

Electronic Supplementary Information

Facile Solid-State Synthesis of a Layered Co-Free, Ni-Rich Cathode Material for All-Solid-State Batteries

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Experimental

LiNi_{0.95}Mn_{0.05}O₂ (NMX9505) Synthesis

Stoichiometric amounts of Ni(OH)₂ (4 μm; BASF SE) and Mn₂O₃ (30 nm; US Research Nanomaterials, Inc.) were mixed in a mortar, and then the required amount of LiOH·H₂O (BASF SE) was added. The powder mixture was thoroughly blended for 5 min using a laboratory blender (KINEMATICA AG), followed by transfer to an alumina crucible. The crucible was heated first at 500 °C for 5 h and then at 780 °C for 15 h under O₂ flow (3 °C min⁻¹ heating rate).

LiNbO₃ Coating

Lithium ethoxide and niobium ethoxide (Sigma-Aldrich) mixtures were added dropwise to the NMX9505 powder in an Ar glovebox (aiming for a 1 wt. % LiNbO₃ coating), and ethanol was added for proper wetting. The powder was then subjected to ultrasonication for 30 min, and the solvent was removed under vacuum overnight. Subsequently, the coated material was ground in a mortar and pestle and heated at 350 °C for 2 h under O₂ flow (5 °C min⁻¹ heating rate).

Electrode Preparation, Cell Assembly and Testing

Liquid electrolyte cell:

NMX9505 was mixed with carbon black (Super C65, Imerys Graphite & Carbon) and PVDF binder (Solef 5130, Solvay GmbH) in a weight ratio of 94:3:3 with the help of a centrifugal planetary mixer (THINKY). The slurry was then cast onto Al foil using a box-type coater (100 μm wet-film thickness; Erichsen Coatmaster 510 film applicator). The electrode tape was dried at 120 °C overnight, followed by calendaring at 30 N mm⁻¹. The NMX9505 loading was 7.5 (± 0.5) mg cm⁻². CR2032 coin cells were assembled using a glass fiber separator (Whatman), a

Li-foil anode and 1 M LiPF₆ in fluoroethylene carbonate (20 wt. %)/diethyl carbonate (80 wt. %) as electrolyte. The cells were cycled at 25 °C between 2.7 and 4.3 V vs. Li⁺/Li.

Solid electrolyte cell:

NMX9505, solid electrolyte (Li₆PS₅Cl, NEI Corp.) and Super C65 were mixed in the ratio 69.3:29.7:1.0 by weight in a planetary ball mill at 140 rpm for 30 min. The same procedure was applied for preparing the anode composition with Li₄Ti₅O₁₂ (NEI Corp.), Li₆PS₅Cl and Super C65 in a weight ratio of 30:65:5. Customized cells with polyether ether ketone sleeve and two stainless steel dies were used for electrochemical testing. At first, the separator layer was cold pressed at a uniaxial pressure of 62 MPa. Then, one side of the separator was filled with 12 mg of cathode composite [10.5 (± 0.5) mg cm⁻² NMX9505 loading] and the other side with 65 mg of anode composite and pressed at 437 MPa. The cells were cycled at 45 °C in the voltage window of 1.15-2.75 V vs. Li₄Ti₅O₁₂/Li₇Ti₅O₁₂ (corresponding to about 2.7-4.3 V vs. Li⁺/Li) under a static pressure of 81 MPa. Impedance tests were carried out using a VMP3 multichannel potentiostat (BioLogic) at an applied AC voltage of 10 mV, with the frequency ranging from 7 MHz to 100 mHz.

Methods

A STOE STADI P diffractometer with a Mo anode ($\lambda = 0.70926 \text{ \AA}$) and a MYTHEN 1 K strip detector (DECTRIS AG) was used for X-ray diffraction (XRD) measurements. Rietveld refinement was performed using GSAS-II.

Particle size distribution measurements were carried out via laser diffraction using a Mastersizer 3000 (Malvern Panalytical), assuming a refractive index of 2.19 and a density of 4.5 g cm⁻³.

Scanning electron microscopy (SEM) imaging was done on a LEO-1530 electron microscope (Carl Zeiss AG) with a field emission source. For cross-sectional SEM, the cathode pellets were polished by ion-milling using an IB-19510CP cross section polisher (JEOL). During transfer, the cathodes were exposed to ambient atmosphere for < 1 min.

