm^{-1}.

Symmetric cell assembly

All operations in this section, except for the testing process, were carried out in a glove box.

A 100 mg portion of the prepared electrolyte was placed into a specialized solid-state battery mold and compressed under an external pressure of 4 T to form a dense electrolyte pellet. Then, Li sheets or Li-In alloy sheets were added to both sides of the electrolyte.

ASSLBs assembly

All operations in this section, except for the testing process, were carried out in a glove box.

The powdered raw materials were weighed according to the mass ratios: LCO:Li_2ZrCl_6 = 7:3, and mixed by grinding in a mortar for 20 minutes. The mixture was set aside for later use.

Similarly, the raw materials were weighed according to the mass ratio of LCO:$Li_2ZrCl_4CN_2$ = 7:3 and ground for 20 minutes. The mixture was set aside for later use.

For the high-voltage cathode, NCM811:$Li_2ZrCl_4CN_2$ = 7:3 ratio, the raw materials were weighed and ground for 20 minutes, then set aside for later use.

For each of the prepared electrolytes, 100 mg was taken and spread into a specialized solid-state battery mold. An external pressure of 1 T was applied to form a dense electrolyte pellet. Then, 10 mg of the corresponding cathode/electrolyte material was added to one side of the electrolyte. A pressure of 4 T was applied to ensure good contact between the electrolyte and the cathode. Finally, lithium metal/Li-In alloy sheet was added to the other side of the electrolyte, and the mold was tightened before test.

Electrochemical measurements

DC Polarization and Electrochemical Impedance Spectroscopy (EIS) test was conducted in Autolab system. 100 mg of the above electrolyte was placed into a specialized mold and subjected to a pressure of 4 T for testing. The conductivity was then calculated using the following formula:

$$\rho = \frac{RS}{L} \tag{1.1}$$

$$\sigma = \frac{1}{\rho} \tag{1.2}$$

Where ρ is the resistivity of the sample and σ is the conductivity.

Galvanostatic Charge-discharge (GCD) and Critical Current Density (CCD) were performed on a cell test system (LAND-CT2001A).

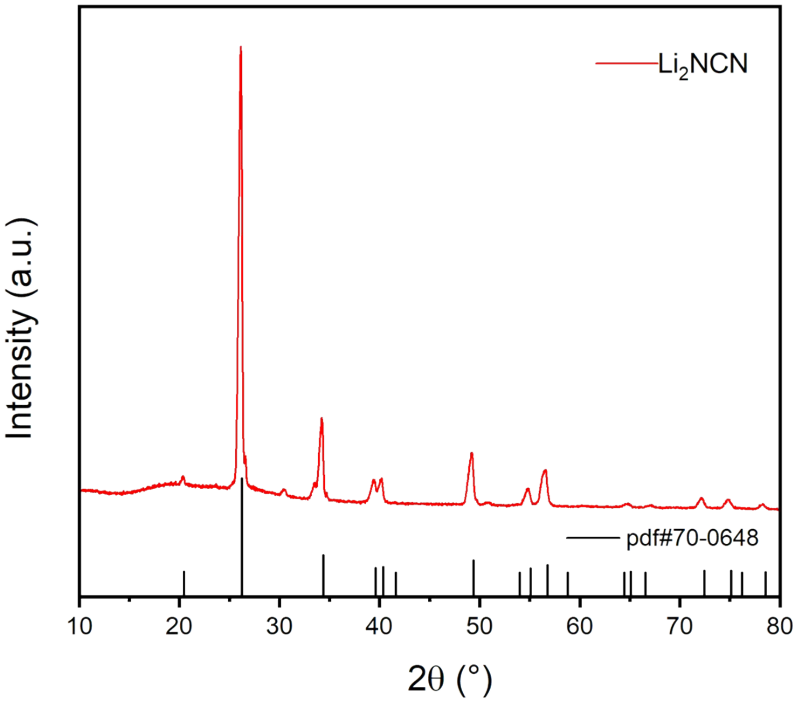

Figure S1 XRD pattern of Li_2NCN.

