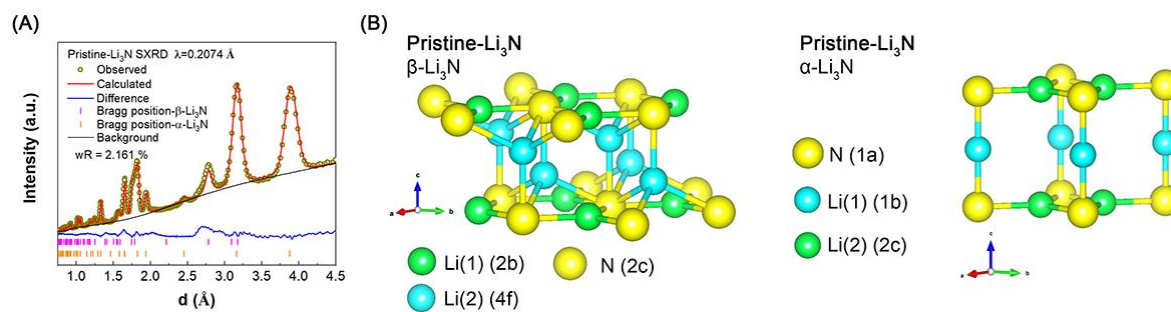


Superionic conducting vacancy-rich β -Li₃N electrolyte for stable cycling of all-solid-state lithium metal batteries

In the format provided by the
authors and unedited

Supplementary Figures, Tables, Notes, and References:



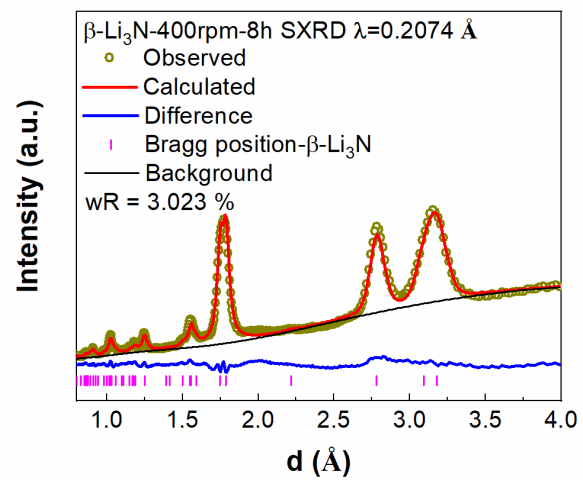
Supplementary Figure 1 SXRD pattern with corresponding Rietveld refinement results for commercial- Li_3N and (B) calculated crystal structure of beta phase and alpha phase in commercial Li_3N .

Supplementary Table 1 Crystallographic data of commercial Li₃N and corresponding refined parameters based on SXRD.

Compound	Li _{2.986(6)} N _{0.995(3)}
α -Li ₃ N, Weight fraction: 63.1(9) wt.%	
Space Group	<i>P6₃/mmm</i>
<i>a</i> = <i>b</i> , Å	3.64895(18)
<i>c</i> , Å	3.87764(5)
α = β , °	90
γ , °	120
<i>V</i> , Å ³	44.718 (8)
β -Li ₃ N, Weight fraction: 36.9(7) wt.%	
Space Group	<i>P6₃/mmc</i>
<i>a</i> = <i>b</i> , Å	3.56941(17)
<i>c</i> , Å	6.35064(3)
α = β , °	90
γ , °	120
<i>V</i> , Å ³	70.0713(7)

Supplementary Table 2 Rietveld refinement analysis results for the SXRD pattern of commercial Li₃N.

α -Li ₃ N, Weight fraction: 63.1(9) wt%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	½	1	0.017(2)	1b	6/mmm	1
Li2	1/3	2/3	0	0.993(4)	0.017(2)	2c	-6m2	2
N3	0	0	0	0.995(2)	0.005(3)	1a	6/mmm	1
β -Li ₃ N, Weight fraction: 36.9(7) wt%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	1/4	1	0.017(1)	2b	-6m2	2
Li2	1/3	2/3	0.58529(2)	0.995(4)	0.017(1)	4f	3m	4
N3	1/3	2/3	1/4	0.997(2)	0.005(2)	2c	-6m2	2



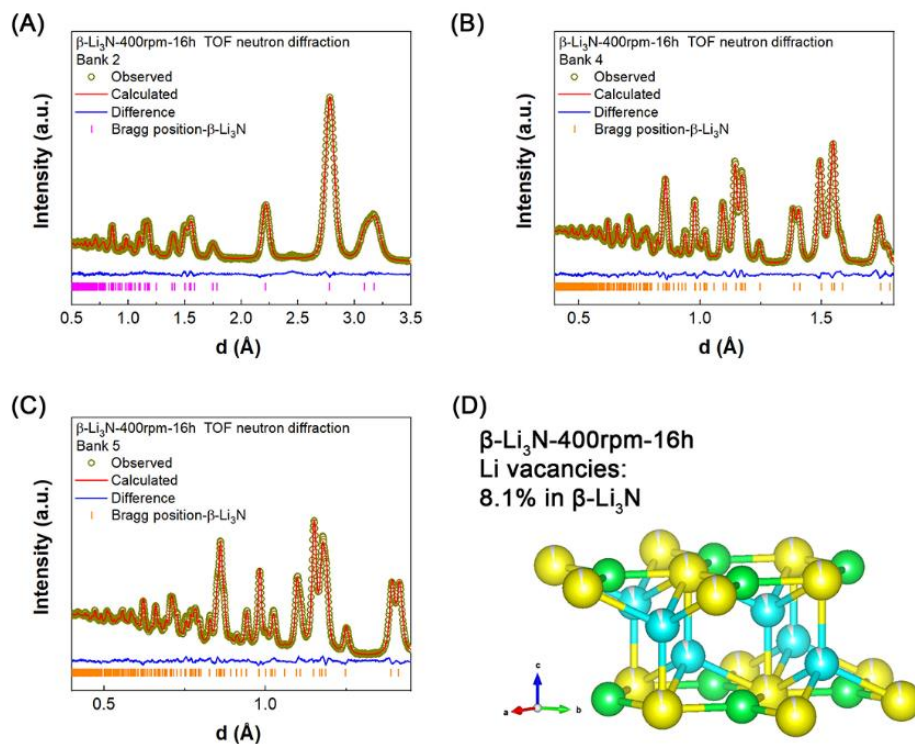
Supplementary Figure 2 SXR D pattern and corresponding Rietveld refinement of β -Li₃N-400rpm-8h sample

Supplementary Table 3 Crystallographic data of β -Li₃N-400rpm-8h and corresponding refined parameters based on SXRD.

Compound	Li _{2.876(9)} N _{0.959(5)}
β -Li ₃ N, Weight fraction: 100 wt%	
Space Group	P6 ₃ /mmc
$a=b$, Å	3.57146(17)
c , Å	6.35700(4)
$\alpha=\beta$, °	90
γ , °	120
V , Å ³	70.221(7)

Supplementary Table 4 Rietveld refinement analysis results for the SXRD pattern of β -Li₃N-400rpm-8h.

β -Li ₃ N, Weight fraction: 100 wt%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	1/4	1	0.005(1)	2b	-6m2	2
Li2	1/3	2/3	0.58300(3)	0.938(6)	0.005(1)	4f	3m	4
N3	1/3	2/3	1/4	0.959(3)	0.009(4)	2c	-6m2	2



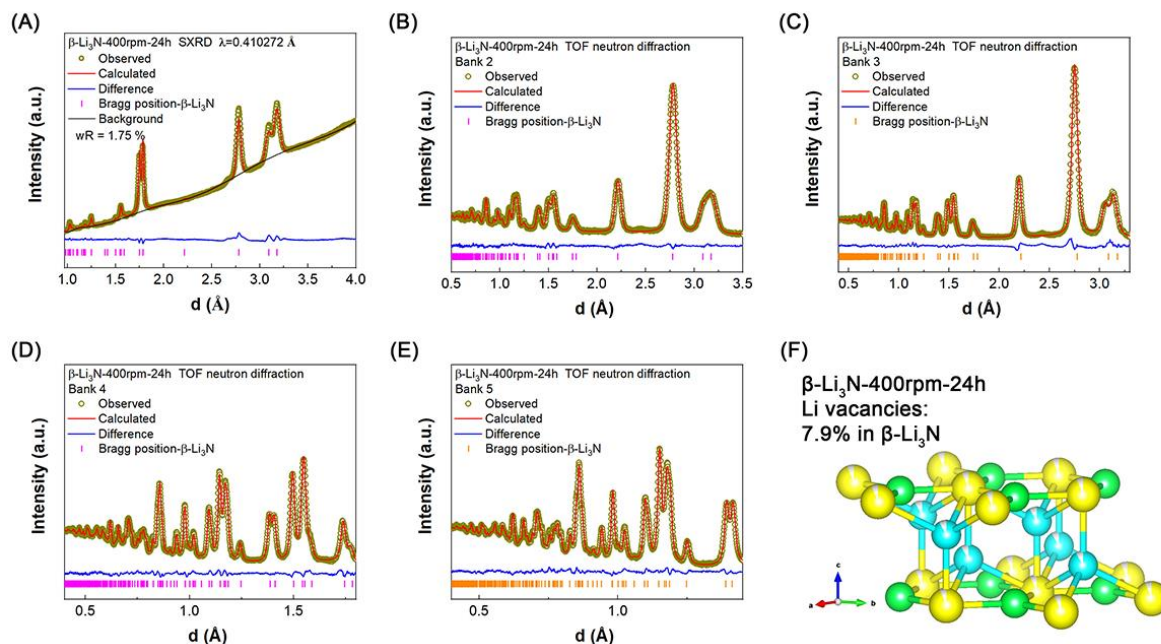
Supplementary Figure 3. Rietveld refinement results for the β -Li₃N-400rpm-16h structure using Time-of-flight (TOF) neutron diffraction data (A) bank 2, (B) bank 4, and (C) bank 5. The total observation-calculation difference, wR is 2.737%. (D) Refined crystal structure of β -Li₃N using the β -Li₃N-400rpm-16h sample.

Supplementary Table 5. Crystallographic data of β -Li₃N-400rpm-16h and corresponding refined parameters based on SXRD and TOF Neutron diffraction.

Compound	Li _{2.838(6)} N _{0.946(3)}
β -Li ₃ N, Weight fraction: 100 wt.%	
Space Group	<i>P</i> 6 ₃ / <i>mmc</i>
<i>a</i> = <i>b</i> , Å	3.57369(19)
<i>c</i> , Å	6.36206(4)
α = β , °	90
γ , °	120
<i>V</i> , Å ³	70.365(9)

Supplementary Table 6. Rietveld refinement analysis results for the SXRD and TOF Neutron diffraction patterns of β -Li₃N-400rpm-16h.

β -Li ₃ N, Weight fraction: 100 wt.%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	$\frac{1}{4}$	1.000	0.005(1)	2b	-6m2	2
Li2	$\frac{1}{3}$	$\frac{2}{3}$	0.58742(3)	0.919(2)	0.005(1)	4f	3m	4
N3	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.946(1)	0.020(9)	2c	-6m2	2



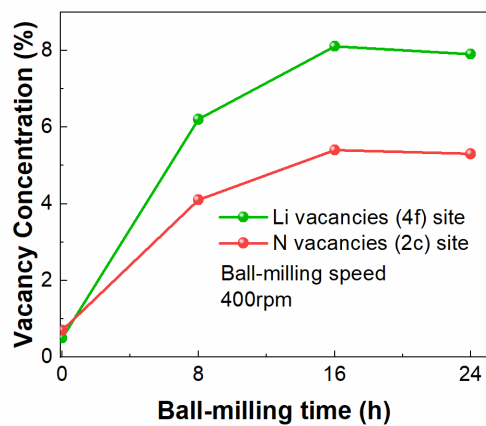
Supplementary Figure 4. (A) SXR D pattern and corresponding Rietveld refinement of β -Li₃N-400rpm-24h; (B–E) TOF neutron diffraction data and corresponding Rietveld refinement of β -Li₃N-400rpm-24h; the total observation-calculation difference, wR is 2.653%; (F) Calculated crystal structure of β -Li₃N using the β -Li₃N-400rpm-24h sample.

Supplementary Table 7. Crystallographic data of β -Li₃N-400rpm-24h and corresponding refined parameters based on SXRD and TOF Neutron diffraction.

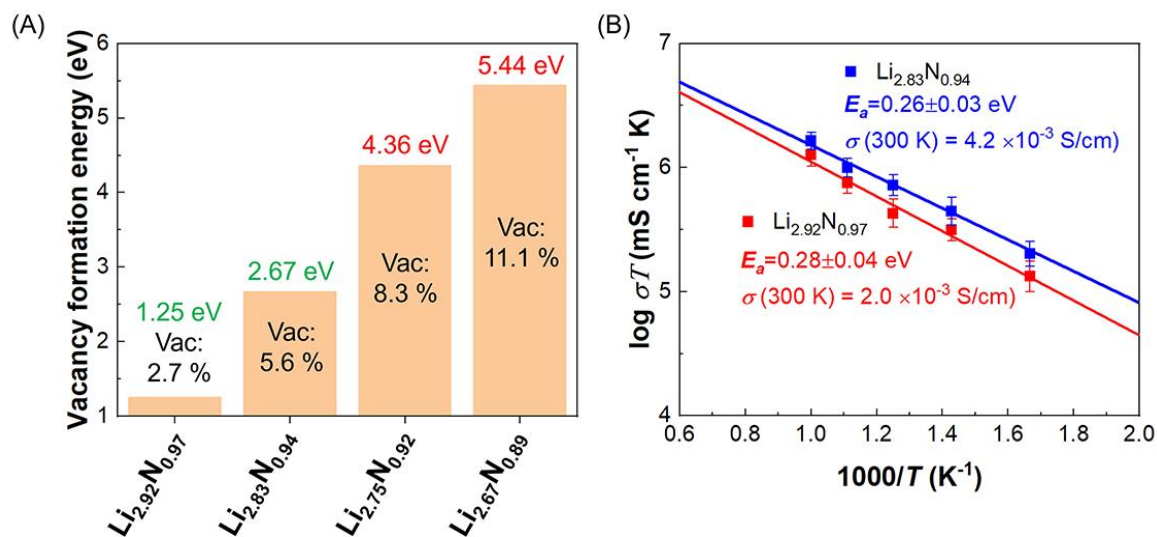
Compound	Li _{2.842(5)} N _{0.947(2)}
β -Li ₃ N, Weight fraction: 100 wt. %	
Space Group	<i>P6₃/mmc</i>
<i>a</i> = <i>b</i> , Å	3.57015(19)
<i>c</i> , Å	6.35712(4)
α = β , °	90
γ , °	120
<i>V</i> , Å ³	70.172(9)

Supplementary Table 8. Rietveld refinement analysis results for the SXRD and TOF Neutron diffraction patterns of β -Li₃N-400rpm-24h.

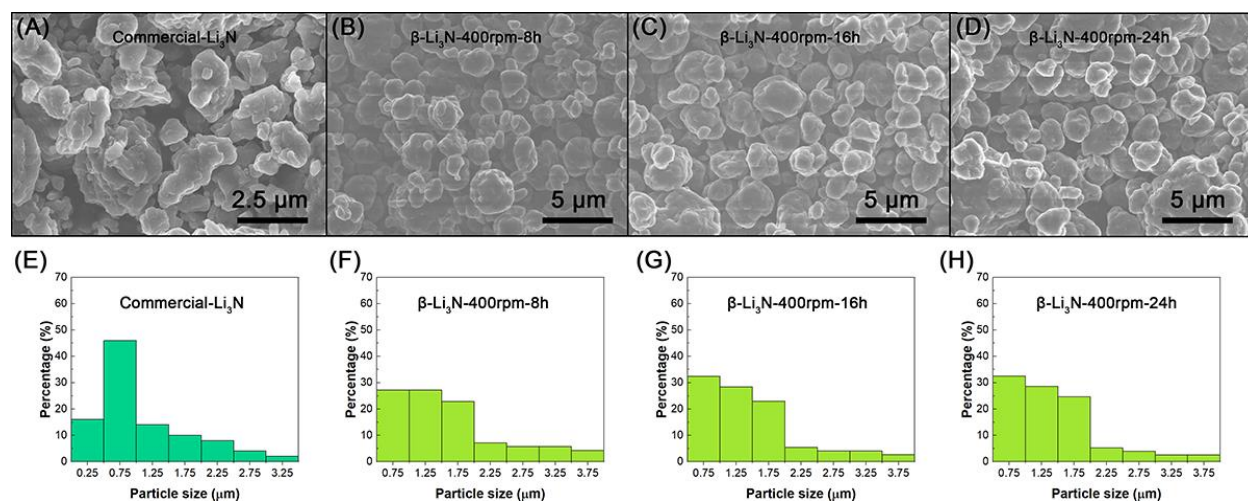
β -Li ₃ N, Weight fraction: 100 wt.%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	$\frac{1}{4}$	1.000	0.005(1)	2b	-6m2	2
Li2	$\frac{1}{3}$	$\frac{2}{3}$	0.58300(3)	0.921(2)	0.005(1)	4f	3m	4
N3	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.947(1)	0.001(9)	2c	-6m2	2



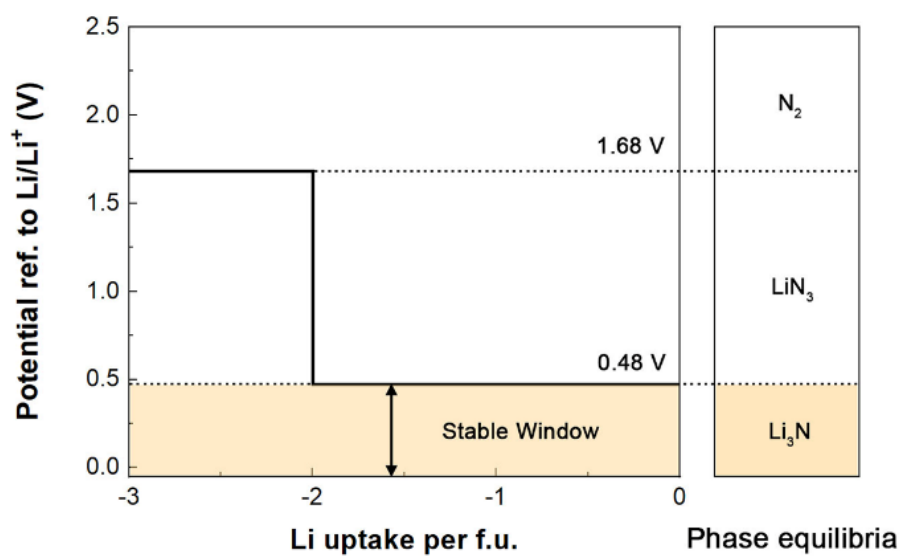
Supplementary Figure 5 Variations in lithium vacancy concentrations at the 4f site and nitrogen vacancy concentrations at the 2c site in β -Li₃N, with respect to ball-milling duration, maintained at a speed of 400 rpm.