The Mn, Ni and Li contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Thermo Fisher Scientific iCAP 7600 DUO.

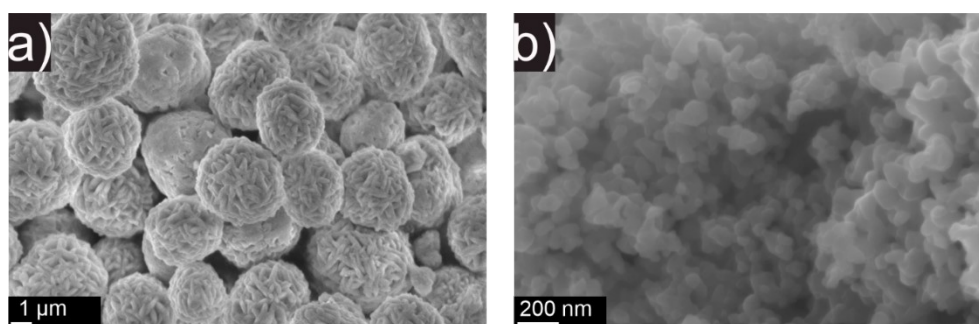


Fig. S1 SEM images of the a) Ni(OH)₂ precursor and b) Mn₂O₃ nanoparticles used in the synthesis of NMX9505.

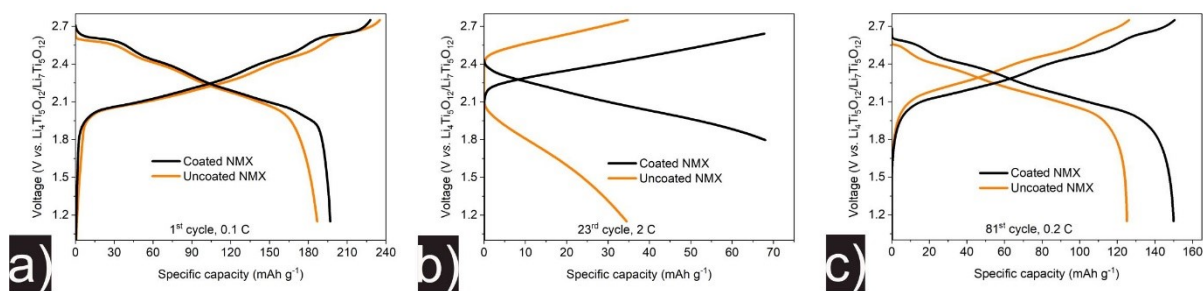


Fig. S2 Voltage profiles of the coated and uncoated NMX9505 cathodes: 1st cycle (0.1C), b) 23rd cycle (2C) and 81st cycle (0.2C).

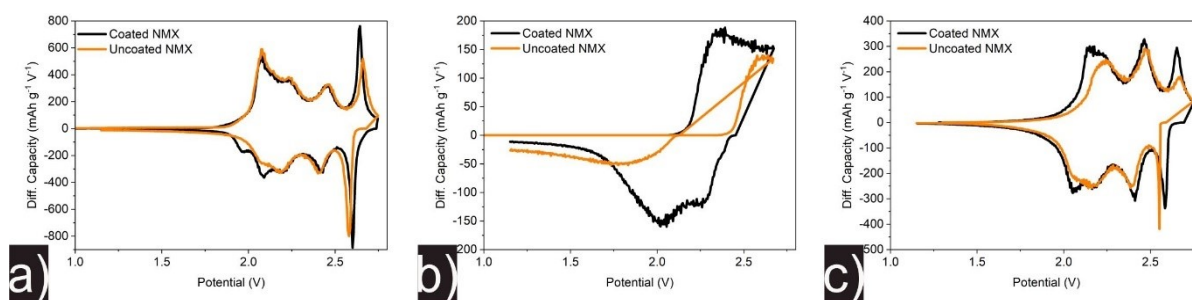


Fig. S3 Differential capacity curves of the coated and uncoated NMX9505 cathodes: a) 1st cycle (0.1C), b) 23rd cycle (2C) and 81st cycle (0.2C).