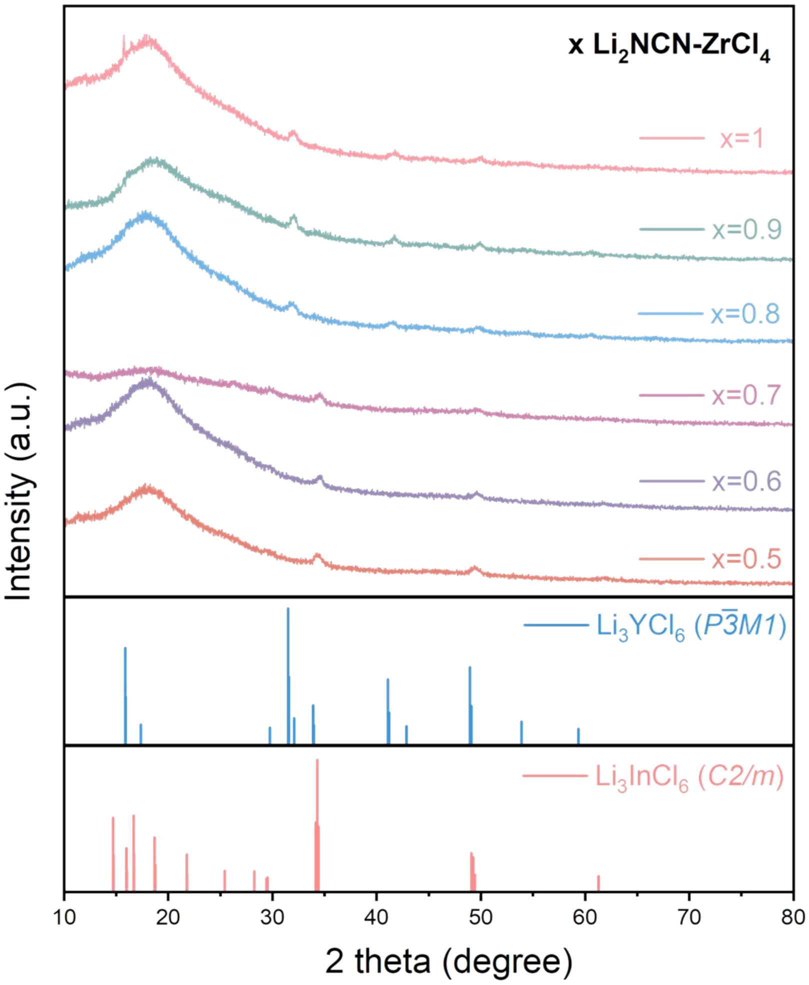

Figure S2 XRD pattern of different ratios of $xLi_2NCN:ZrCl_4$

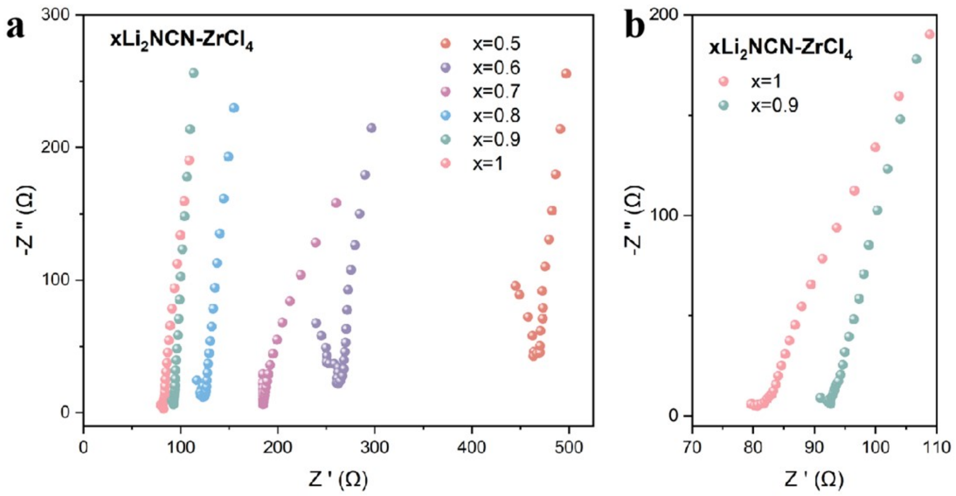

Figure S3 (a) EIS pattern of different ratios of $xLi_2NCN:ZrCl_4$. (b) Localized magnified image of different ratios.