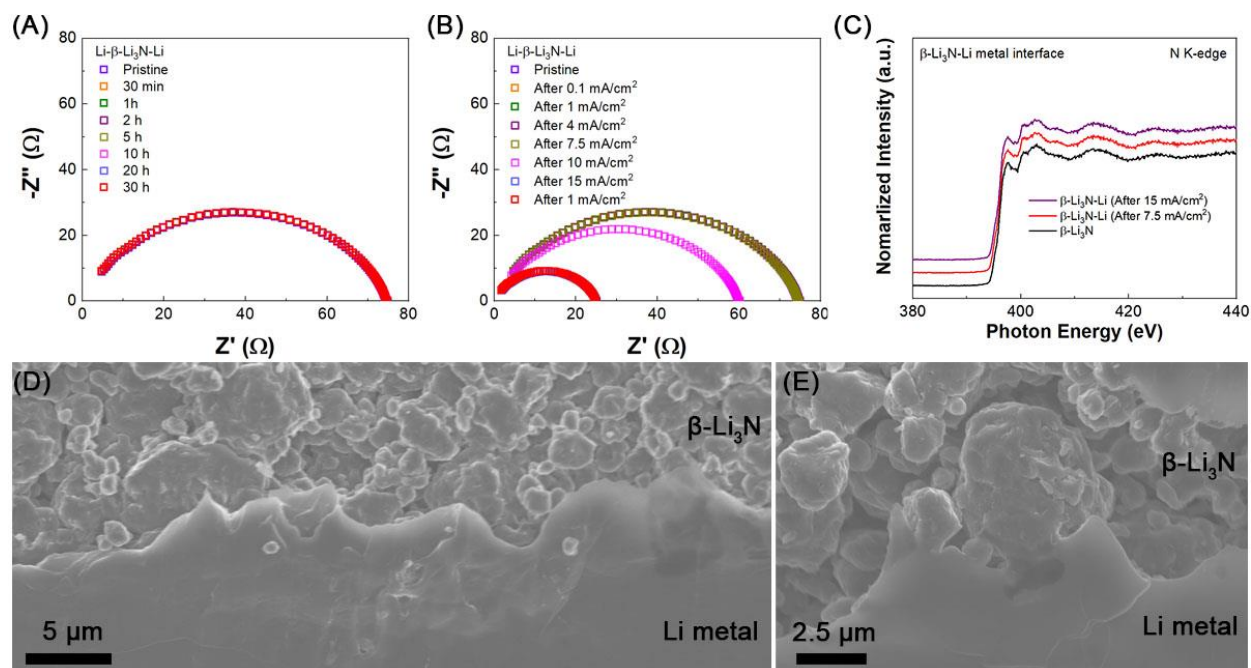
Supplementary Figure 6. Computation of formation energy and ion diffusion in vacancy-rich β - Li_3N . (A) The formation energy of vacancy-rich β - Li_3N with vacancy concentrations of 2.7% for $\text{Li}_{2.92}\text{N}_{0.97}$, 5.6% for $\text{Li}_{2.83}\text{N}_{0.94}$, 8.3% for $\text{Li}_{2.75}\text{N}_{0.92}$, and 11.1% for $\text{Li}_{2.67}\text{N}_{0.89}$. (B) Arrhenius plots of lithium-ion diffusivity in vacancy-rich β - Li_3N with $\text{Li}_{2.92}\text{N}_{0.97}$ (vacancy concentration 2.7%) and $\text{Li}_{2.83}\text{N}_{0.94}$ (vacancy concentration 5.6%) in AIMD simulations.



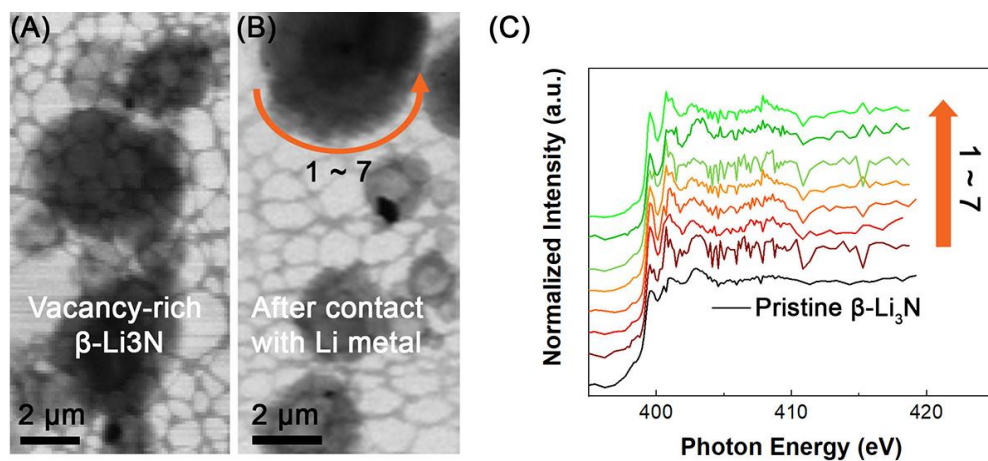
Supplementary Figure 7 Morphology characterization of a series of Li_3N SSE. Scanning electron microscopy images of the commercial Li_3N raw material, and prepared $\beta\text{-Li}_3\text{N}$ SSEs, (A) commercial Li_3N , (B) $\beta\text{-Li}_3\text{N}$ -400rpm-8h, (C) $\beta\text{-Li}_3\text{N}$ -400rpm-16h, and (D) $\beta\text{-Li}_3\text{N}$ -400rpm-24h. Particle size distribution of the pristine commercial Li_3N raw material, and prepared $\beta\text{-Li}_3\text{N}$ SSEs, (E) commercial Li_3N , (F) $\beta\text{-Li}_3\text{N}$ -400rpm-8h, (G) $\beta\text{-Li}_3\text{N}$ -400rpm-16h, and (H) $\beta\text{-Li}_3\text{N}$ -400rpm-24h.



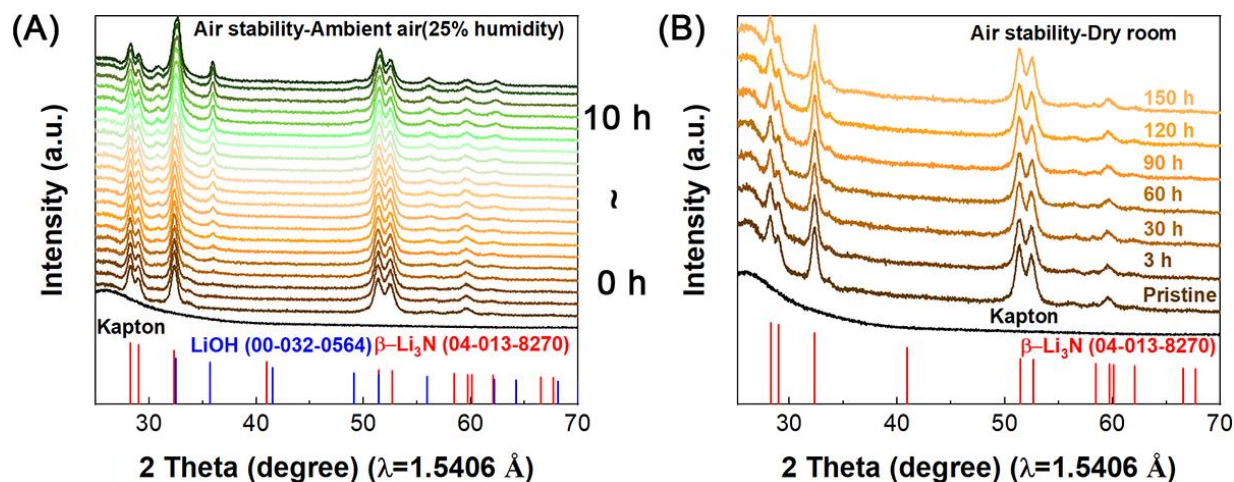
Supplementary Figure 8 Calculated thermodynamic equilibrium voltage profile and phase equilibria of β - Li_3N .



Supplementary Figure 9 (A) Time-dependent electrochemical impedance spectroscopy of Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells at rest for 30 h. (B) Time-dependent electrochemical impedance spectroscopy of Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells cycled at step-increased current densities and capacity (fixed 1 h time for Li plating/stripping) as shown in Figure 4C. (C) N K-edge XANES spectra comparison of vacancy-rich β -Li₃N and vacancy-rich β -Li₃N-lithium metal anode interfaces in the Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells cycled at step-increased current densities and capacity (fixed 1 h time for Li plating/stripping) as shown in Figure 4C. N K-edge XANES spectra were collected in the TEY mode. (D) and (E) Cross-sectional Scanning Electron Microscopy (SEM) images of vacancy-rich β -Li₃N-lithium metal anode interfaces in the Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells cycled at step-increased current densities and capacity (fixed 1 h time for Li plating/stripping) as shown in Figure 4C: (D) after 10 mA/cm², (E) after 15 mA/cm².

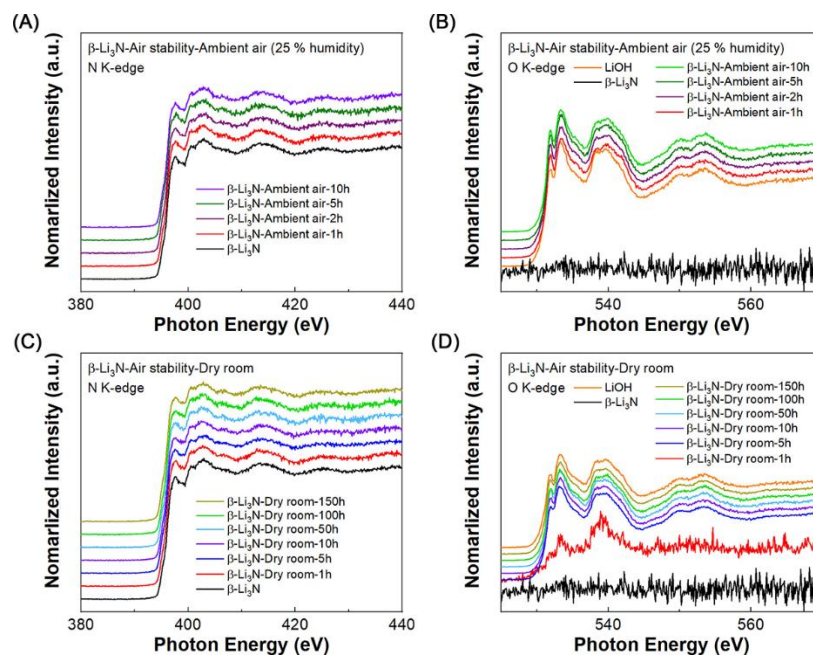


Supplementary Figure 10 Ex-situ scanning transmission X-ray microscopy study of (A) the vacancy-rich β - Li_3N sample and (B) the vacancy-rich β - Li_3N sample after contact with lithium (acquired at photon energy of 395 eV). The minor spectral fluctuations are attributed to the STXM technique's photon energy resolution limits. (C) Normalized nitrogen K-edge XANES spectra of pristine vacancy-rich β - Li_3N and the regions 1–7 marked in (B) for the vacancy-rich β - Li_3N sample after contact with lithium. Data are collected at photon energies spanning from 395 to 418 eV^{1,2}.

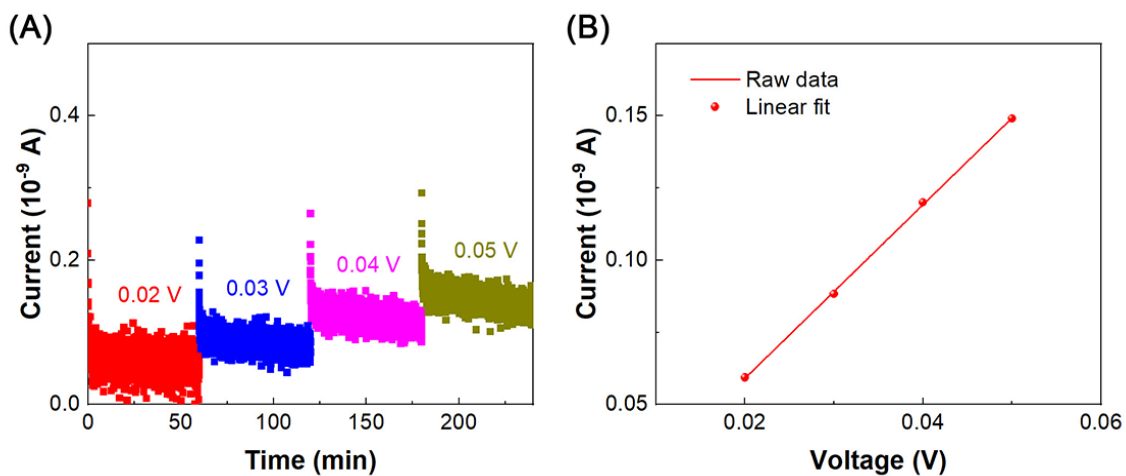


Supplementary Figure 11 (A) Operando X-ray diffraction pattern evolution of vacancy-rich β - Li_3N during exposure process to air with 25% relative humidity for 10 h. (B) In-situ X-ray diffraction pattern evolution of vacancy-rich β - Li_3N upon different exposure times in a dry room with a low dew point of -50 to -60 °C (< 0.3 % relative humidity) for 150 h.

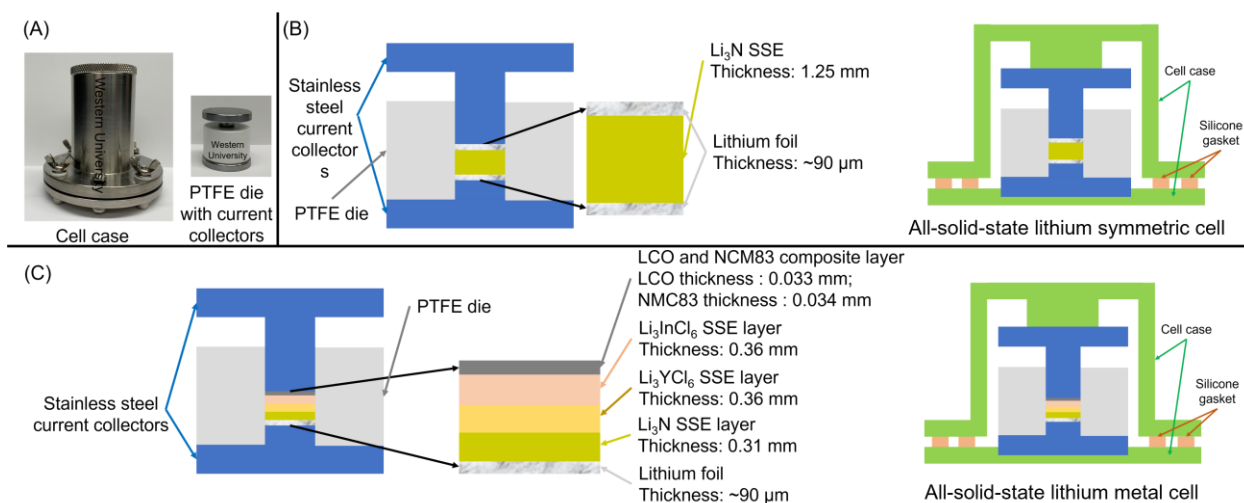
Note: For the operando XRD analysis of the vacancy-rich β - Li_3N , the XRD pattern evolution was monitored in real-time during the sample's exposure to air at 25% relative humidity. In the in-situ XRD study, changes in the XRD pattern were tracked over a 150-hour exposure of the same sample in a dry room. After designated exposure durations in the dry room, the sample was sealed using Kapton tape to prevent potential contamination from the ambient environment within the XRD instrument room. Notably, Kapton tape does not exhibit distinct sharp XRD peaks but presents a broad hump around 2θ of approximately 26 degrees.



