Supporting Information

Molten salt synthesis of a single-crystal $LiNi_{0.5}Mn_{1.5}O_4$ cathode with an in-situ construction stable interface for 4.8 V-class all-solid-state batteries

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Experimental Section

Materials Synthesis

The scLNMO@Li_2MoO_4 cathode was synthesized in three steps. First, a stoichiometric amount of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}$] $\cdot 4H_2O$ (Beijing Innochem Technology Co., Ltd) was dissolved in 20 ml of deionized water, into which 0.5 g of LNMO (Canrd New Energy Technology Corporation) was added and stirred for half an hour. The mixture was then vigorously stirred at 80 ℃ for 5 h until the deionized water was completely evaporated. The resulting powder was subsequently mixed with LiOH (Beijing Innochem Technology Co., Ltd) and processed through ball-milling (200 rpm) for 5 h. Then, the as-recived powder was further heated to 500 ℃ for 6 h and 830 ℃ for 12 h with a ramp rate of 3 ℃·min^{-1} in an air atmosphere.

Materials Characterization

X-ray diffraction (XRD) measurements for all materials were carried out by using an X-ray diffractometer (Bruker D8 Advance) with Cu Kα radiation (λ = 1.5405 Å). The corresponding rietveld refinement was conducted using General Structure Analysis System (GSAS) II. The electron micrographs of powder samples were acquired by scanning electron microscopy (SEM, Zeiss G300) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 TWIN). X-ray photoelectron spectroscopy (XPS, American Thermo Fisher Scientific ESCALAB 250Xi) was applied to identify the surface and depth profiling of the elemental composition (Ni 2p, Mn 2p, and Mo 3d). The etching speed utilized for scLNMO@Li_2MoO_4 powder samples were 0.5 nm s^{-1} for the referenced Ta_2O_5. The chamber pressure was < 5×10^{-8} torr. The binding energy was calibrated with the C 1s peak at 284.8 eV. Sample transfer from an Ar-filled glovebox to the instrument was conducted within an air-tight box.

Assembly of ASSLBs and Electrochemical Measurements

All the solid-state cells were assembled in an argon-filled glovebox. The composite cathode mixture, consisting of LNMO, LIC, and VGCF in a 50:45:5 weight ratio, was obtained by hand-mixing for 30 min. Following that, LIC (40 mg) and LPSCl (40 mg) were sequentially added to a PEEK cylinder with diameter of 10 mm and pressed at 2 tons. Then, the as-prepared composite cathode (about 5 mg) was uniformly spread on one side of the LIC pellet and compacted at 2 tons. Finally, a bilayer of In foil (with a diameter of 10 mm and a thickness of 100 μm) and Li foil (with a diameter of 10 mm and a thickness of 50 μm) was placed on the side of the LPSCl pellet and pressed at 0.35 tons as an Li-In alloy anode to form the cells. The cells were assembled and left for 24 hours in order to ensure a homogeneous Li-In alloy anode before electrochemical testing. The applied pressure for the ASSLBs and testing temperature were fixed at 0.35 tons and 30 ℃, respectively. The cell was cycled between 3-4.8 V (vs. Li/Li^+) at a rate of 0.1 C (1 C = 145 mA g^{-1}) with a constant voltage cut-off of 3.5 mA g^{-1} at the end of charging. The galvanostatic intermittent titration technique (GITT) was performed with a 300 s charge/discharge at 0.1 C followed by 7200 s of relaxation. Both galvanostatic charge/discharge and GITT were carried out on a NEWARE (C-4008) battery tester within a voltage range of 3-4.8 V (vs. Li/Li^+). Cyclic voltammetry (CV) measurements were conducted on a potentiostat (Biologic VMP-3) at a scan rate of 1 mV s−1 over the voltage range of 3-4.8 V (vs. Li/Li^+). For in situ galvanostatic electrochemical impedance spectra (GEIS), a frequency range of 1 MHz to 1 Hz and an perturbation of 20 mA were chosen, and the measurements are conducted during the charging and discharging process with an equal interval time of 10 minutes.