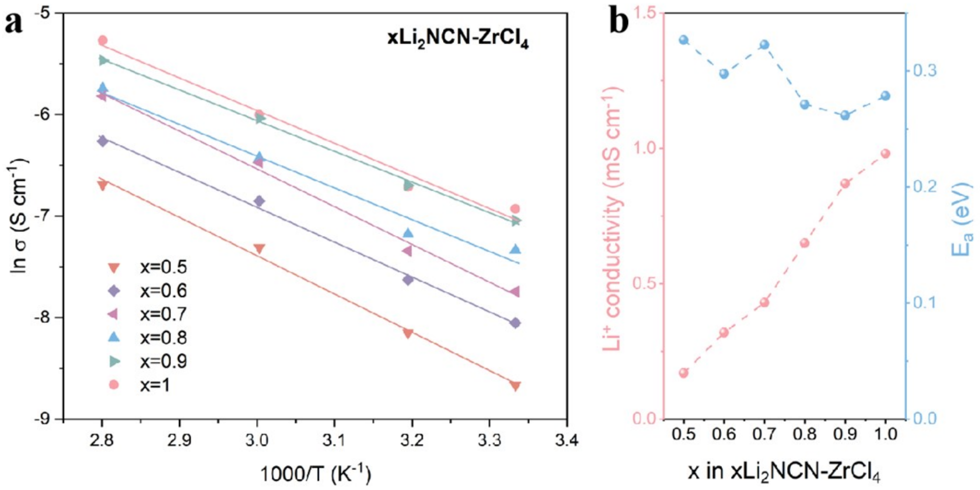

Figure S4 (a) Test diagram of the product conductivity varies with temperature of different ratios. (b) Comparison of conductivity and activation energy of products of different ratios.

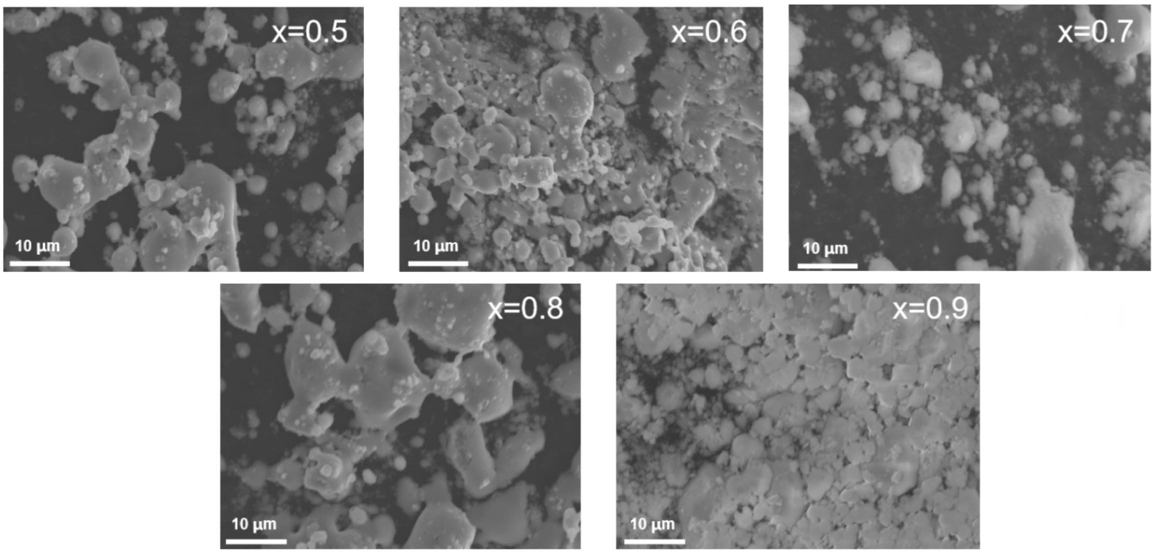

Figure S5 The morphology of the products when x = 0.5 , 0.6, 0.7, 0.8 and 0.9.