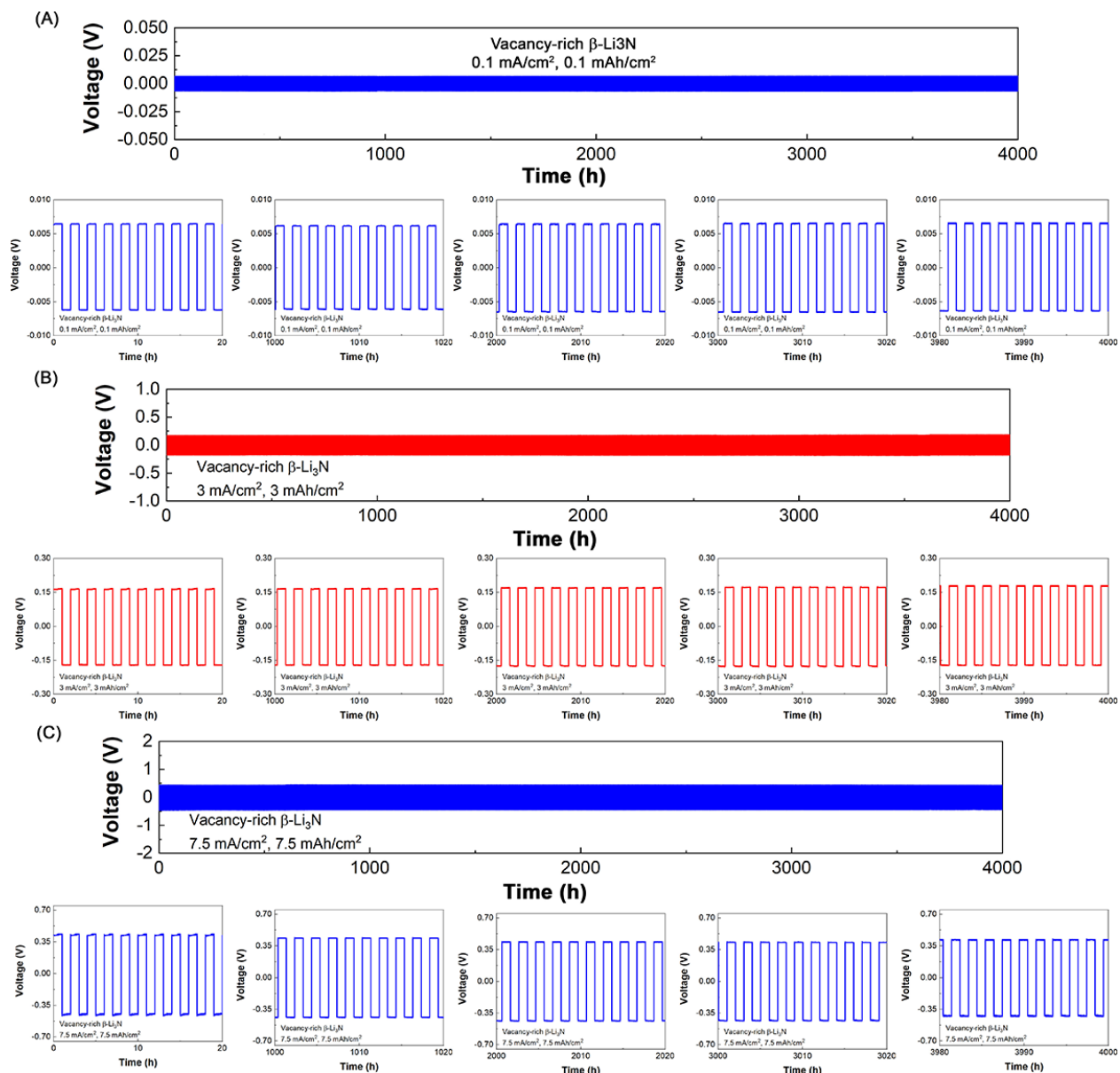
Supplementary Figure 12 Ex-situ (A) N K-edge, and (B) O K-edge XANES studies of this vacancy-rich β -Li₃N during exposure process to air with 25% relative humidity for 10 h. Ex-situ (C) N K-edge, and (D) O K-edge XANES studies of this vacancy-rich β -Li₃N upon different exposure times in a dry room with a low dew point of -50 to -60 °C (< 0.3 % relative humidity) for 150 h. N K-, and O K- edge XANES spectra were collected in the TEY mode.



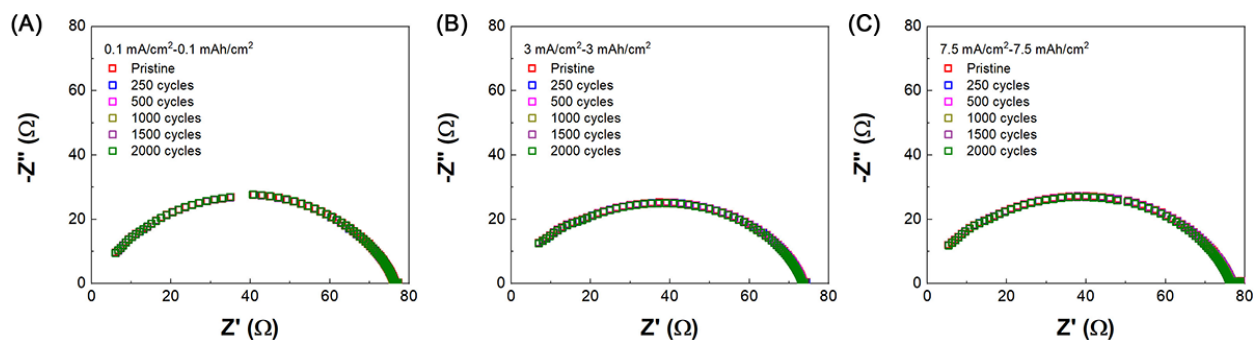
Supplementary Figure 13 Direct current (DC) polarization curves of the vacancy-rich β -Li₃N sample using lithium blocking symmetric cells at different voltages. (b) Equilibrium current response of vacancy-rich β -Li₃N symmetric cells at different voltages.



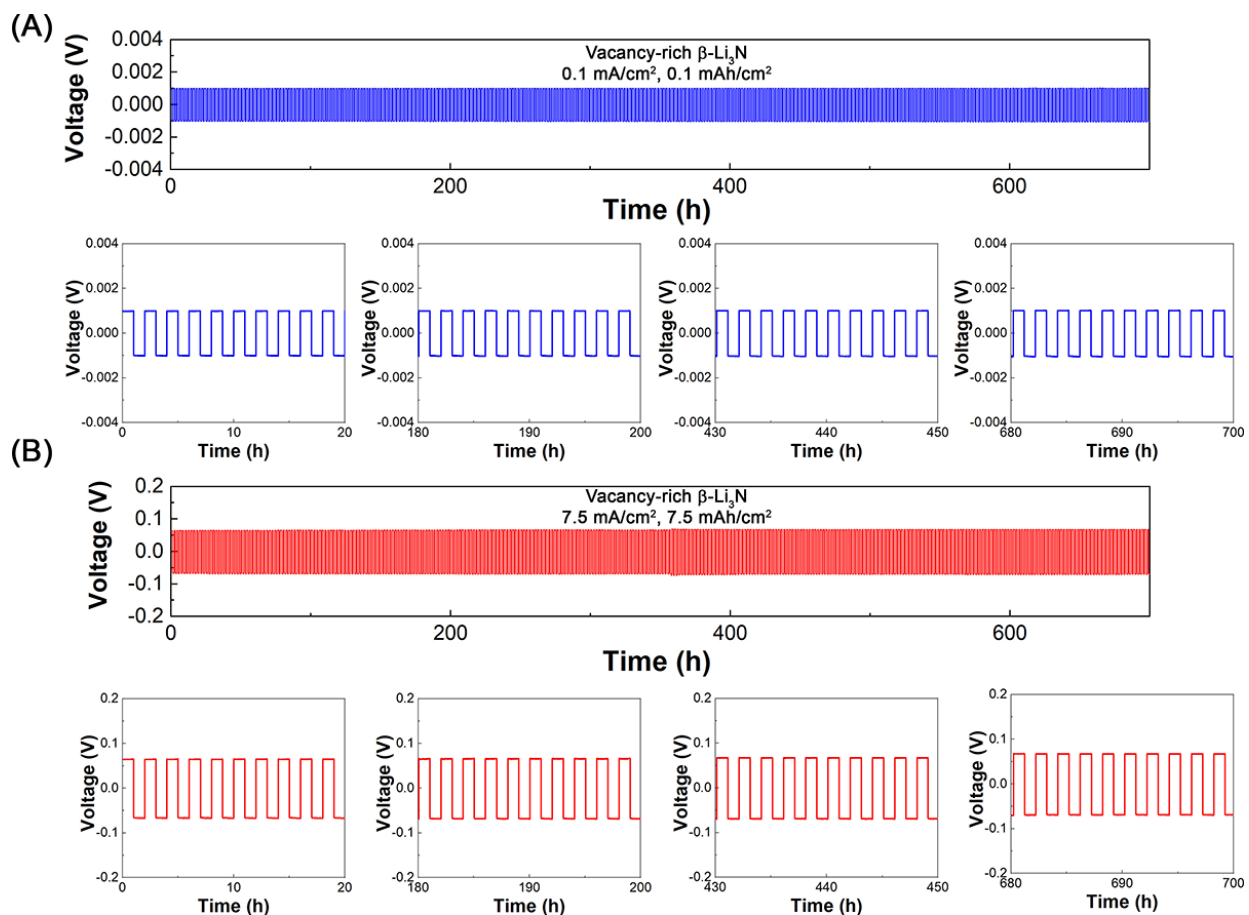
Supplementary Figure 14 (A) Digital photograph of the in-house fabricated all-solid-state cell and the PTFE die Schematic illustration of (B) all-solid-state lithium symmetric cells and (C) all-solid-state lithium metal cells.



Supplementary Figure 15 Voltage profiles of Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cell with (A) a current density of 0.1 mA/cm² and a fixed capacity of 0.1 mAh/cm², (B) a current density of 3 mA/cm² and a fixed capacity of 3 mAh/cm², and (C) a current density of 7.5 mA/cm² and a fixed capacity of 7.5 mAh/cm².

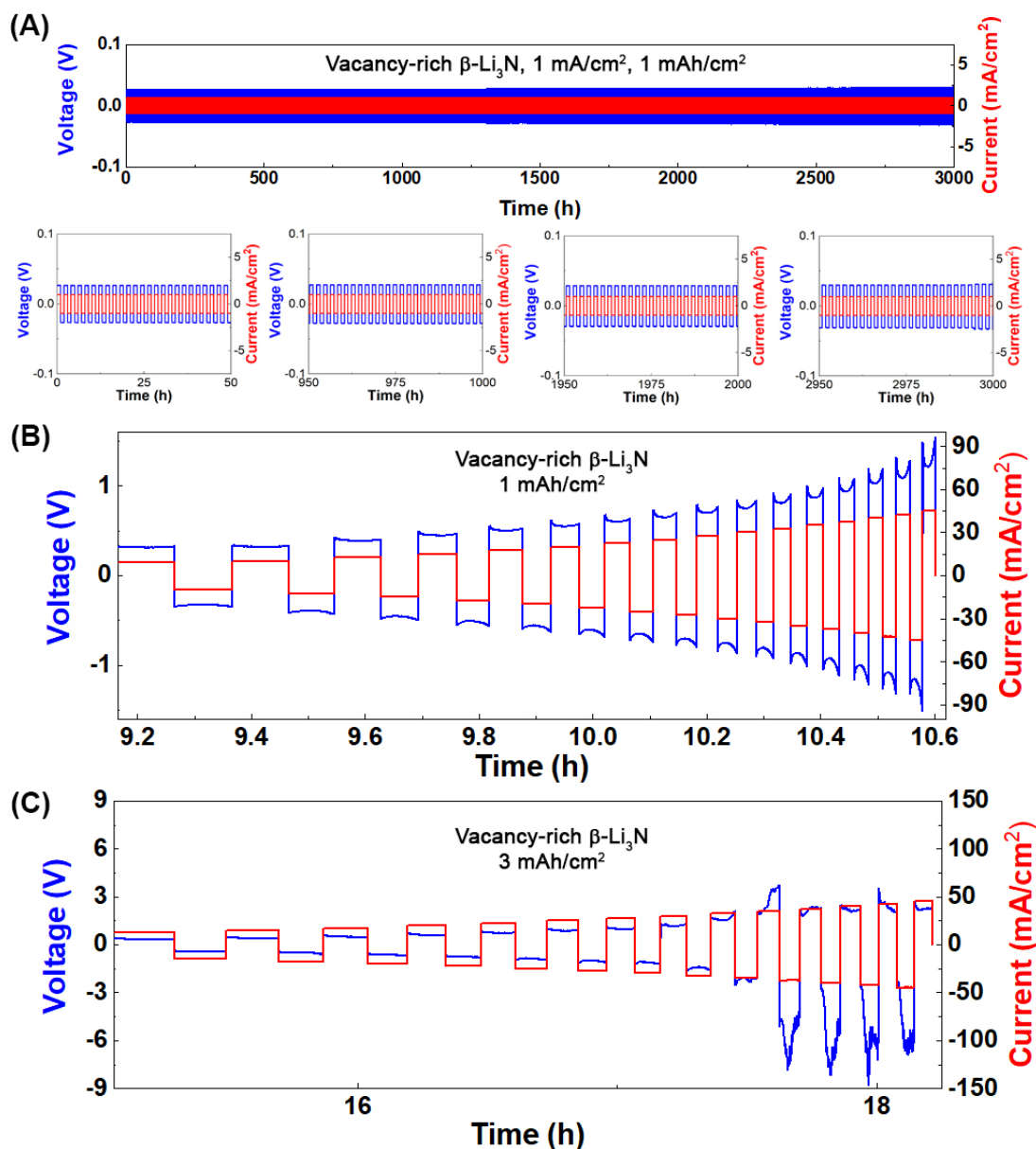


Supplementary Figure 16 Time-dependent electrochemical impedance spectroscopy of Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells cycled at (A) a current density of 0.1 mA/cm² and a fixed capacity of 0.1 mAh/cm², (B) a current density of 3 mA/cm² and a fixed capacity of 3 mAh/cm², and (C) a current density of 7.5 mA/cm² and a fixed capacity of 7.5 mAh/cm² as shown in Supplementary Figure 15.

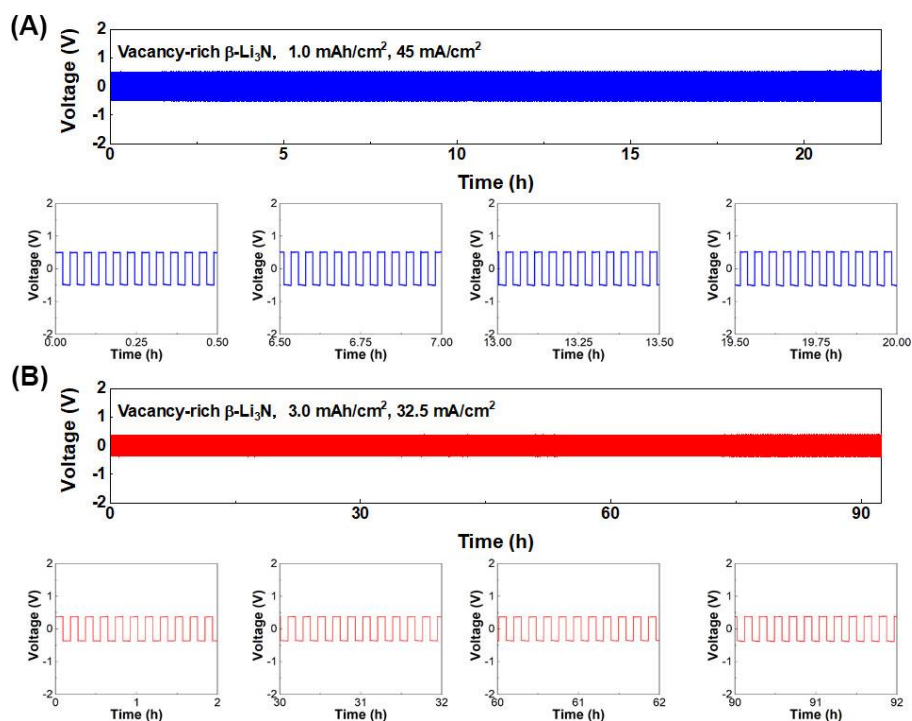


Supplementary Figure 17 Voltage profiles of Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cell with (A) a current density of 0.1 mA/cm² and a fixed capacity of 0.1 mAh/cm², and (B) a current density of 7.5 mA/cm² with a fixed capacity of 7.5 mAh/cm².