Supplementary Figures

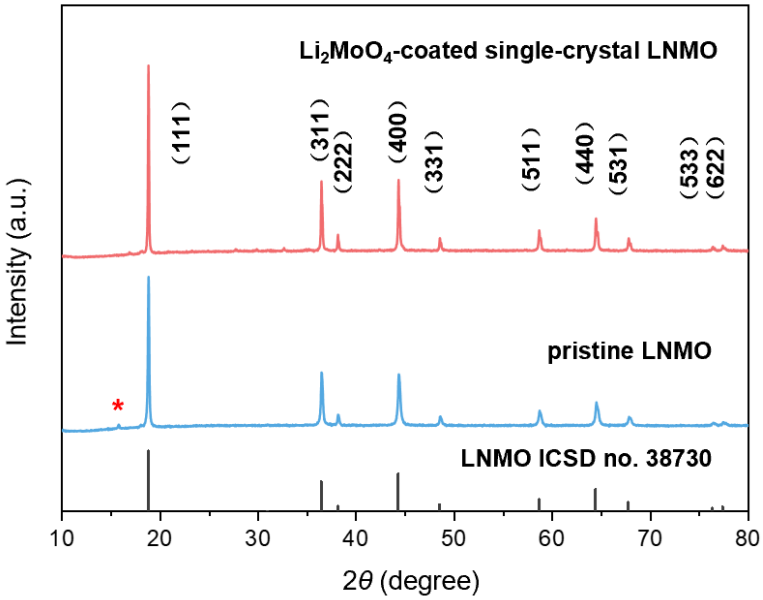

Figure S1. XRD patterns of pristine LNMO and Li_2MoO_4-coated single-crystal LNMO.

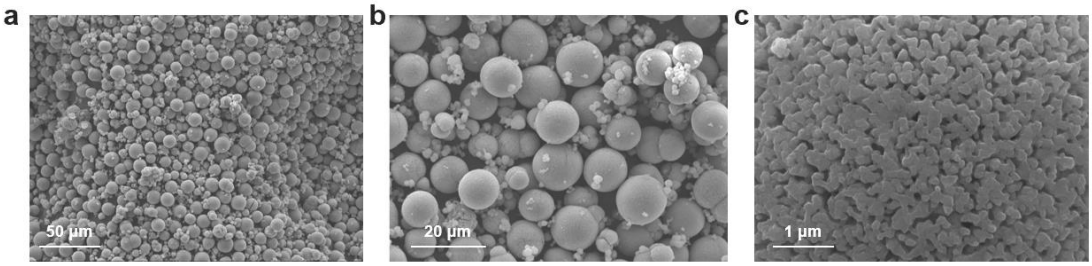

Figure S2. a-c) SEM images with different magnifications of pristine polycrystalline LNMO particles.

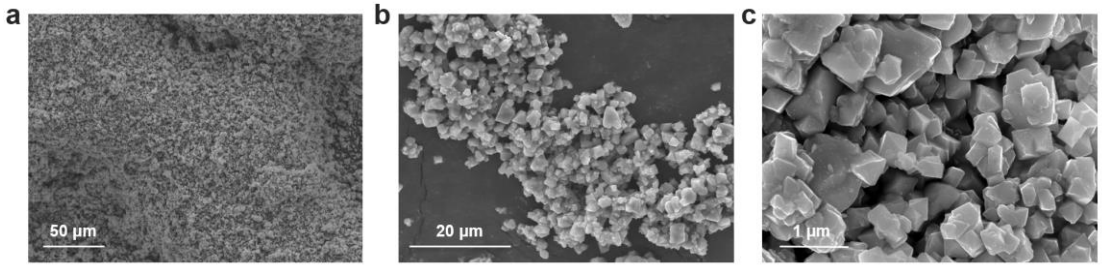

Figure S3. a-c) SEM images with different magnification of the Li_2MoO_4-coated single-crystal LNMO particles synthesized through molten salt annealing approach using the polycrystalline LNMO particles as precursors.