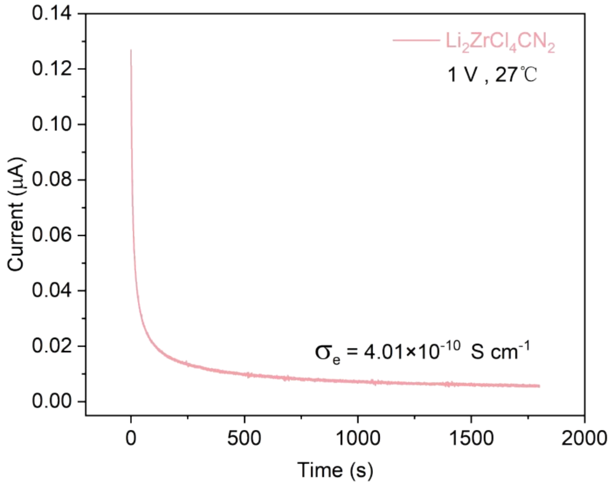

Figure S6 I-T curve of LZCN-18 .

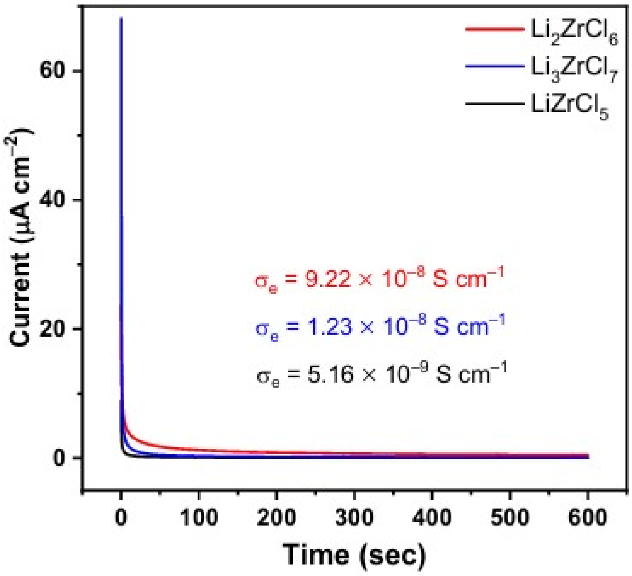

Figure S7 I-T curve of LZC.[1]

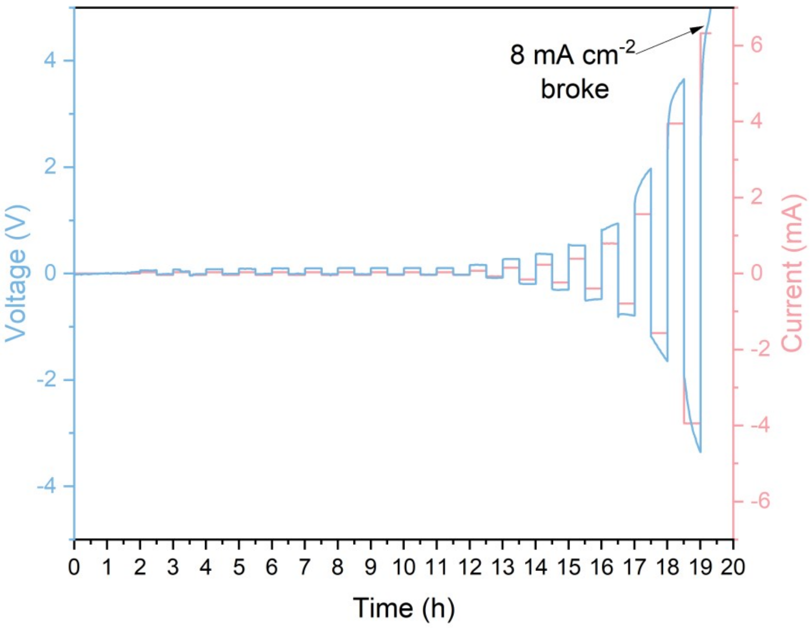

Figure S8 Critical current density tests on Li-Li symmetric cells with LZCN-18.