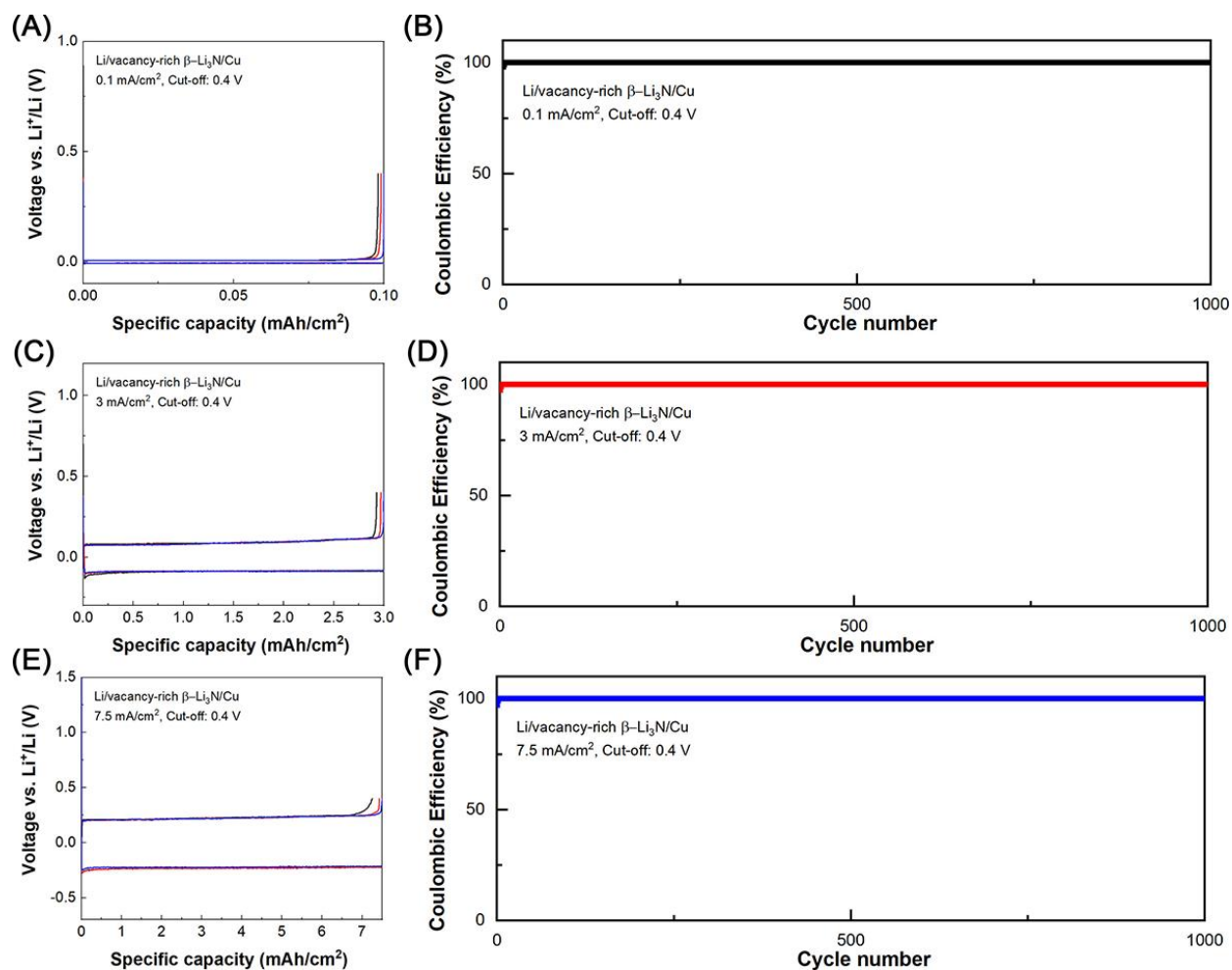
Note: For practical applications, it is imperative to minimize the overpotential of the Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells. To achieve this objective, solid-state electrolyte layers were fabricated to possess lower overall resistance. Specifically, these layers incorporated 15 mg of vacancy-rich β -Li₃N, resulting in a thickness of approximately 0.25 mm in the symmetric cells instead of 100 mg of vacancy-rich β -Li₃N for regular lithium symmetric cell measurements.



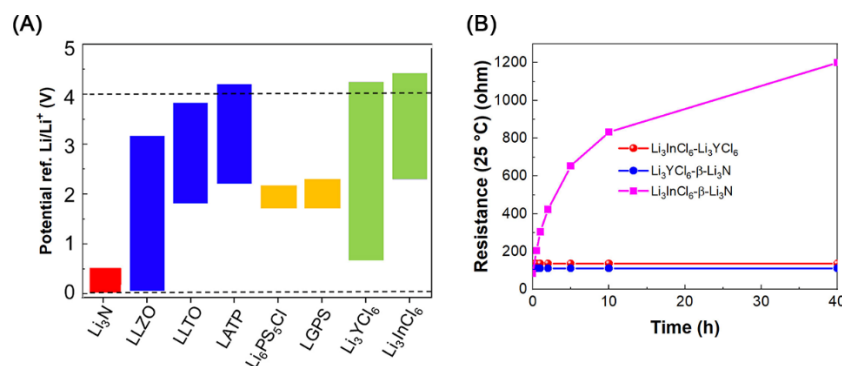
Supplementary Figure 18 Voltage profiles of the Li/vacancy-rich $\beta\text{-Li}_3\text{N}$ /Li symmetric all-solid-state cells with (A) a current density of 1 mA/cm² and a fixed capacity of 1 mAh/cm² after incremental current densities and capacity symmetric cell testing as shown in Figure 4C, (B) a fixed capacity of 1 mAh/cm² and incremental current densities, and (C) a fixed capacity of 3 mAh/cm² and incremental current densities.



Supplementary Figure 19 Voltage profiles of the Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells with (A) a current density of 45 mA/cm² and a fixed capacity of 1 mAh/cm² for 500 cycles and (B) a current density of 32.5 mA/cm² and a fixed capacity of 3 mAh/cm² for 500 cycles. Note: For practical applications, it is imperative to minimize the overpotential of the Li/vacancy-rich β -Li₃N/Li symmetric all-solid-state cells, especially at elevated current densities of 45 and 32.5 mA/cm². To achieve this objective, solid-state electrolyte layers were fabricated to possess lower overall resistance. Specifically, these layers incorporated 15 mg of vacancy-rich β -Li₃N, resulting in a thickness of approximately 0.25 mm in the symmetric cells instead of 100 mg of vacancy-rich β -Li₃N for regular lithium symmetric cell measurements.

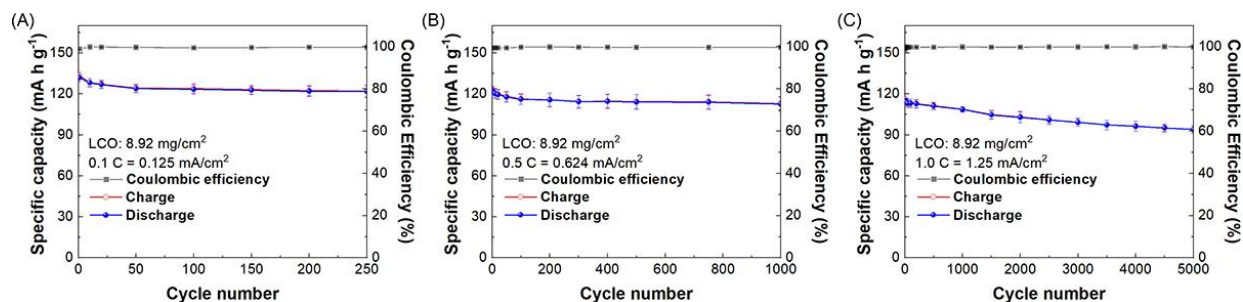


Supplementary Figure 20 Voltage profiles and corresponding Coulombic efficiency for the $\text{Li}/\text{vacancy-rich } \beta\text{-Li}_3\text{N}/\text{Cu}$ asymmetric all-solid-state cells cycled at (A) and (B) a current density of $0.1 \text{ mA}/\text{cm}^2$ and a fixed capacity of $0.1 \text{ mAh}/\text{cm}^2$, (C) and (D) a current density of $3 \text{ mA}/\text{cm}^2$ and a fixed capacity of $3 \text{ mAh}/\text{cm}^2$, and (E) and (F) a current density of $7.5 \text{ mA}/\text{cm}^2$ and a fixed capacity of $7.5 \text{ mAh}/\text{cm}^2$.

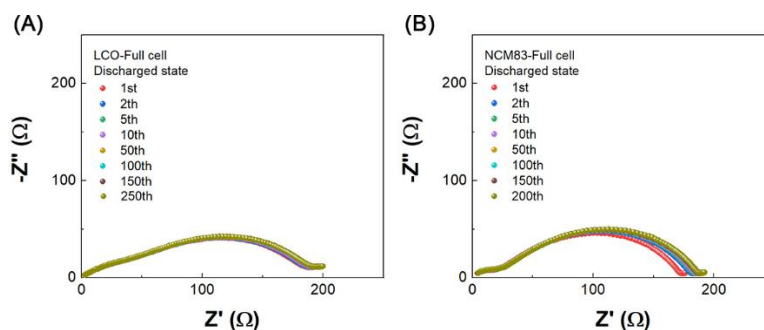


Supplementary Figure 21 (A) Calculation of the intrinsic thermodynamic electrochemical windows for this vacancy-rich β -Li₃N compared with other common SSEs, encompassing oxides, sulfides, and halides. (B) Time-dependent evolution of lithium-ion conductive resistance in layer-by-layer assembled configurations of Li₃InCl₆(60 mg)-Li₃YCl₆(60 mg), Li₃YCl₆(60 mg)- β -Li₃N(25 mg), and Li₃InCl₆(60 mg)- β -Li₃N(25 mg).

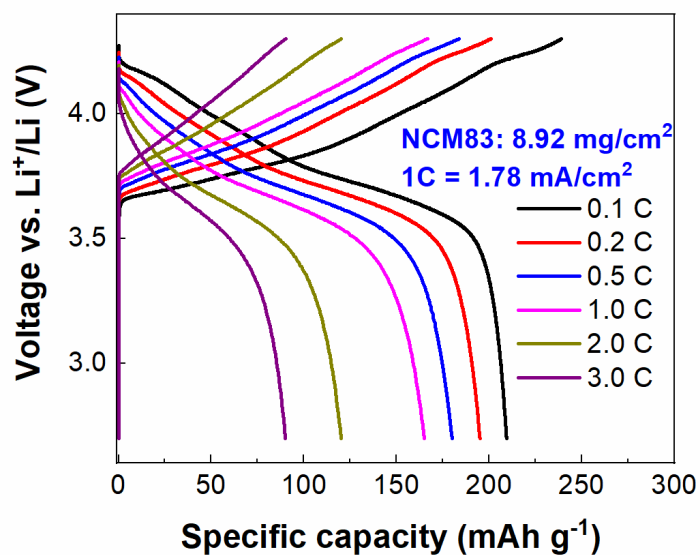
Notes: The electrochemical window mismatch between the high-voltage cathode-compatible Li₃InCl₆ and lithium-metal-compatible β -Li₃N induces severe interfacial reactions, resulting in elevated interfacial resistance. Conversely, the layer-by-layer assembled configurations of Li₃InCl₆ (60 mg)- Li₃YCl₆ (60 mg) and Li₃YCl₆ (60 mg)- β -Li₃N (25 mg) exhibit stable resistance for a duration of 40 hours, indicative of interfacial stability. Consequently, Li₃YCl₆ serves as an effective buffer layer mitigating interfacial reactions between Li₃InCl₆ and β -Li₃N SSEs.



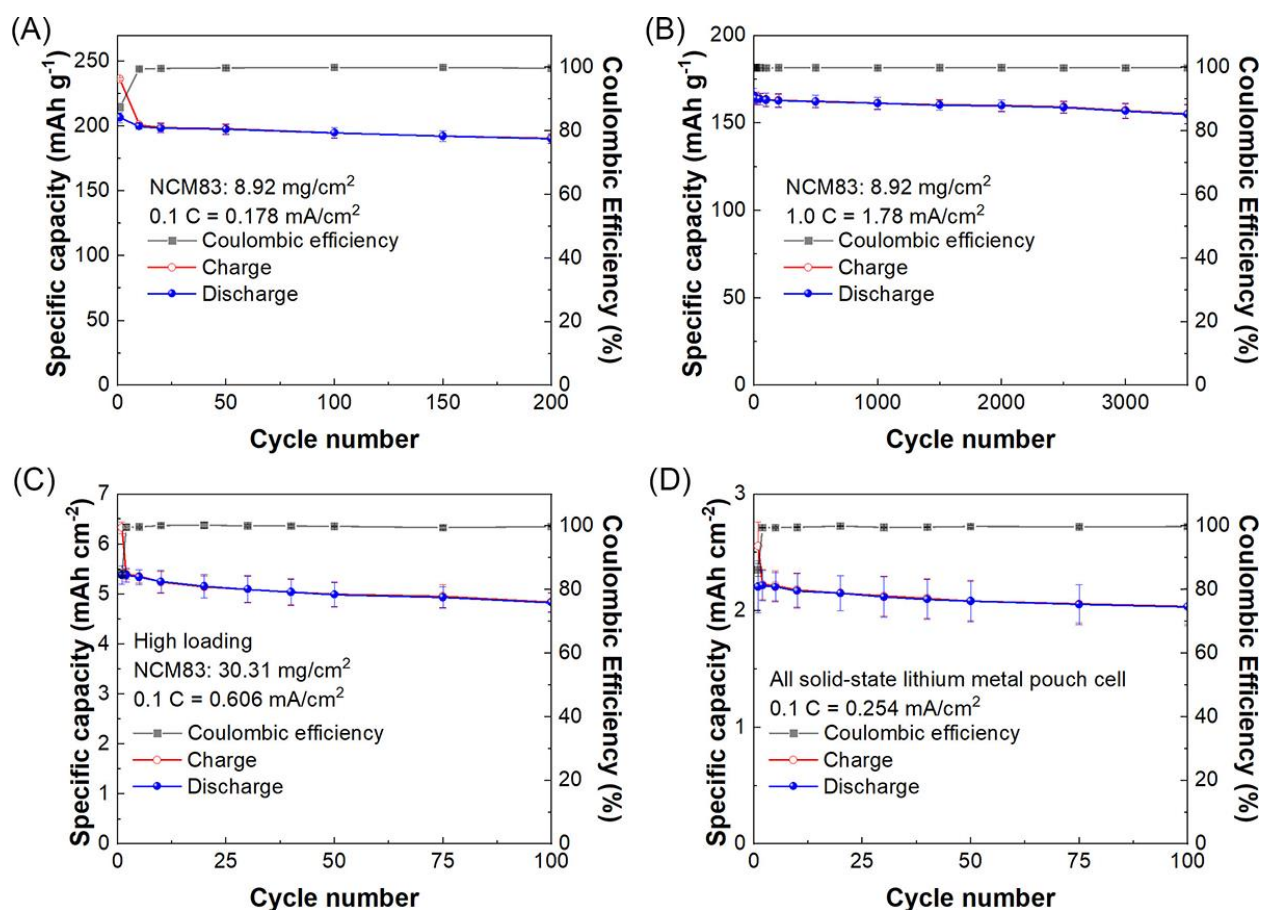
Supplementary Figure 22 Long-term electrochemical performance of LCO/Li₃InCl₆/Li₃YCl₆/vacancy-rich β-Li₃N/Li all-solid-state lithium metal batteries, featuring a cathode loading of 8.92 mg/cm², tested at an ambient temperature of 25 °C within an operational voltage range of 4.2 V to 2.7 V. The evolution of both the average charge-discharge capacity and the average Coulombic efficiency as a function of cycle number for batteries subjected to cycling at rates of (A) 0.1 C, (B) 0.5 C, and (C) 1.0 C. The data encapsulated in Supplementary Figure 23 were garnered from all-solid-state pellet-type cells, with the analysis based on 10 cells for each specified cycling condition. The points represent the average values of the 10 cells, and the error bars denote their standard deviation.



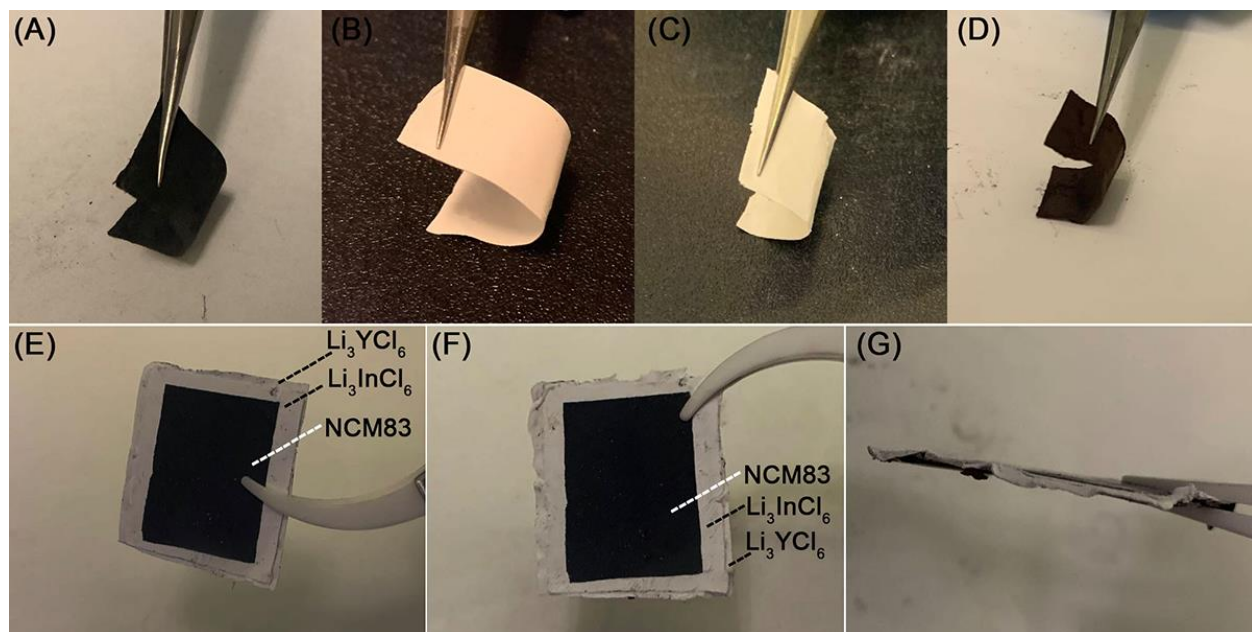
Supplementary Figure 23 All-solid-state lithium metal batteries impedance evolution during cycling at a 0.1 C rate. (A) Nyquist plots of an LCO/halide/vacancy-rich β - $\text{Li}_3\text{N}/\text{Li}$ all-solid-state lithium metal cell with LCO loading of 8.92 mg/cm^2 at 25°C with an operating voltage window between 4.2 V and 2.7 V for 250 cycles and equilibrated at full discharge. (B) Nyquist plots of an NCM83/halide/vacancy-rich β - $\text{Li}_3\text{N}/\text{Li}$ all-solid-state lithium metal cell at 25°C with an operating voltage window between 4.3 V and 2.7 V for 200 cycles and equilibrated at full discharge.