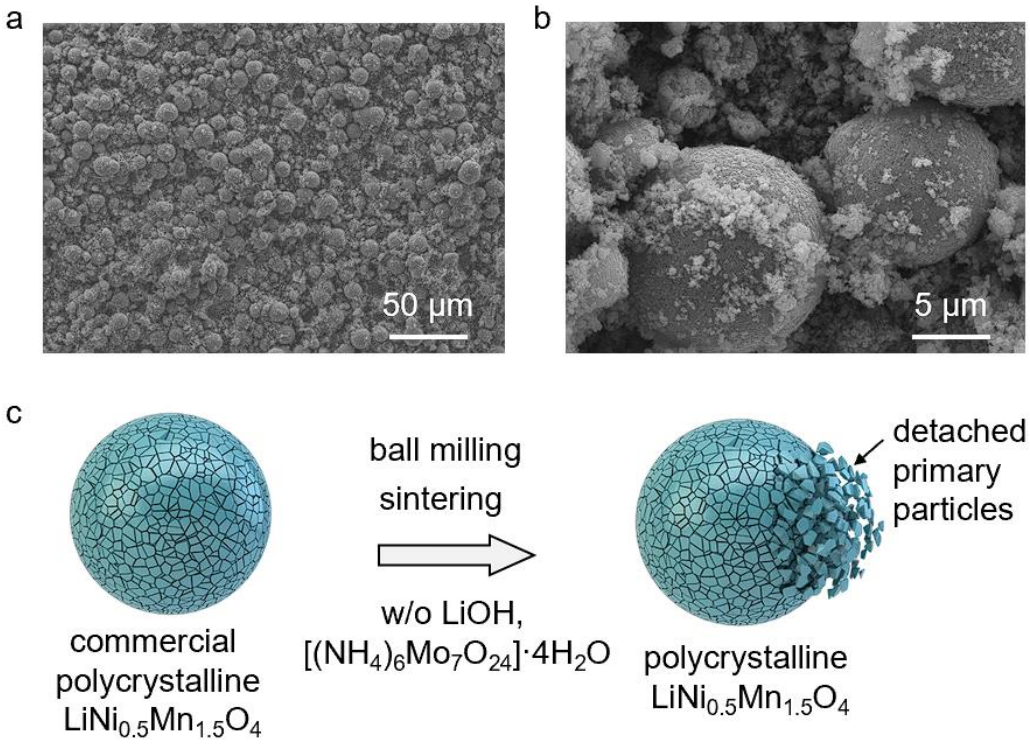

Figure S4. a, b) SEM images of the LNMO particels synthesized without LiOH and $[(NH_4)_6Mo_7O_{24}]\cdot 4H_2O$. c) Schematic illustration of the synthesized LNMO particels without LiOH and $[(NH_4)_6Mo_7O_{24}]\cdot 4H_2O$.

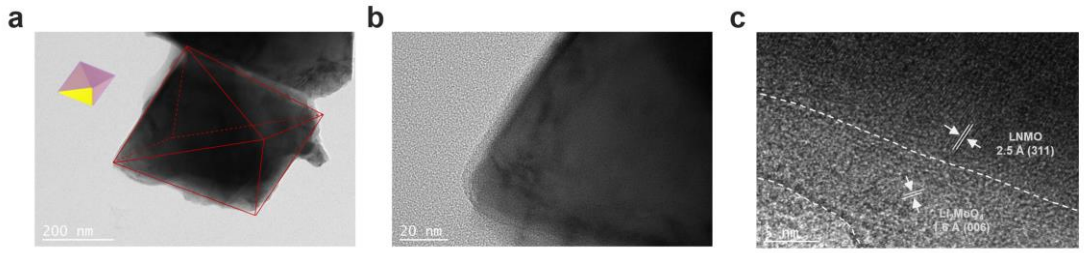

Figure S5. a, b) TEM and c) High-resolution TEM images of scLNMO@Li_2MoO_4.