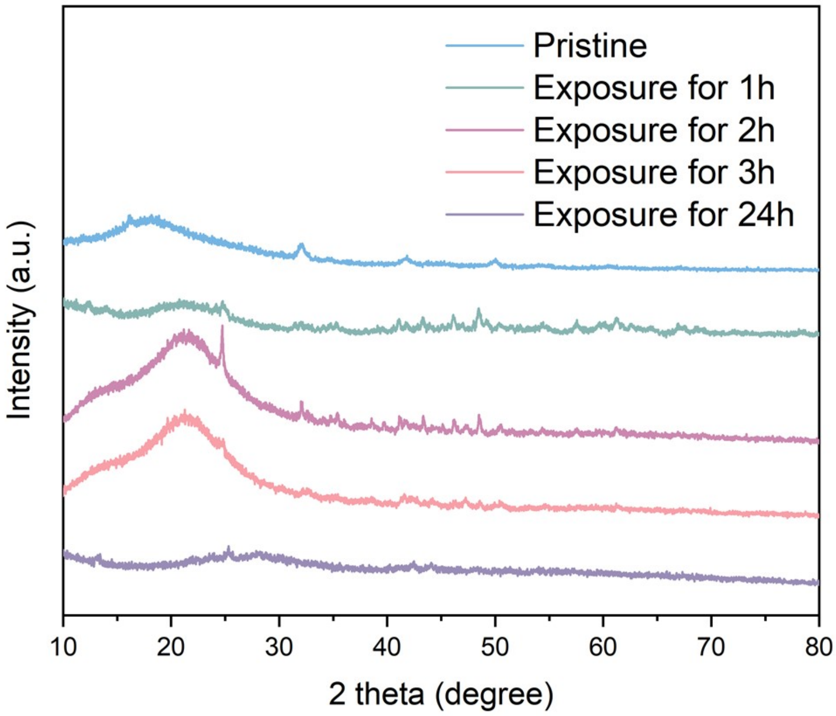

Figure S9 XRD patterns of LZC electrolyte film exposed for different durations.

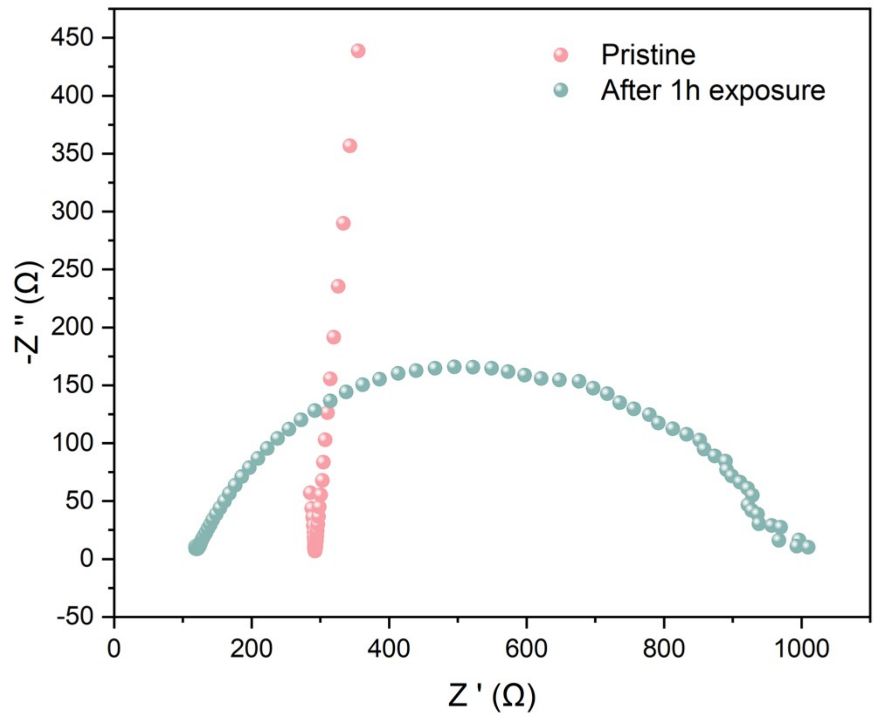

Figure S10 Impedance changes of LZC electrolyte film after exposure for 1h.