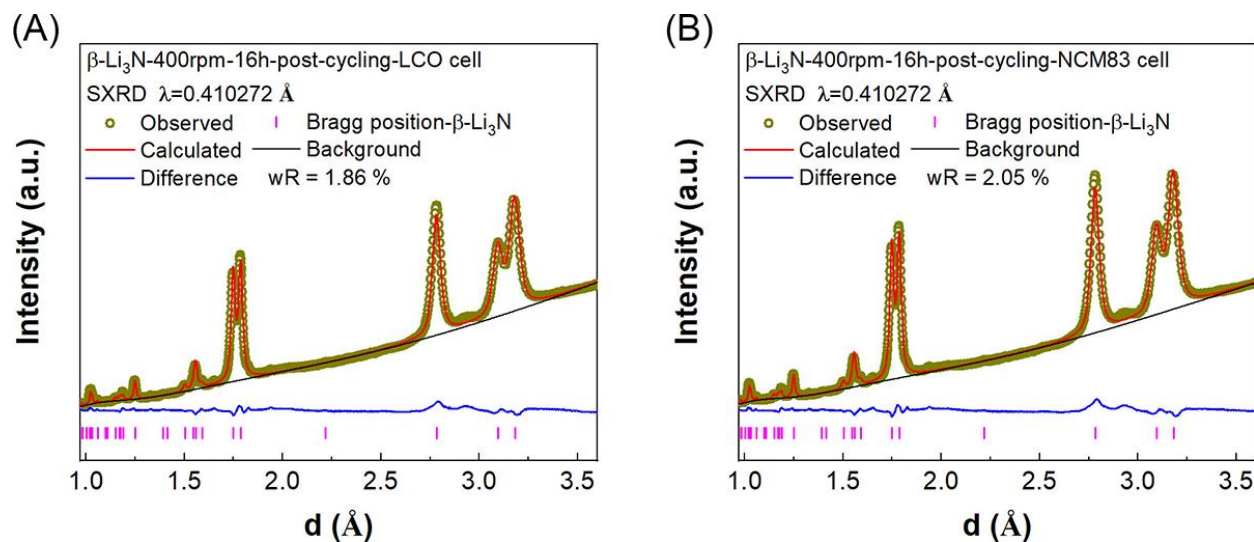
Supplementary Figure 24 Electrochemical performance of the NCM83/Li₃InCl₆/Li₃YCl₆/vacancy-rich β -Li₃N/Li all-solid-state lithium metal batteries at 25 °C with an operating voltage window between 4.3 V and 2.7 V and the NCM83 loading of 8.92 mg/cm²: The charge/discharge curves at incremental cycling rates up to 3.0 C.



Supplementary Figure 25 Long-term electrochemical performance of NCM83/Li₃InCl₆/Li₃YCl₆/vacancy-rich β -Li₃N/Li all-solid-state lithium metal batteries at 25°C, operating within a voltage range of 4.3 V to 2.7 V with an NCM83 cathode loading of 8.92 mg/cm². The average charge-discharge capacity and Coulombic efficiency over cycle numbers for batteries cycled at (A) 0.1 C, and (B) 1.0 C, and (C) the performance of high-loading all-solid-state lithium metal batteries (areal loading of NCM83: 30.31 mg/cm²). (D) The average charge-discharge capacity and Coulombic efficiency over cycle numbers for an all-solid-state pouch cell. Data for Figures S26A to S26D were acquired using all-solid-state pellet-type cells, with averages calculated from 10 cells under each specified cycling condition. The points represent the average values of the 10 cells, and the error bars denote their standard deviation.



Supplementary Figure 26 Digital photographs showcasing dry films of: (A) NCM83 cathode, (B) Li_3InCl_6 , (C) Li_3YCl_6 , and (D) vacancy-rich $\beta\text{-Li}_3\text{N}$ solid-state electrolytes (SSEs) halide. Additionally, images of the assembled dry-film based cell with the configuration NCM83/LIC/LYC/vacancy-rich $\beta\text{-Li}_3\text{N}$ /Li before cycling (E) and after cycling (F and G)



Supplementary Figure 27 SXR D pattern and corresponding Rietveld refinement of β -Li₃N-400rpm-16h post cycling in the (A) LCO/Li₃InCl₆/Li₃YCl₆/vacancy-rich β -Li₃N/Li all-solid-state lithium metal cells and (B) NCM83/Li₃InCl₆/Li₃YCl₆/vacancy-rich β -Li₃N/Li all-solid-state lithium metal cells with cathode loading of 8.92 mg/cm² before cycling and after cycling at 0.1 C for 200, and 250 cycles, respectively.

Supplementary Table 9. Crystallographic data of β -Li₃N-400rpm-16h-post cycling-LCO cell and corresponding refined parameters based on SXRD.

Compound	Li _{2.840(6)} N _{0.947(7)}
β -Li ₃ N, Weight fraction: 100 wt. %	
Space Group	<i>P6₃/mmc</i>
<i>a</i> = <i>b</i> , Å	3.5710(6)
<i>c</i> , Å	6.3556(5)
α = β , °	90
γ , °	120
<i>V</i> , Å ³	70.188(18)

Supplementary Table 10. Rietveld refinement analysis results for the SXRD patterns of β -Li₃N-400rpm-16h-post cycling-LCO cell

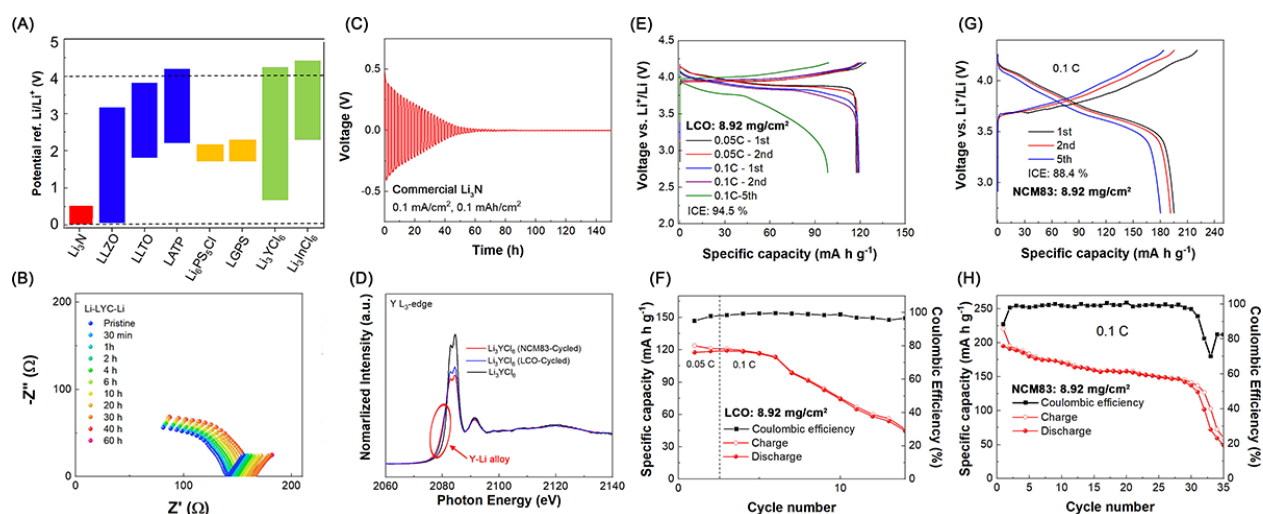
β -Li ₃ N, Weight fraction: 100 wt.%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	$\frac{1}{4}$	1.000	0.0435(11)	2b	-6m2	2
Li2	$\frac{1}{3}$	$\frac{2}{3}$	0.58742(3)	0.920(6)	0.0435(11)	4f	3m	4
N3	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.947(7)	0.0119(10)	2c	-6m2	2

Supplementary Table 11. Crystallographic data of β -Li₃N-400rpm-16h-post cycling-NCM83 cell and corresponding refined parameters based on SXRD.

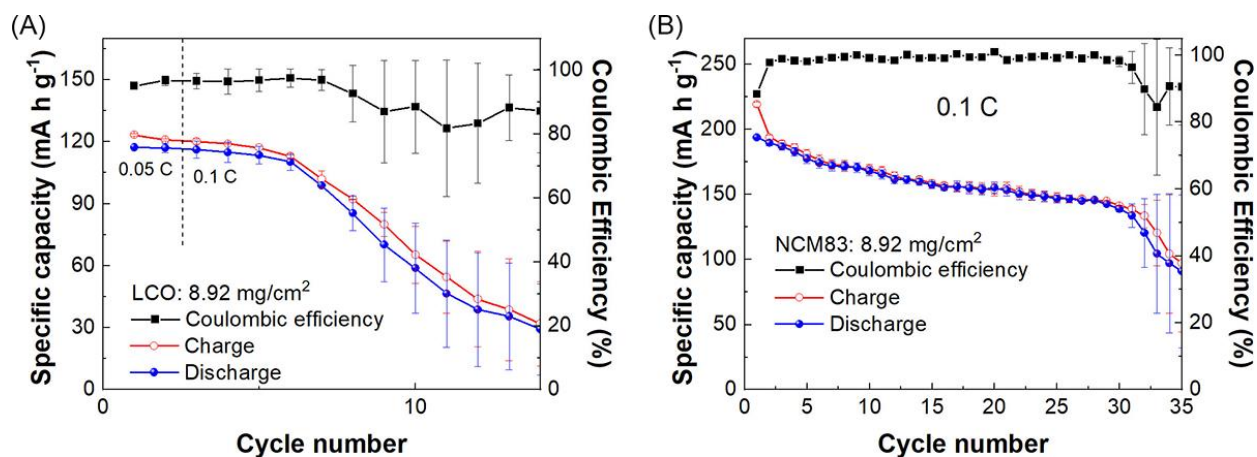
Compound	Li _{2.836(7)} N _{0.94(5)}
β -Li ₃ N, Weight fraction: 100 wt. %	
Space Group	<i>P6₃/mmc</i>
$a=b$, Å	3.5710(6)
c , Å	6.3556(5)
$\alpha=\beta$, °	90
γ , °	120
V , Å ³	70.190(18)

Supplementary Table 12. Rietveld refinement analysis results for the SXRD patterns of β -Li₃N-400rpm-16h-post cycling-NCM83 cell

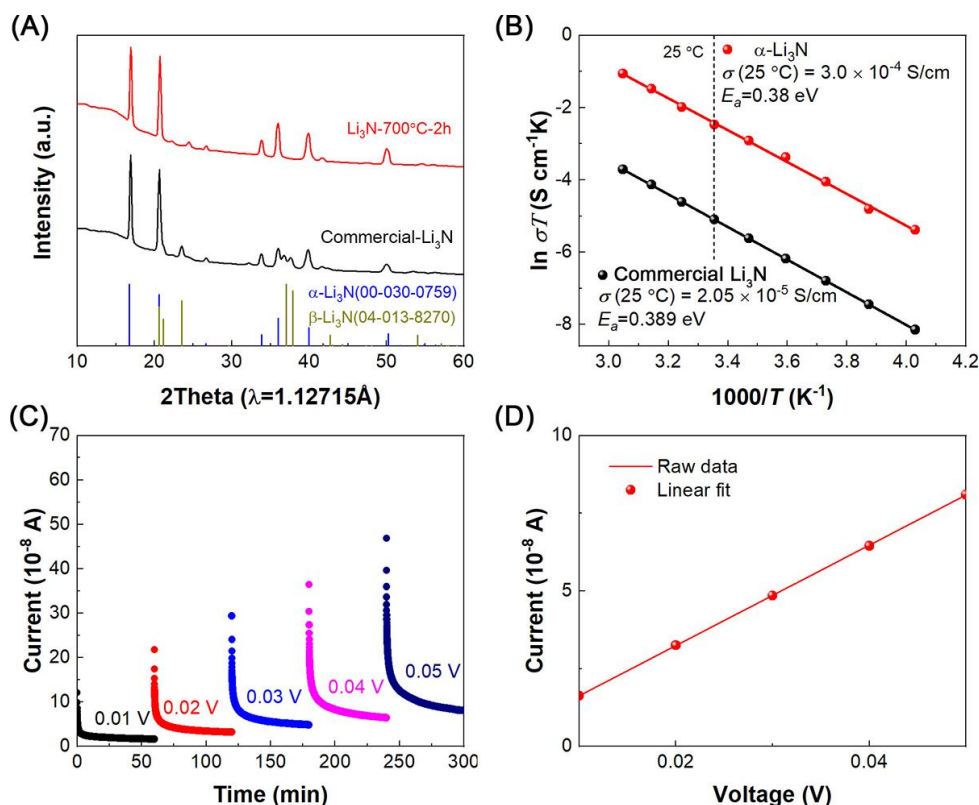
β -Li ₃ N, Weight fraction: 100 wt.%								
Atom	x	y	z	<i>Occ.</i>	U	Site	Sym.	Mult.
Li1	0	0	$\frac{1}{4}$	1.000	0.0423(11)	2b	-6m2	2
Li2	$\frac{1}{3}$	$\frac{2}{3}$	0.58742(3)	0.918(7)	0.0423(11)	4f	3m	4
N3	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.945(5)	0.0112(9)	2c	-6m2	2



Supplementary Figure 28 (A) Calculation of the intrinsic thermodynamic electrochemical windows for this vacancy-rich $\beta\text{-Li}_3\text{N}$ compared with other common SSEs, encompassing oxides, sulfides, and halides. (B) Time-resolved EIS spectra of the $\text{Li/Li}_3\text{YCl}_6(\text{LYC})/\text{Li}$ symmetric cell at rest for 60 h. (C) Voltage profiles of $\text{Li}/\text{commercial-Li}_3\text{N}/\text{Li}$ symmetric all-solid-state cell with a current density of 0.1 mA/cm^2 and a fixed capacity of 0.1 mAh/cm^2 . (D) Y $\text{L}_{3\text{-edge}}$ XANES spectra of the Li_3YCl_6 SSE and SSE layers in the LCO and NCM83/ $\text{Li}_3\text{InCl}_6/\text{Li}_3\text{YCl}_6/\text{commercial-Li}_3\text{N}/\text{Li}$ cells with LCO and NCM83 loading of 8.92 mg/cm^2 after cycling at 0.1 C for 15 and 35 cycles, respectively. Y $\text{L}_{3\text{-edge}}$ XANES spectra were collected in the TEY mode. (E ~ H) Electrochemical performance of the LCO and NCM83/ $\text{Li}_3\text{InCl}_6/\text{Li}_3\text{YCl}_6/\text{commercial-Li}_3\text{N}/\text{Li}$ all-solid-state lithium metal batteries with cathode loading of 8.92 mg/cm^2 at 25°C . (E) The charge/discharge curves at 0.05 and 0.1 C of $\text{LCO}/\text{Li}_3\text{InCl}_6/\text{Li}_3\text{YCl}_6/\text{commercial-Li}_3\text{N}/\text{Li}$ cycled an operating voltage window between 4.2 V and 2.7 V . (F) Charge-discharge capacity and the Coulombic efficiency as a function of cycle number for $\text{LCO}/\text{Li}_3\text{InCl}_6/\text{Li}_3\text{YCl}_6/\text{commercial-Li}_3\text{N}/\text{Li}$ cycled at 0.1 C . (G) The charge/discharge curves at 0.1 C of $\text{NCM83}/\text{Li}_3\text{InCl}_6/\text{Li}_3\text{YCl}_6/\text{commercial-Li}_3\text{N}/\text{Li}$ cycled an operating voltage window between 4.3 V and 2.7 V . (H) Charge-discharge capacity and the Coulombic efficiency as a function of cycle number for $\text{NCM83}/\text{Li}_3\text{InCl}_6/\text{Li}_3\text{YCl}_6/\text{commercial-Li}_3\text{N}/\text{Li}$ cycled at 0.1 C .

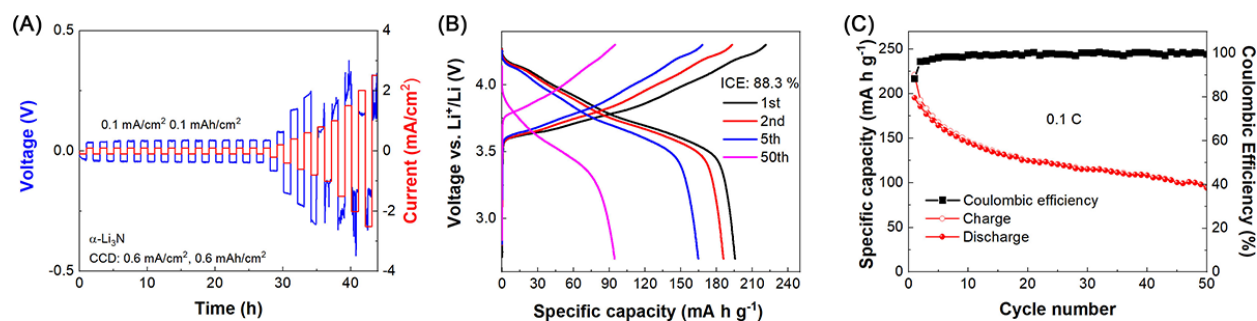


Supplementary Figure 29 The average charge-discharge capacity and the average Coulombic efficiency as a function of cycle number for (A) LCO/Li₃InCl₆/Li₃YCl₆/commercial-Li₃N/Li cycled at 0.1 C and (B) NCM83/Li₃InCl₆/Li₃YCl₆/commercial-Li₃N/Li cycled at 0.1 C. The points represent the average values of the 10 cells, and the error bars denote their standard deviation.