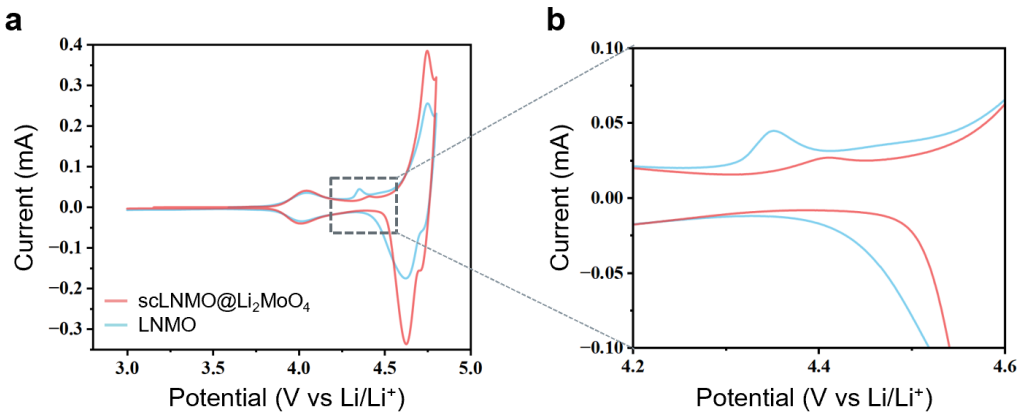

Figure S6. a) The first-cycle CV curves of the pristine LNMO and scLNMO@Li_2MoO_4 with a scan rate of 0.1 mV s^{-1}. b) Localized enlargement of the boxed portion of a).

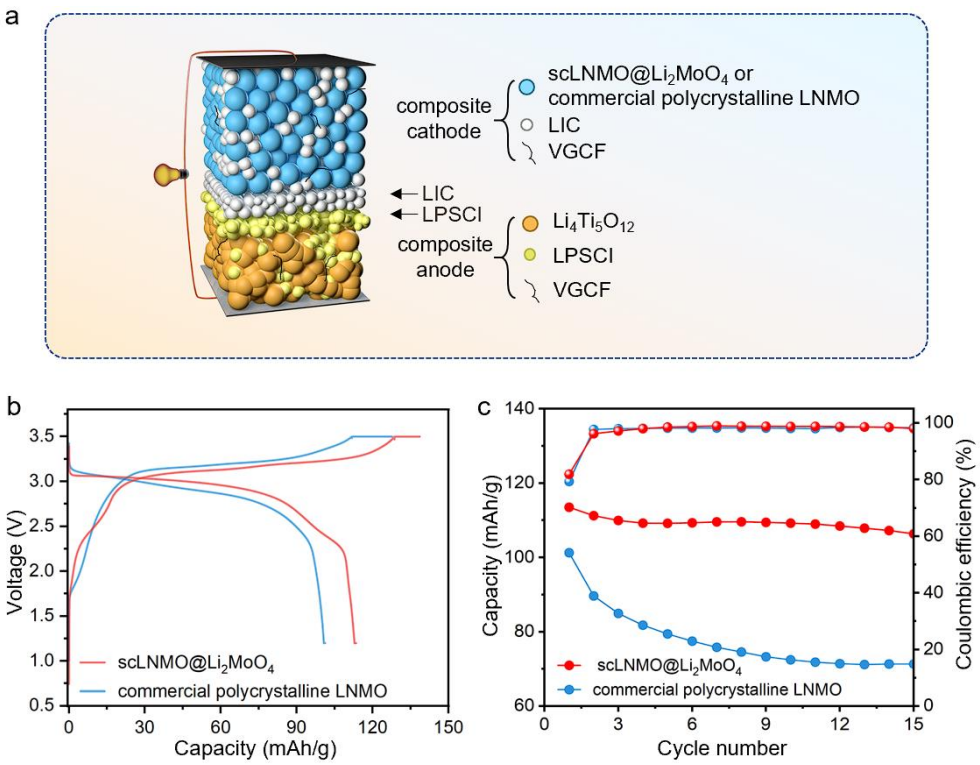

Figure S7. a) Schematic diagram of the all-solid-state full-cell configuration. b) The first charge-discharge voltage profiles and c) cycling stability of the commercial polycrystalline LNMO||LTO and scLNMO@Li_2MoO_4||LTO cells at 0.1 C.