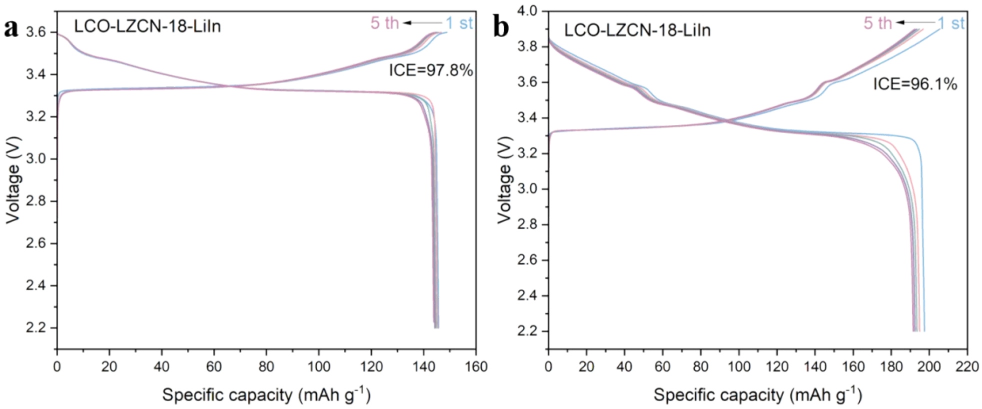

Figure S11 Charge-discharge curves of the LCO/LZCN-18/Li-In battery for the first five cycles (a) 2.2 V -3.6 V. (b) 2.2 V -3.96 V.

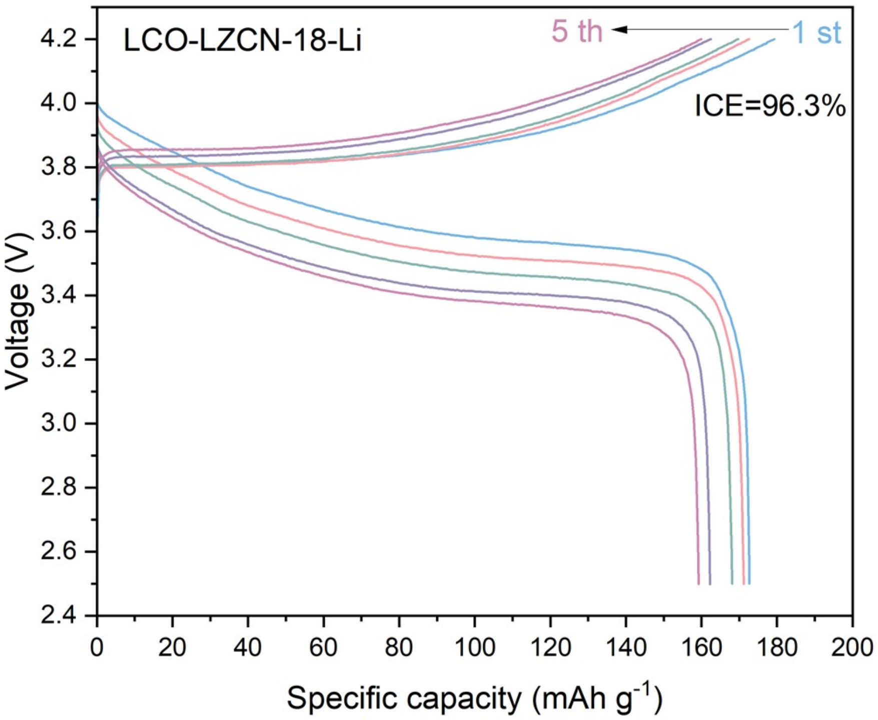

Figure S12 Charge-discharge curves between 2.5 V- 4.2 V of the LCO/LZCN-18/Li battery for the first five cycles