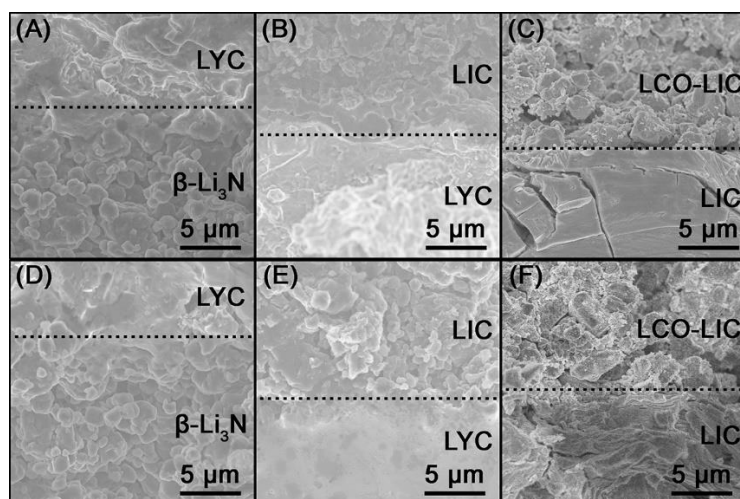


Supplementary Figure 30 (A) The XRD patterns of the $\alpha\text{-Li}_3\text{N}$ samples processed by annealing at 700°C for 2 h and the commercial Li_3N raw materials. (B) Arrhenius plots of $\alpha\text{-Li}_3\text{N}$ and the commercial Li_3N . (C) Direct current (DC) polarization curves of the $\alpha\text{-Li}_3\text{N}$ sample using lithium blocking symmetric cells at different voltages. (D) Equilibrium current response of the $\alpha\text{-Li}_3\text{N}$ symmetric cells at different voltages.

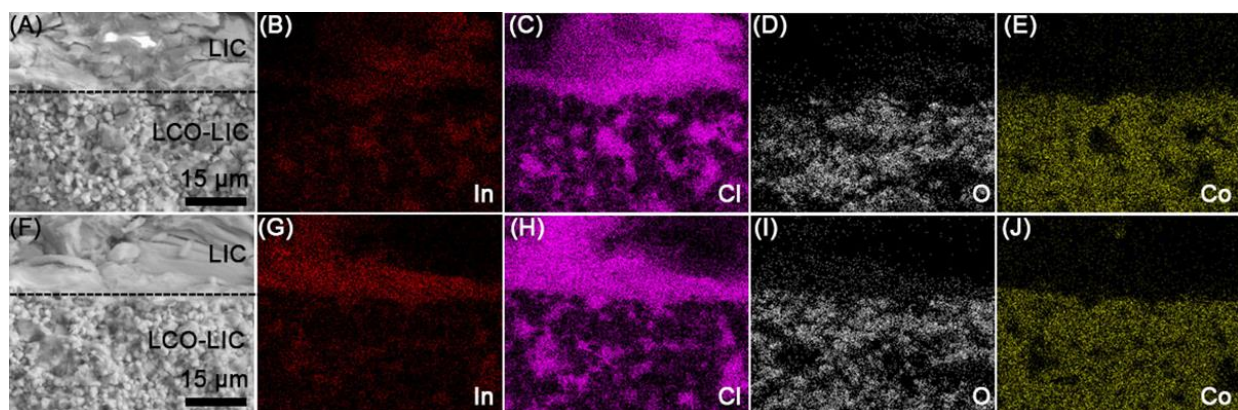
Note: The $\alpha\text{-Li}_3\text{N}$ sample was prepared by annealing the commercial Li_3N raw materials under vacuum at 700°C for 2 h. The heating rate was 5°C/min .



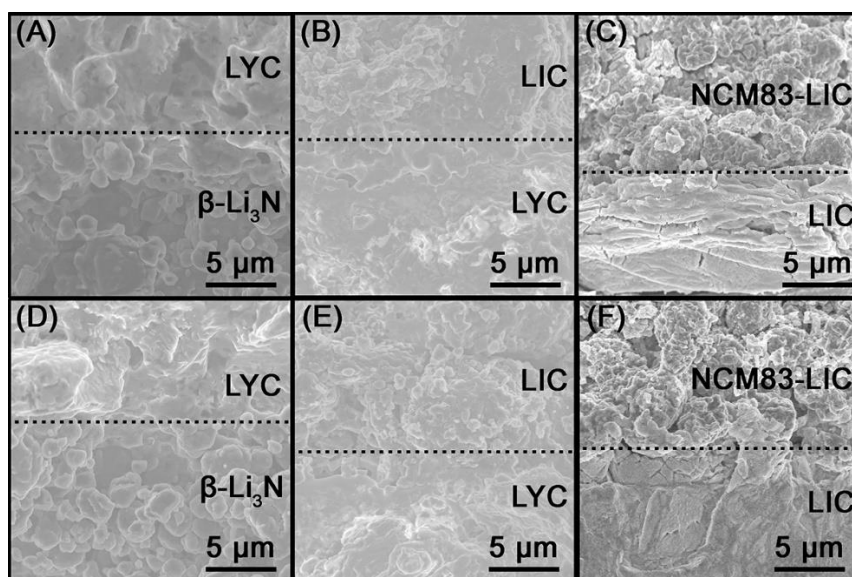
Supplementary Figure 31 (A) Voltage profiles of Li/α-Li₃N/Li symmetric all-solid-state cell with incremental current densities and capacities (lithium plating/stripping for fixed 1 h). (B) The charge/discharge curves at 0.1 C and (C) charge-discharge capacity and the Coulombic efficiency as a function of cycle number cycled at 0.1 C of the NCM83/Li₃InCl₆/Li₃YCl₆/α-Li₃N/Li all-solid-state lithium metal batteries at 25 °C with an operating voltage window between 4.3 V and 2.7 V and the NCM83 loading of 8.92 mg/cm².



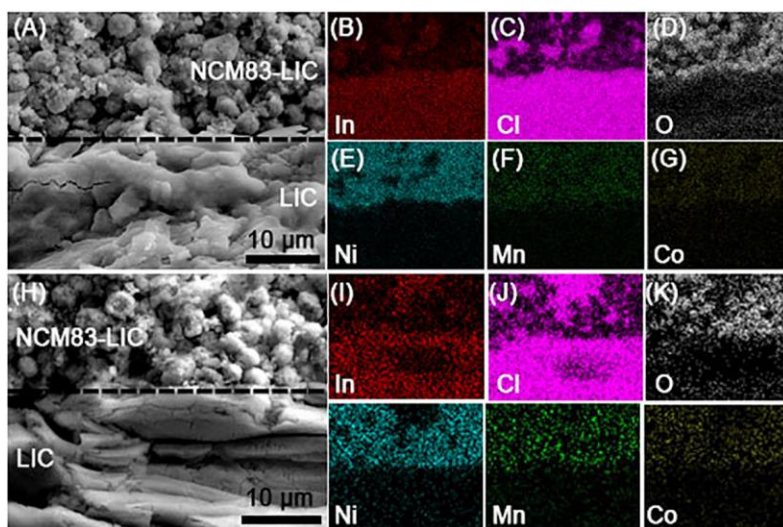
Supplementary Figure 32 Cross-sectional Scanning Electron Microscopy (SEM) images of LCO/ Li_3InCl_6 (LIC)/ Li_3YCl_6 (LYC)/vacancy-rich $\beta\text{-Li}_3\text{N}$ /Li cells with LCO loading of 8.92 mg/cm^2 (A, B, and C) before cycling and (D, E, and F) after cycling at 0.1 C with an operating voltage window between 4.2 V and 2.7 V for 250 cycles, showcasing the (A, and D) $\beta\text{-Li}_3\text{N}$ /LYC, (B, and E) LYC/LIC, (C, and F) LIC/LCO-LIC interfaces.



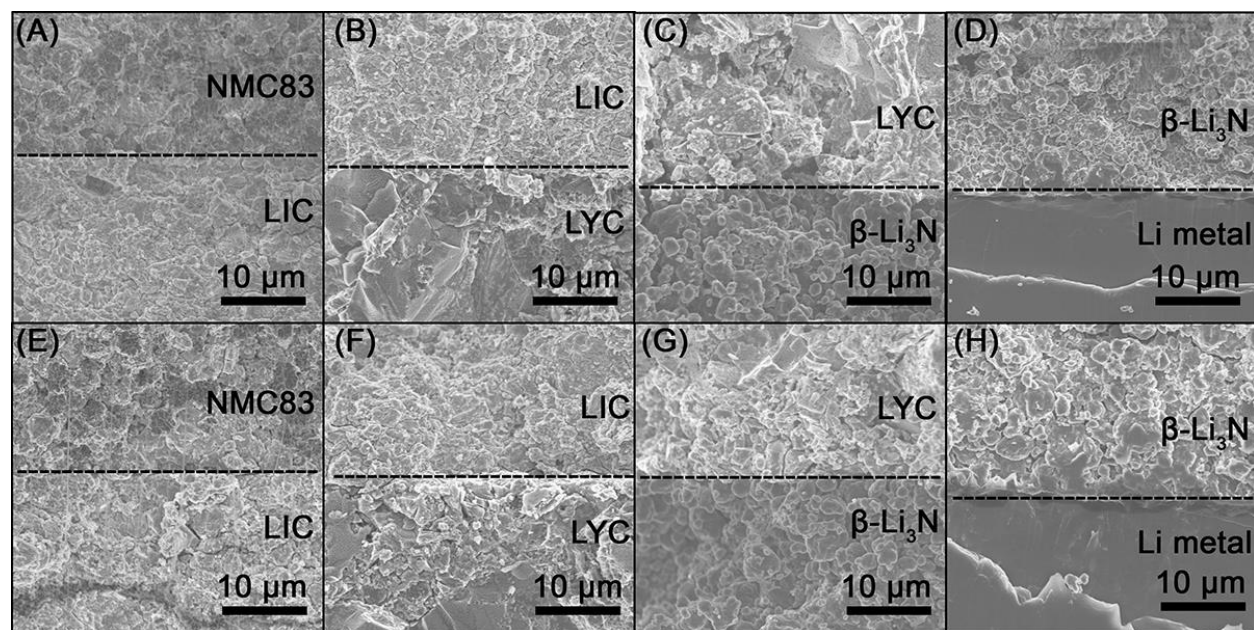
Supplementary Figure 33 SEM images and the corresponding Energy-Dispersive X-ray (EDX) mapping of elements for the LIC/LCO-LIC interfaces in the LCO/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/vacancy-rich β -Li₃N/Li cells with LCO loading of 8.92 mg/cm² (A ~ E) before cycling and (F ~ J) after cycling at 0.1 C with an operating voltage window between 4.2 V and 2.7 V for 250 cycles: (B and G) Indium (In), (C and H) Chlorine (Cl), (D and I) Oxygen (O), and (E and J) Cobalt (Co).



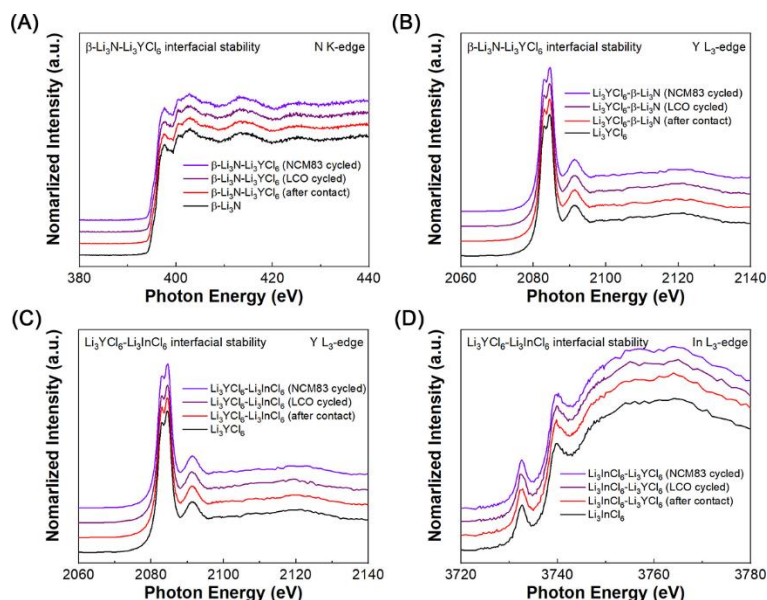
Supplementary Figure 34 Cross-sectional Scanning Electron Microscopy (SEM) images of NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/vacancy-rich $\beta\text{-Li}_3\text{N}$ /Li cells with NCM83 loading of 8.92 mg/cm² (A, B, and C) before cycling and (D, E, and F) after cycling at 0.1 C with an operating voltage window between 4.3 V and 2.7 V for 200 cycles, showcasing the (A, and D) $\beta\text{-Li}_3\text{N}$ /LYC, (B, and E) LYC/LIC, (C, and F) LIC/NCM83-LIC interfaces.



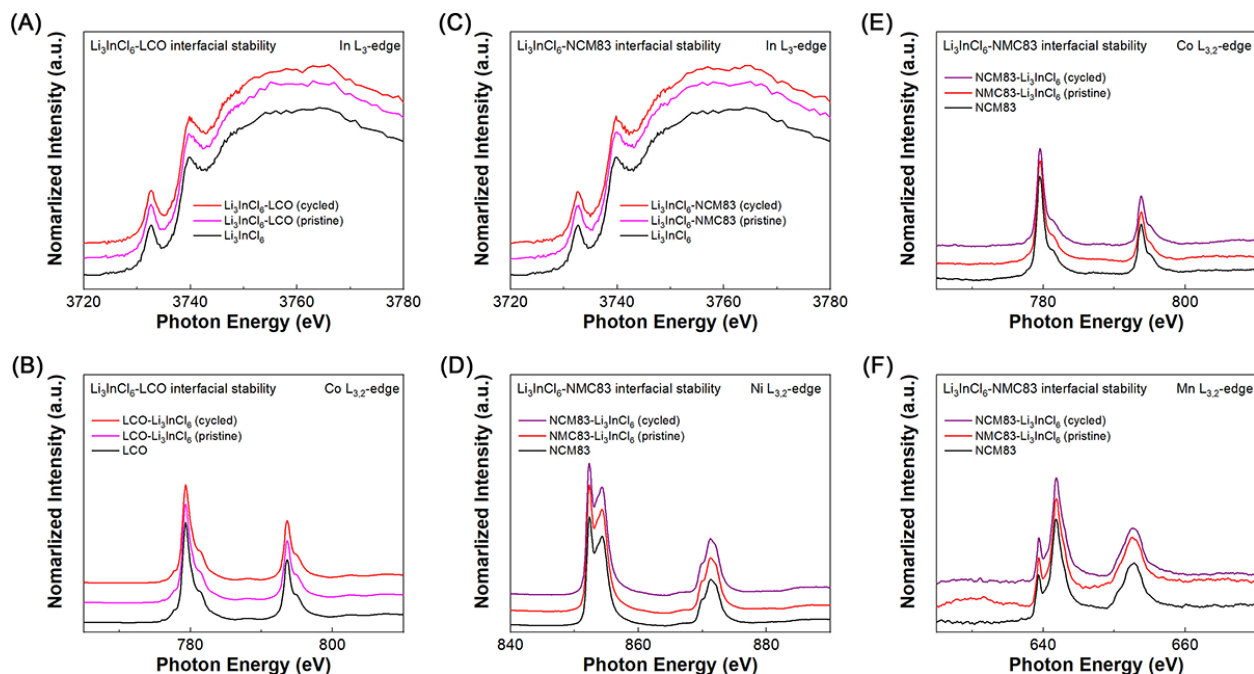
Supplementary Figure 35 SEM images and the corresponding EDX mapping of elements for the LIC/NCM83-LIC interfaces in the NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/vacancy-rich β -Li₃N/Li cells with NCM83 loading of 8.92 mg/cm² (A ~ G) before cycling and (H ~ N) after cycling at 0.1 C with an operating voltage window between 4.3 V and 2.7 V for 250 cycles: (B and I) Indium (In), (C and J) Chlorine (Cl), (D and K) Oxygen (O), (E and L) Nickel (Ni), (F and M) Manganese (Mn), and (G and N) Cobalt (Co).