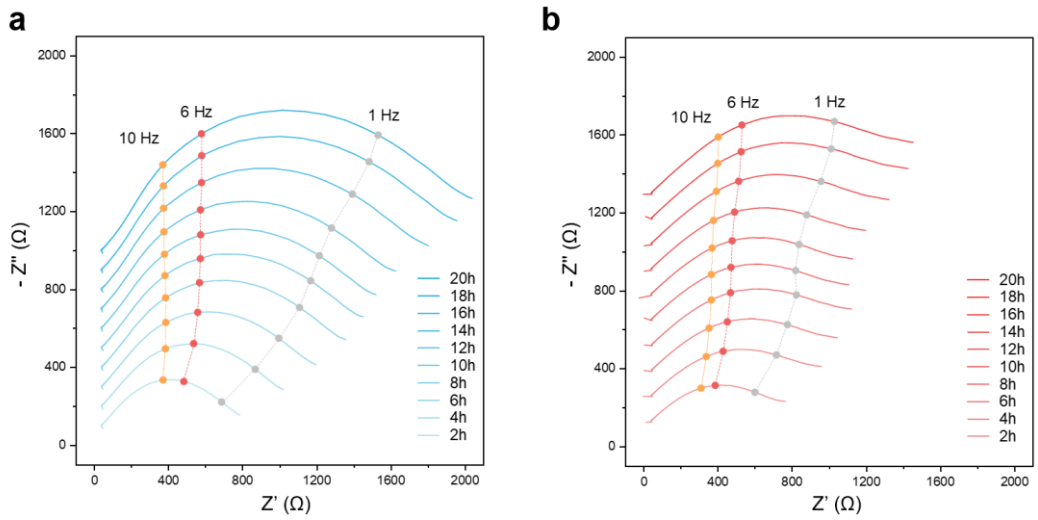

Figure S8. Nyquist plots of the a) LNMO and b) scLNMO@Li_2MoO_4 cells charged to 4.8 V in the first cycle and held for several hours.

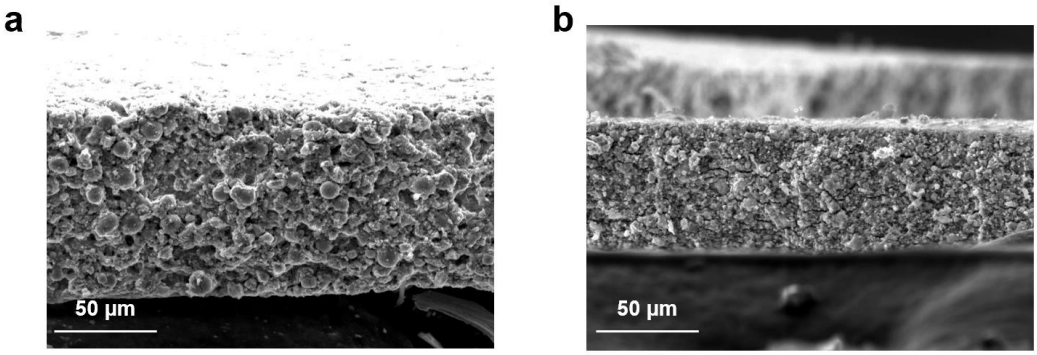

Figure S9. Cross-sectional SEM images of h) LNMO and i) scLNMO@Li_2MoO_4 composite cathodes before cycling.

Table S1. The lattice parameters of the pristine LNMO and Li_2MoO_4-coated single-crystal LNMO through Rietveld refinement analysis on XRD patterns.

Sample	**Space group**	**a [Å]**	**V [Å^3]**	**R_{wp} [%]**
LNMO	$Fd\bar{3}m$	8.16465	544.267	3.07
scLNMO@Li_2MoO_4	$Fd\bar{3}m$	8.16860	545.058	3.29

Table S2. Summary of electrochemical test condition and performance of inorganic SEs-based ASSLBs with LNMO cathode

Cathode	SE	Specific capacity [mAh g^{-1}]/Current density	Anode	Ref.
$LiNbO_3$-coated LNMO	$Li_{10}GeP_2S_{12}$	80/0.05C	Li-In	[1]
$LiNbO_3$-coated LNMO	LPSCl	115/0.1C	Li	[2]
Li_3PO_4-coated LNMO	LPSCl	49.9/0.1C	Li	[2]
$Li_4Ti_5O_{12}$-coated LNMO	LPSCl	7/0.1C	Li	[2]
Sulfurized LNMO	LPSCl	77.9 /0.1C	$Li_4Ti_5O_{12}$	[3]
$LiNbO_3$-coated LNMO	Li_3YCl_6	91.0/20 mA g^{-1}	Li-In	[4]
Al_2O_3-H-LNMO (pellet type)	LPSCl	105.5/0.1C 92.4/0.2C	Li-In	[5]
Al_2O_3-H-LNMO (film type)	LPSCl	89.8/0.1C 82.1/0.2C	Li-In	[5]
Li_3PO_4- coated LNMO (Fe doped)	Li_3InCl_6	94/0.05C	Li-In	[6]
scLNMO@Li_2MoO_4	Li_3InCl_6	128.8/0.1C	Li-In	This work

References

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