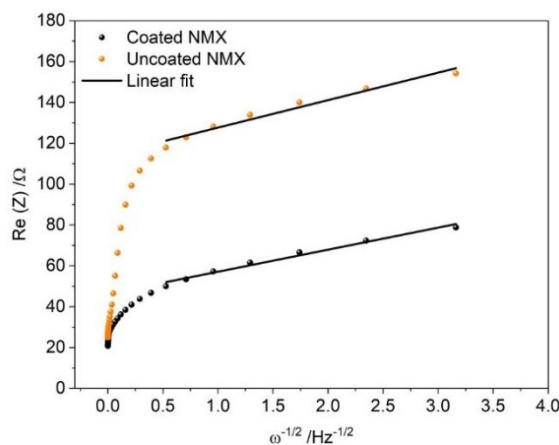


Fig. S4 Real part of the impedance versus reciprocal root square of the frequency and corresponding linear fits to the data at low frequencies.

$$Z_{RE}(\omega) = R_{SE} + R_{CT} + \sigma \cdot \frac{1}{\sqrt{\omega}} \quad \text{Eqn. S1}$$

$$\sigma = \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_i \sqrt{D_i}} \right) \quad \text{Eqn. S2}$$

Z_{RE} – real part of the impedance, R_{SE} – bulk resistance, R_{CT} – charge-transfer resistance, σ – Warburg coefficient, ω – frequency, R – gas constant, T – absolute temperature, n – number of electrons, A – contact area, F – Faraday constant, D_i – Li-ion diffusion coefficient and C_i – concentration of Li-ions.

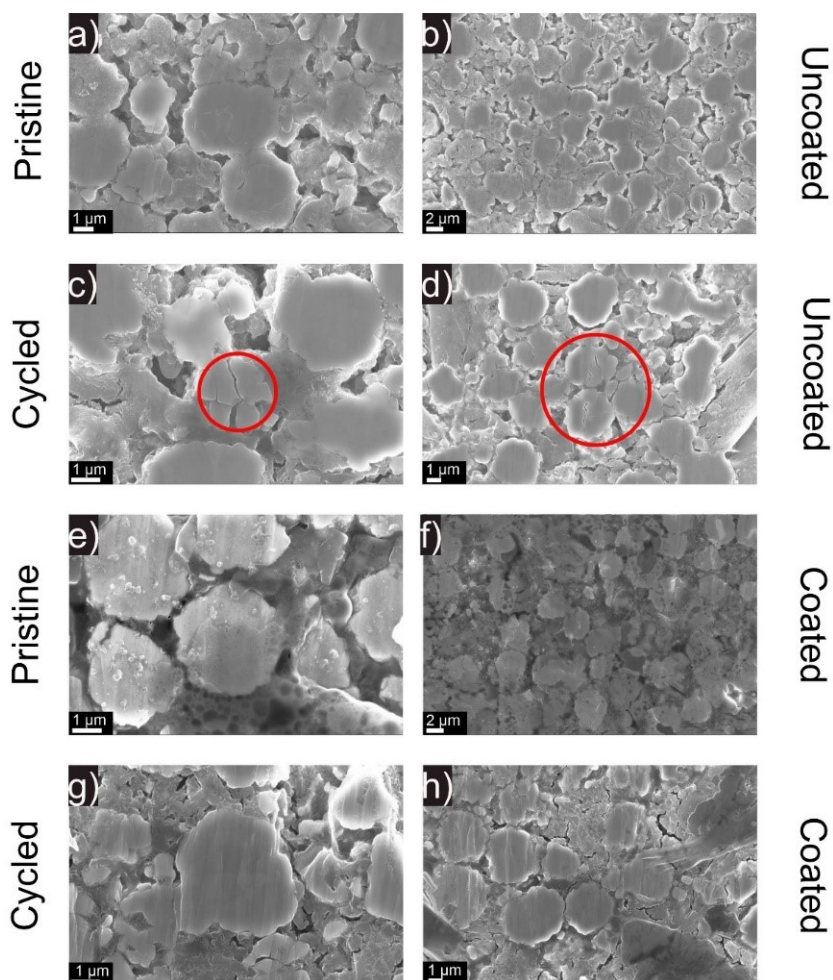


Fig. S5 Cross-sectional SEM images collected from the coated and uncoated NMX9505 cathodes before and after cycling. Cracked particles are indicated by red circles.

Tab. S1 ICP-OES results for the NMX9505 cathode material employed in this work.

Element	Li	Mn	Ni
wt. %	7.45 ± 0.14	2.47 ± 0.05	54.4 ± 1.0