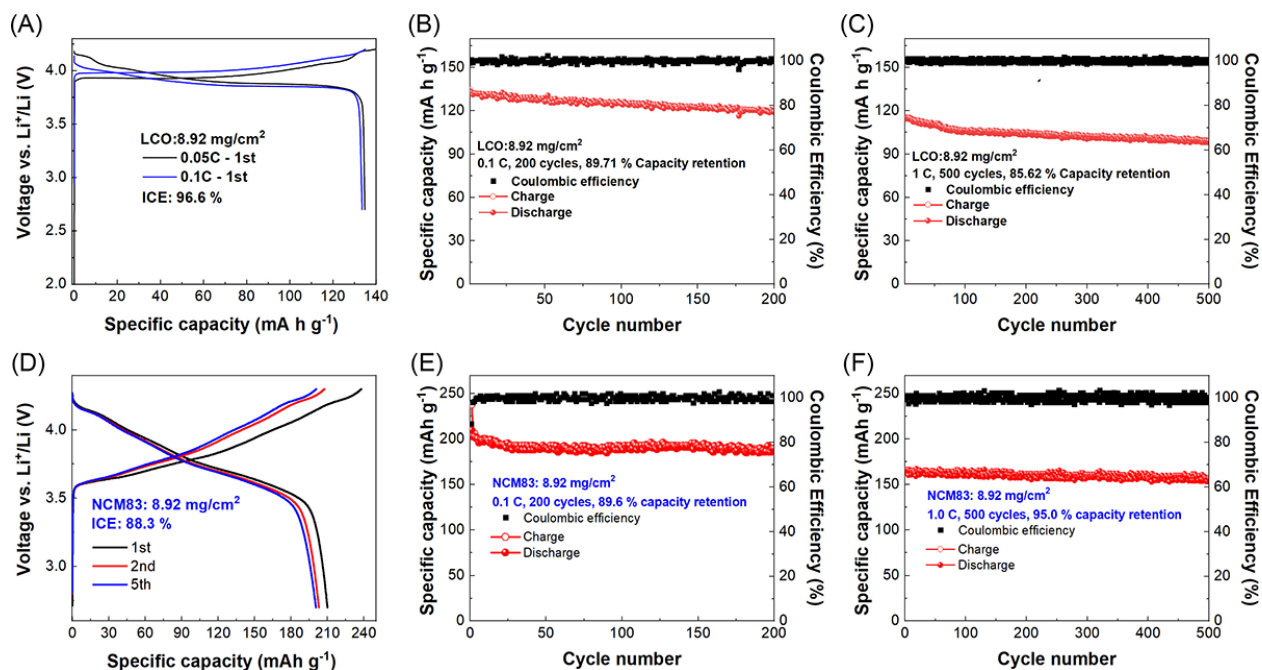
Supplementary Figure 36 Cross-sectional Scanning Electron Microscopy (SEM) images of NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/vacancy-rich β-Li₃N/Li pouch cells (A, B, C, and D) before cycling and (E, F, G, and H) after cycling at 0.1 C with an operating voltage window between 4.3 V and 2.7 V for 80 cycles, showcasing the (A, and E) NCM83-LIC/LIC, (B, and F) LIC/LYC, (C, and G) LYC /vacancy-rich β-Li₃N, and (D, and H) vacancy-rich β-Li₃N/Li interfaces.



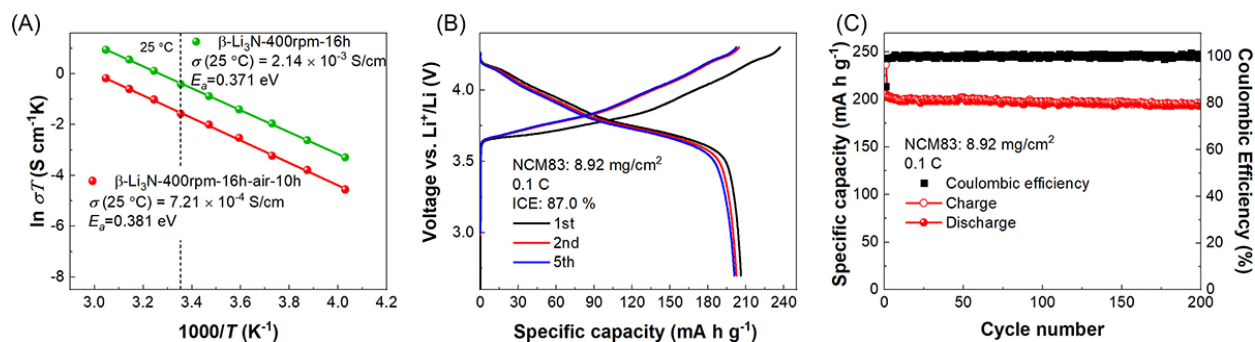
Supplementary Figure 37 XANES studies of interfacial chemical stability across the layered $\text{Li}_3\text{InCl}_6(\text{LIC})$ / $\text{Li}_3\text{YCl}_6(\text{LYC})$ /vacancy-rich $\beta\text{-Li}_3\text{N}$ SSEs in the LCO/ $\text{Li}_3\text{InCl}_6(\text{LIC})$ / $\text{Li}_3\text{YCl}_6(\text{LYC})$ /vacancy-rich $\beta\text{-Li}_3\text{N}/\text{Li}$ all-solid-state lithium metal cells, and NCM83/ $\text{Li}_3\text{InCl}_6(\text{LIC})$ / $\text{Li}_3\text{YCl}_6(\text{LYC})$ /vacancy-rich $\beta\text{-Li}_3\text{N}/\text{Li}$ cells with cathode loading of 8.92 mg/cm^2 before cycling and after cycling at 0.1 C for 200, and 250 cycles, respectively. (A) N K-edge and (B) Y L_3 -edge XANES studies of the vacancy-rich $\beta\text{-Li}_3\text{N-Li}_3\text{YCl}_6$ interfaces, (C) Y L_3 -edge and (D) In L_3 -edge XANES studies of the $\text{Li}_3\text{InCl}_6\text{-Li}_3\text{YCl}_6$ interfaces. N K-, Y L_3 - and In L_3 - edge XANES spectra were collected in the TEY mode.



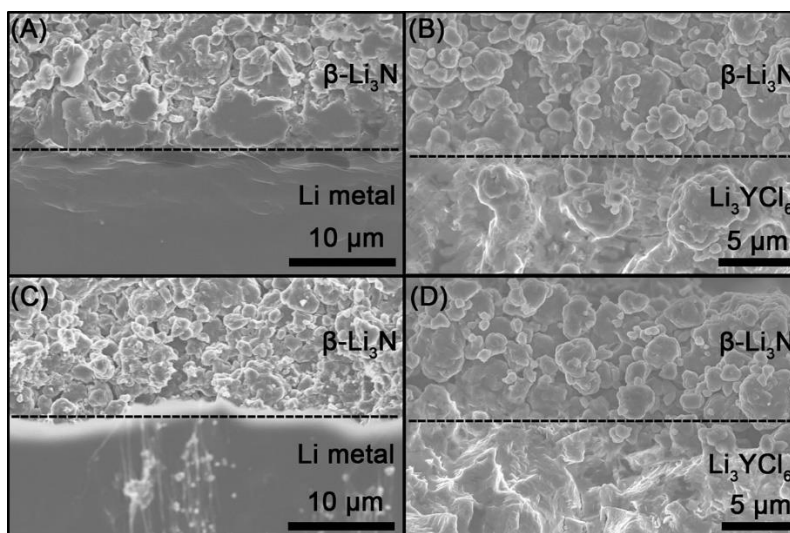
Supplementary Figure 38 XANES studies of interfacial chemical stability between Li_3InCl_6 and cathodes in the LCO/ Li_3InCl_6 (LIC)/ Li_3YCl_6 (LYC)/vacancy-rich $\beta\text{-Li}_{1-x}\text{N}/\text{Li}$ all-solid-state lithium metal cells, and NCM83/ Li_3InCl_6 (LIC)/ Li_3YCl_6 (LYC)/vacancy-rich $\beta\text{-Li}_{1-x}\text{N}/\text{Li}$ all-solid-state lithium metal cells with cathode loading of 8.92 mg/cm^2 before cycling and after cycling at 0.1 C with an operating voltage window between 4.2 V and 2.7 V for 200, and 250 cycles, respectively. (A) In $L_{3,2}$ -edge, and (B) Co $L_{3,2}$ -edge XANES studies of the LCO- Li_3InCl_6 interfaces, (C) In $L_{3,2}$ -edge, (D) Ni $L_{3,2}$ -edge, (E) Co $L_{3,2}$ -edge, and (F) Mn $L_{3,2}$ -edge XANES studies of the NCM83- Li_3InCl_6 interfaces. Ni $L_{3,2}$ -, Co $L_{3,2}$ -, Mn $L_{3,2}$ -, and In $L_{3,2}$ - edge XANES spectra were collected in the TEY mode.



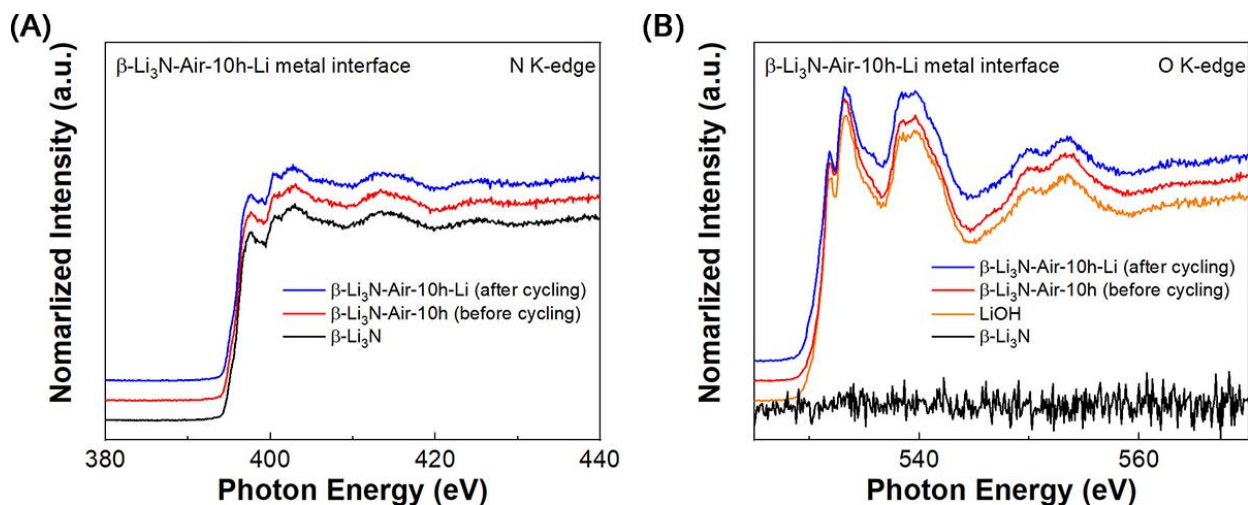
Supplementary Figure 39 (A ~ C) Electrochemical performance of the LCO/Li₆PS₅Cl/Li₃YCl₆(LYC)/vacancy-rich β -Li₃N/Li all-solid-state lithium metal batteries at 25 °C with an operating voltage window between 4.2 V and 2.7 V and the cathode loading of 8.92 mg/cm²: (A) The charge/discharge curves at 0.05, and 0.1 C. Charge-discharge capacity and the Coulombic efficiency as a function of cycle number for all-solid-state lithium metal batteries cycled at (B) 0.1 C, and (C) 1 C. (D ~ E) Electrochemical performance of the NCM83/Li₆PS₅Cl/Li₃YCl₆(LYC)/vacancy-rich β -Li₃N/Li all-solid-state lithium metal batteries at 25 °C with an operating voltage window between 4.3 V and 2.7 V and the cathode loading of 8.92 mg/cm²: (D) The charge/discharge curves at 0.1 C. Charge-discharge capacity and the Coulombic efficiency as a function of cycle number for all-solid-state lithium metal batteries cycled at (E) 0.1 C, and (F) 1 C.



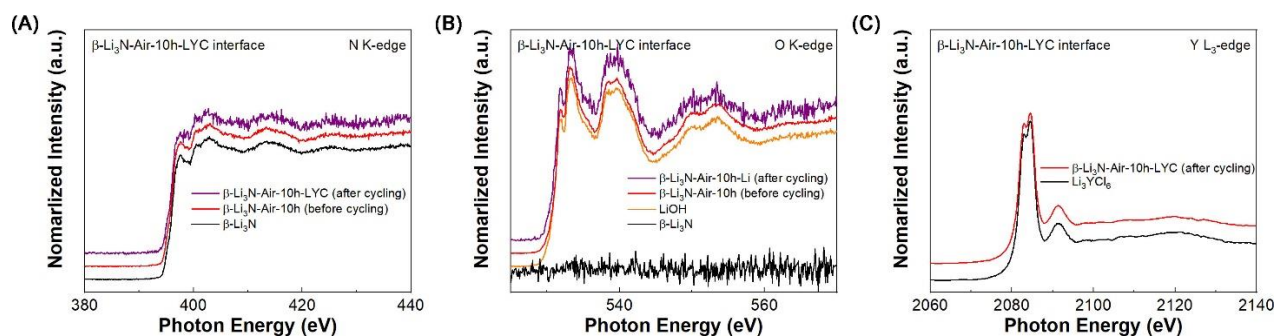
Supplementary Figure 40 (A) Arrhenius plots of β -Li₃N-400rpm-16h, and β -Li₃N-400rpm-16h-air-10h (denoted as β -Li₃N-air-10h). (B) and (C) long-term electrochemical performance of the NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/ β -Li₃N-air-10h/Li all-solid-state lithium metal batteries at 25 °C with an operating voltage window between 4.3 V and 2.7 V and the NCM83 loading of 8.92 mg/cm²: (B) the charge/discharge curves at 0.1 C, and (C) charge-discharge capacity and the Coulombic efficiency as a function of cycle number for all-solid-state lithium metal batteries cycled at 0.1 C.



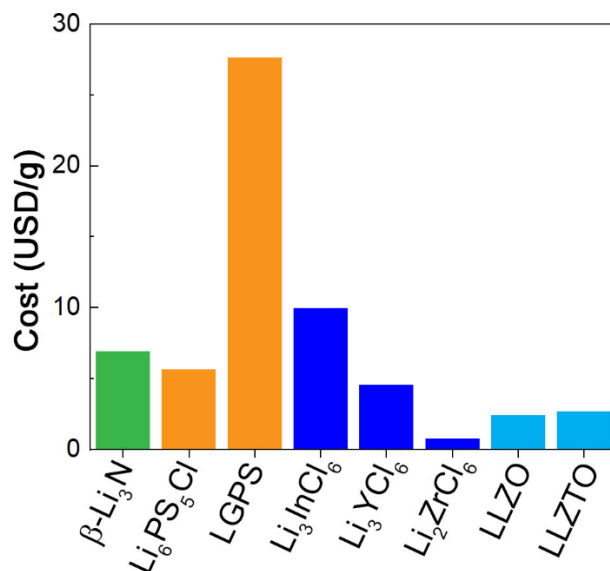
Supplementary Figure 41 Cross-sectional Scanning Electron Microscopy (SEM) images of NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/β-Li₃N-air-10h/Li cells with NCM83 loading of 8.92 mg/cm² (A, and B) before cycling and (C, and D) after cycling at 0.1 C with an operating voltage window between 4.3 V and 2.7 V for 200 cycles, showcasing the (A, and C) β-Li₃N-air-10h/Li, and (B, and D) β-Li₃N-air-10h/LYC.



Supplementary Figure 42 XANES studies of interfacial chemical stability across the β -Li₃N-air-10h-lithium metal interfaces in the NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/ β -Li₃N-air-10h/Li cells with NCM83 loading of 8.92 mg/cm² before cycling and after cycling at 0.1 C with an operating voltage window between 4.3 V and 2.7 V for 200 cycles. (A) N K-edge and (B) O K-edge XANES studies of β -Li₃N-air-10h-lithium metal interfaces. N K-, and O K- edge XANES spectra were collected in the TEY mode.



Supplementary Figure 43 XANES studies of interfacial chemical stability across the β -Li₃N-air-10h-Li₃YCl₆ interfaces in the NCM83/Li₃InCl₆(LIC)/Li₃YCl₆(LYC)/ β -Li₃N-air-10h/Li cells with NCM83 loading of 8.92 mg/cm² before cycling and after cycling at 0.1 C with an operating voltage window between 4.3 V and 2.7 V for 200 cycles. (A) N K-edge, (B) O K-edge, and (C) Y L₃-edge XANES studies of β -Li₃N-air-10h-Li₃YCl₆ interfaces. N K-, O K-, and Y L₃- edge XANES spectra were collected in the TEY mode.



Supplementary Figure 44 A cost comparison of β -Li₃N with several common types of solid-state electrolytes, including sulfides (e.g., Li₆PS₅Cl, and Li₁₀GeP₂S₁₂ (LGPS)), halides (e.g., Li₃InCl₆, Li₃YCl₆, Li₂ZrCl₆), and oxides (e.g., La₃Li₇O₁₂Zr₂ (LLZO), Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO)). The cost estimates are based on the prices of raw materials sourced from Fisher Scientific. **Supplementary Table 13** provides additional information on these chemicals, including stock numbers, quantities purchased, and purities.

Supplementary Table 13 Laboratory-scale prices utilized for cost estimation in Supplementary Figure 44

. All prices referenced are sourced from Fisher Scientific.