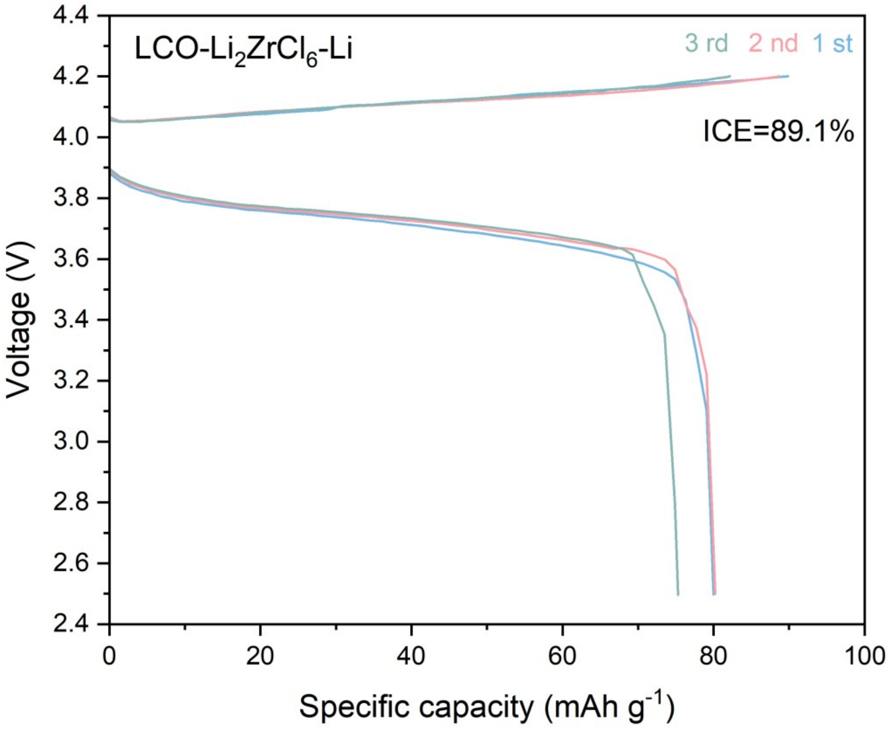

Figure S13 Charge-discharge curves between 2.5 V- 4.2 V of the LCO/LZC/Li battery for the first three cycles

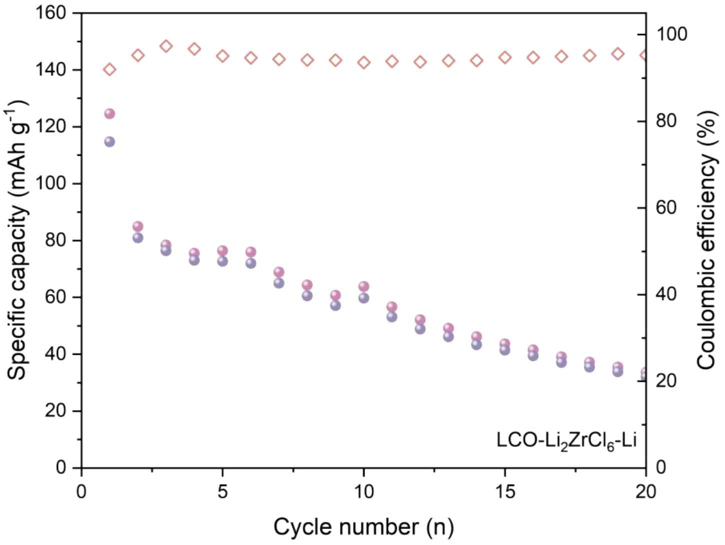

Figure S14 Cycle performance of the LCO/LZC/Li battery.

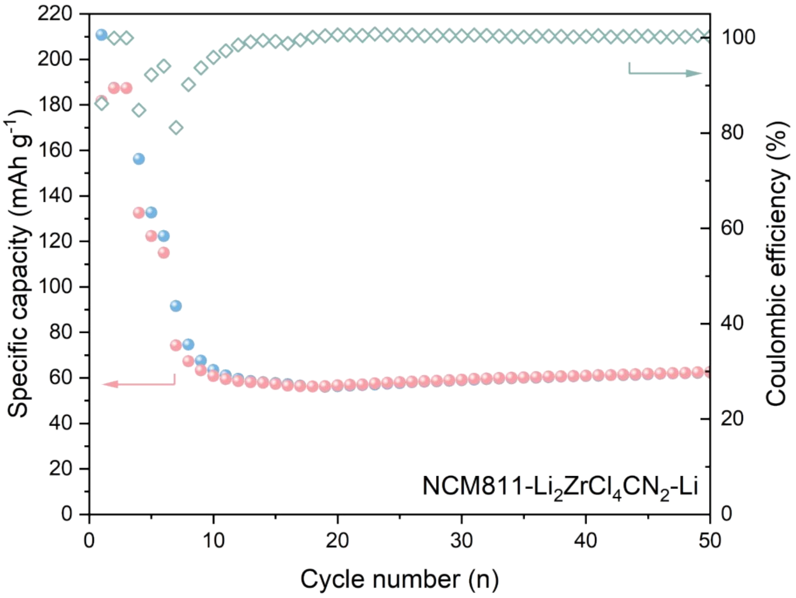

Figure S15 Cycle performance of the NCM811/LZC/Li battery.

References

1 K. Wang, Q. Ren, Z. Gu, C. Duan, J. Wang, F. Zhu, Y. Fu, J. Hao, J. Zhu, L. He, C. Wang, Y. Lu, J. Ma and C. Ma, *Nat. Commun.,*2021, **12**, 4410.