Chemicals	Catalog No.	Quantity / g	Price / USD
Lithium nitride, 99.4% (metals basis)	03547918	50	343.00
Lithium sulfide, 99.9% (metal basis)	01283918	50	630.00
Lithium chloride, 98+%,	A1053122	100	45.00
Phosphorus pentasulfide, 98+%	AC196725000	500	80.00
Germanium Disulfide, 99.99%	50-177-0098	5	485.98
Indium (III) chloride, 99.999%	AA1185618	50	638.00
Yttrium(III) chloride, 99.9%	AA1868209	50	315.00
Zirconium(IV) chloride, 99.5+%	AA1210422	100	82.00
Zirconium(IV) oxide, 98.5%	AC190522500	250	71.75
Lanthanum(III) oxide, 99.9+%	L0235500G	25	56.00
Lithium hydroxide, 98.0+%,	L022525G	25	45.25
Tantalum(V) oxide, 99% (metals basis)	AA1470918	50	185.00

Supplementary Note 1: The commercially available Li_3N is usually prepared through the reaction between molten lithium metal and pure nitrogen gas, resulting in a mixture of α - and β -phases. β - Li_3N is favorable because of the higher ionic conductivity with high vacancy concentrations under high-energy ball-milling process. Based on the reported structural evolution of Li_3N under pressure, α - Li_3N (space group: P6/mmm) can transform into β - Li_3N (space group: P6₃/mmc) at an increased pressure of 0.4 ~ 0.7 GPa; and the β - Li_3N phase is stable up to at least 8 GPa.^{3,4} Increasing the ball-milling speed from 200 to 400 rpm leads to a gradual transformation of the α -phase into the β -phase (**Figure 1A**). Pure β - Li_3N is obtained by ball-milling at 400 rpm for 8 h, denoted by β - Li_3N -400rpm-8h. When the ball-milling speed is further increased to 500 and 600 rpm, an additional Li_2N_2 phase occurs and a mixture of Li_2N_2 and β - Li_3N is formed, whereas the Li_2N_2 phase is a mixed electronic/ionic conductor and cannot maintain a stable interface with lithium metal.⁵

Supplementary Note 2: The presence of lithium vacancies at the 4f site rather than the 2b site can be ascribed to the comparatively weaker bonding of N^{3-} with Li^+ at the 4f site in comparison to the bonding strength at the 2b site. The interatomic distances from the N atom at the 2c site to Li(1) at the 2b site and Li(2) at the 4f site are 2.062(1) Å and 2.117(3) Å, respectively. The chemical bond between N and Li(2) is less robust than that with Li(1), making it more favorable for Li(2) to vacate, leading to a higher prevalence of lithium vacancies at the 4f site. To corroborate this theory, we calculated the formation energy for a single lithium vacancy at the 2b and 4f sites using the DFT method, as illustrated in **Figure 1E**.^{6,7} The lithium vacancy formation energy at the 4f site, 0.81 eV, is lower than the 1.43 eV at the 2b site, aligning with the observed loss of lithium atoms from 4f sites in the experimentally refined structure. The mechanism behind the formation of lithium vacancies in vacancy-rich β - Li_3N aligns with findings reported for α - Li_3N .⁸ Additionally, within vacancy-rich β - Li_3N , lithium vacancies coexist alongside a substantial concentration of nitrogen vacancies, which have a vacancy formation energy of 3.28 eV.

Supplementary Note 3: By comparing the trends of lithium and nitrogen vacancy concentrations, ionic conductivity, and activation energy for the vacancy-rich β - Li_3N SSEs. Lithium-ion diffusion can be described by Arrhenius relationship (equations (1) and (2)):

$$\sigma = \frac{\sigma_0}{T} e^{-E_a/k_B T} \quad (1)$$

$$\sigma_0 = z \frac{ne^2}{k_B} e^{\Delta S_m/k_B} \alpha_0^2 v_0 \quad (2)$$

with σ_0 the pre-factor, T the temperature, E_a the activation energy for lithium-ion conduction, k_B the Boltzmann constant, z the geometric factor, n the concentration of mobile lithium ions, ΔS_m the entropy of lithium-ion hopping, α_0 the lithium-ion hopping distance, and v_0 the attempt frequency.⁹ As shown in **Figure 1F**, vacancy-rich β -Li₃N owns higher n values due to higher lithium vacancy population. Moreover, nitrogen vacancies in the crystal structure may give more space for lithium-ion diffusion and reduce lithium ion hopping energy (E_{HOP}) between sites. As E_a corresponds to mobile defect formation energy (E_f) and E_{HOP} , vacancy-rich β -Li₃N presents lower E_a values. Higher n values and lower E_a values result in much higher ionic conductivity in vacancy-rich β -Li₃N.

Supplementary Note 4: In β -Li₃N crystals, lithium-ion diffusion is mediated by the lithium-ion hopping across the vacancy sites. Typically, reduced lattice parameters correspond to an elevated barrier for lithium transport across grains, manifesting impediments such as grain boundaries and voids. This subsequently amplifies the diffusion gap energy and diminishes the ionic conductivity.¹⁰ The morphologies of both raw commercial Li₃N and β -Li₃N synthesized via ball milling were analyzed using Scanning Electron Microscopy (SEM). The images, as depicted in **Supplementary Figure 7**, exhibit characteristic polyhedral particles. For the raw commercial Li₃N, the dominant particle size predominantly falls within the range of 0.5-1.0 μm . Following the ball-milling procedure, which prompts a phase transition from α -Li₃N to β -Li₃N (specifically in the β -Li₃N-400rpm-8h sample), the dominant particle size expands, predominantly spanning the range of 0.5-1.5 μm . As ball-milling duration increases, this size range persists, but the distribution skews towards the smaller end. A deeper analysis, probing the interrelationship between lithium-ion diffusion, particle size, and vacancy concentration, pinpoints an elevated vacancy concentration as a crucial determinant of enhanced lithium-ion diffusion within the β -Li₃N SSEs.

Supplementary Note 5: As discussed above, vacancy-rich β -Li₃N SSEs with fine-tuned lithium and nitrogen vacancies showed high ionic conductivity, good lithium metal compatibility, and good air stability. In addition to those favorable features, low electronic conductivity of SSE is also a critical factor for realizing stable lithium stripping and plating at high current densities and capacities. As high electronic conductivity can lead to growth of lithium dendrites inside the SSE

layer, the requirement of electronic conductivity should be below $10^{-10} - 10^{-12}$ S/cm for dendrite-free lithium plating performance at high current densities.¹¹

Supplementary Note 6: The EIS spectra exhibit consistent impedance values up to the critical current and capacity thresholds of 7.5 mA/cm² and 7.5 mAh/cm², respectively. Beyond these thresholds, up to 15 mA/cm² and 15 mAh/cm², a discernible reduction in impedance is observed, suggesting the formation of lithium dendrites. Importantly, this reduction does not lead to hard short circuiting, a conclusion supported by the impedance data (**Supplementary Figure 9**). Additionally, XANES evaluations confirmed the interface stability between the vacancy-rich β -Li₃N SSE and lithium metal across cycling, even subsequent to dendrite formation.

Supplementary Note 7: For application in all-solid-state lithium metal batteries, it is imperative to integrate the lithium-metal-compatible, vacancy-rich β -Li₃N SSE with an SSE that is compatible with the cathode, to span the full electrochemical window requisite for functional batteries.¹²⁻¹⁴ The incorporation of dual halide SSEs is justified by the necessity for high-voltage-stable Li₃InCl₆ to match the electrochemical cycling windows of the selected cathodes (LCO: 2.7–4.2 V vs. Li⁺/Li; NCM83: 2.7–4.3 V vs. Li⁺/Li). This strategy mitigates the electrochemical window mismatch between β -Li₃N and Li₃InCl₆, with Li₃YCl₆ serving as an intermediary buffer layer, as illustrated in **Supplementary Figure 21**.

Supplementary Note 8: The diminished ICE of 87.6% can be attributed to the loss of contact between certain NCM83 particles and the Li₃InCl₆ SSE particles. This contact disruption is a consequence of the anisotropic volume changes induced by the unstable Ni⁴⁺ species in Ni-rich NMC during the charge-discharge process, a phenomenon further supported by the marginal rise in impedance of the all-solid-state cell post initial cycles, as illustrated in **Supplementary Figure 23**.^{16,17} Following these initial cycles, the composite cathode structure, comprising both NCM83 and Li₃InCl₆ SSE particles, achieves stability. As a result, the irreversible capacity attributable to the contact loss diminishes, leading the Coulombic efficiency of the early cycles to stabilize around 100%. This enhancement in Coulombic efficiency during the initial cycles is also observable with increased cathode loading, as demonstrated in **Figures 6E and 6G**.

Supplementary Note 9: The structural stability of this vacancy-rich β -Li₃N SSE during electrochemical cycling is systematically examined using SXRD, as depicted in **Supplementary Figure 27, Supplementary Tables 9 ~ 12**. Results from the corresponding Rietveld refinement, along with intricate crystallographic structures presented in **Supplementary Tables S9 ~ S12**, corroborate that the nitrogen and lithium vacancy concentrations remain largely invariant over extended cycling periods. This consistency suggests the enduring stability of high ionic conductivity in the vacancy-rich β -Li₃N SSE throughout the cycling process. The lithium metal compatibility of the β -Li₃N SSE, which can be delineated into two essential attributes: chemical stability toward lithium metal and enhanced dendrite suppression capability. This compatibility of the vacancy-rich β -Li₃N SSE with lithium metal has been corroborated by the DFT calculations and STXM results and been further studied by electrochemical performing and XANES as shown in **Supplementary Figure 28**. Electrochemical window calculations for Li₃N and Li₃YCl₆ SSEs (**Supplementary Figure 28A**) confirm the chemical stability of Li₃N SSEs towards lithium metal. In contrast, Li₃YCl₆ is susceptible to significant interfacial reactions with lithium metal, leading to a gradual increase in impedance, as evidenced in (**Supplementary Figure 28B**). Although chemically stable towards lithium metal, commercial-Li₃N exhibits a decline in overpotential during cycling in lithium-symmetric cells, indicating problematic lithium dendrite growth (**Supplementary Figure 28C**). When commercial-Li₃N SSEs are utilized in all-solid-state lithium metal batteries, lithium dendrites penetrate the commercial-Li₃N layer and react with Li₃YCl₆ during cycling, causing adverse interfacial reactions (**Supplementary Figure 28D**). A shoulder peak in the Y L₃-edge XANES confirms the formation of Y-Li alloys post-cycling. This dendritic growth in the commercial-Li₃N SSE layer consequently leads to rapid performance degradation in LCO and NCM83/LIC/LYC/commercial-Li₃N/Li all-solid-state cells. This degradation is shown in **Supplementary Figure 28E to 28H**, with the average electrochemical performance detailed in **Supplementary Figure 29**. Additionally, our analysis highlights that the low electronic conductivity of the vacancy-rich β -Li₃N SSE plays a pivotal role in its compatibility with lithium metal anodes. In comparison, another extensively studied phase of Li₃N SSEs, α -Li₃N, also demonstrates a high room-temperature ionic conductivity of approximately 10⁻⁴ S/cm and noteworthy chemical stability against lithium metal.^{10,18} As illustrated in **Supplementary Figure 30**, the synthesized α -Li₃N showcases a room-temperature ionic conductivity of 3.0×10⁻⁴ S/cm and an activation energy of 0.38 eV. However, its electronic conductivity, measured at 2.6×10⁻⁷ S/cm,

significantly exceeds the desired threshold (ideally below $10^{-10} \sim 10^{-12}$ S/cm) for dendrite-free lithium plating at elevated current densities.¹¹ Due to this elevated electronic conductivity, the critical current density and critical lithium stripping/plating capacity of the Li/ α -Li₃N/Li all-solid-state symmetric cells are restricted to just 0.6 mA/cm² and 0.6 mAh/cm², respectively, as detailed in **Supplementary Figure 31**. This is considerably lower than that of the vacancy-rich β -Li₃N SSE, which registers values of 7.5 mA/cm² and 7.5 mAh/cm². Owing to the compromised compatibility with lithium-anodes, all-solid-state full cells featuring the NCM83/halides/ α -Li₃N/Li configuration exhibited rapid degradation as shown in **Supplementary Figure 31**. Additional validation for the remaining factors is provided through impedance studies, SEM and EDX and XANES analyses. **Supplementary Figure 23** delineates the impedance evolution for the two fabricated all-solid-state lithium metal cells—LCO/halides/vacancy-rich β -Li₃N/Li and NCM83/halides/vacancy-rich β -Li₃N/Li—during cycling at a 0.1 C rate for 250 and 200 cycles, respectively. The impedance remains stable throughout extended cycling after initial cycles, underscoring stable interfacial interactions within the Li₃InCl₆/Li₃YCl₆/vacancy-rich β -Li₃N layers and between Li₃InCl₆ and the cathode materials (LCO and NCM83). SEM and EDX mapping, specifically targeting the interfaces as illustrated in **Supplementary Figures S32–S36**, indicate no notable structural degradation or elemental interdiffusion, thereby verifying sustained structural stability over time. Nonetheless, the diminished contact between certain cathode particles and the SSEs leads to a gradual decline in capacity at a rate of 0.1C. This sustained structural stability is also evident in the pouch cells, as delineated in **Supplementary Figures 26 and 36**. After cycling at 0.1 C for 100 cycles, the assembled all-solid-state full cell remains stable. The morphologies of the NCM83/Li₃InCl₆, Li₃InCl₆/Li₃YCl₆, Li₃YCl₆/vacancy-rich β -Li₃N, and β -Li₃N/Li interfaces maintain close contact, further attesting to the prolonged structural robustness. The chemical stability at the interfaces was rigorously assessed using XANES analyses, as detailed in **Supplementary Figures 37 and 38**. Initially, the focus was on the interfacial stability within the layered Li₃InCl₆/Li₃YCl₆/vacancy-rich β -Li₃N SSEs. This was achieved by acquiring XANES spectra at the N K-edge for the vacancy-rich β -Li₃N-Li₃YCl₆ interfaces, and at the Y L₃-edge and In L₃-edge for the Li₃InCl₆-Li₃YCl₆ interfaces. Subsequently, the XANES spectra, captured at the In L₃-edge and Co L_{3,2}-edge, were analyzed to evaluate the interfacial stability between Li₃InCl₆ and the LCO cathode. For the NCM83-Li₃InCl₆ interfaces, XANES spectra were acquired at the In L₃-edge, Ni L_{3,2}-edge, Co L_{3,2}-edge, and Mn L_{3,2}-edge. Remarkably, these XANES spectra

exhibited negligible variations when compared before and after extended cycling—250 cycles for the LCO cell and 200 cycles for the NCM83 cell—thereby corroborating the interfacial chemical stability within the layered SSEs as well as the effective compatibility between Li_3InCl_6 and the respective cathode materials.

Supplementary Note 10: Specifically, the LCO/ $\text{Li}_6\text{PS}_5\text{Cl}$ /LYC/vacancy-rich $\beta\text{-Li}_3\text{N}$ /Li configurations demonstrated a high capacity retention of 89.71% over 200 cycles at 0.1 C, and an 85.62% retention over an extended 500 cycles at a 1 C rate, as evidenced in **Supplementary Figures 39A ~ 39C**. Similarly, the NCM83/ $\text{Li}_6\text{PS}_5\text{Cl}$ /LYC/ $\beta\text{-Li}_3\text{N}$ /Li configurations exhibited an impressive capacity retention of 89.6% over 200 cycles at 0.1 C and 95.0% retention over 500 cycles at 1 C, as detailed in **Supplementary Figures 39D ~ 39F**. To mitigate potential interfacial reactivity between the cathode materials and $\text{Li}_6\text{PS}_5\text{Cl}$, cathode particles were strategically coated with a protective LiNbOx layer of approximately 5 nm thickness using atomic layer deposition (ALD) methods.¹⁹ The exceptional electrochemical performance observed in batteries utilizing Li_3InCl_6 or $\text{Li}_6\text{PS}_5\text{Cl}$ SSEs, alongside vacancy-rich $\beta\text{-Li}_3\text{N}$ SSEs compatible with lithium metal anodes, underscores the potential of vacancy-rich $\beta\text{-Li}_3\text{N}$ as a stable SSE layer within all-solid-state lithium metal batteries. However, the electrochemical stability window of vacancy-rich $\beta\text{-Li}_3\text{N}$ SSEs, limited to 0-0.48 V versus Li^+/Li , necessitates careful selection of an additional SSE that is compatible with both the cathode materials and the vacancy-rich $\beta\text{-Li}_3\text{N}$ SSEs, meeting specific criteria for successful integration. Enhancing the applicability of vacancy-rich $\beta\text{-Li}_3\text{N}$ SSEs further requires expanding their electrochemical window, potentially through doping or the addition of a passivating layer.²⁰

Supplementary Note 11: To address the critical requirement for air stability in SSEs for practical applications, a comprehensive evaluation was conducted on the lithium-ion diffusion characteristics, electrochemical performance, and interfacial stability of vacancy-rich $\beta\text{-Li}_3\text{N}$ SSEs post-exposure to ambient air for a duration of 10 hours, hereafter referred to as $\beta\text{-Li}_3\text{N}$ -air-10h. **Supplementary Figure 40A** depicts the Arrhenius plot for $\beta\text{-Li}_3\text{N}$ -air-10h, which retains a high ionic conductivity of 7.21×10^{-4} S/cm at room temperature (25°C) with an activation energy of 0.381 eV, in comparison to its commercial counterpart ($\beta\text{-Li}_3\text{N}$ -air-400rpm-16h). Subsequently, $\beta\text{-Li}_3\text{N}$ -air-10h was employed as the SSE for lithium metal anodes in all-solid-state lithium metal

batteries, configured as NCM83/Li₃InCl₆/Li₃YCl₆/β-Li₃N-air-10h/Li, as illustrated in **Supplementary Figures 40B and 40C**. These full cells were cycled at 0.1 C (1 C = 200 mA/g) between 2.7 and 4.3 V vs. Li⁺/Li at room temperature with a NCM83 loading of 8.92 mg/cm². The reversible capacity was observed to be approximately 206 mAh/g with an initial Coulombic efficiency (ICE) of 87.0% and was maintained at about 195 mAh/g over 200 cycles. A subsequent focus was placed on examining the interfacial stability of the full cells, encompassing both interfacial morphology and chemical reactions. **Supplementary Figure 41** delineates the interfacial morphology at the β-Li₃N-air-10h-lithium metal and β-Li₃N-air-10h-LYC interfaces pre- and post-cycling. No discernible lithium dendrite growth or cracking was observed, thus indicating favorable interfacial morphological stability. Additional scrutiny was afforded through XANES. **Supplementary Figure 42** presents the N K-edge and O K-edge XANES across the β-Li₃N-air-10h-lithium metal interfaces before and after cycling, while **Supplementary Figure 43** displays the N K-edge, O K-edge, and Y L₃-edge XANES across the β-Li₃N-air-10h-LYC interfaces. No significant alterations in the XANES spectra were evident, suggesting robust chemical stability this β-Li₃N-air-10h SSE against lithium metal and Li₃YCl₆ through the cycling processes.

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