Electronic Supplementary Information

Realizing reversible anionic redox based on a Na–O–Li configuration for Nalayered oxide cathodes with solid-solution reaction

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Experimental Section

Material synthesis. A powder sample of Na_{0.6}MnO₂ (NMO), Na_{0.6}Li_{0.2}Mn_{0.8}O₂ (NLMO), Na_{0.6}Mn_{0.8}Ti_{0.2}O₂ (NMTO), and Na_{0.6}Li_{0.2}Mn_{0.6}Ti_{0.2}O₂ (NLMTO) were synthesized using the solid-state reaction method. For each material, stoichiometric amounts of the respective raw materials, sourced from Aladdin Bio-Chem Co., Ltd. (Shanghai) with high purities (sodium carbonate \geq 99.8%, lithium carbonate \geq 99.8%, manganese trioxide \geq 99.9%, titanium dioxide \geq 99.5%), were ground for one hour. The resulting mixtures were then pressed into cylinders under a pressure of 10 MPa (with a diameter of 25 mm and thickness of 5 mm). All samples were calcined at 1000 °C in air for 15 hours and subsequently cooled to room temperature in the furnace. To prevent moisture exposure, the final products were stored in an argon glove box where O₂ and H₂O levels were maintained below 0.1 ppm. The synthesis of the four materials, NLMTO, NLMO, NMTO, and NMO, differed only in the choice of chemicals and stoichiometry.

Material Characterizations. X-ray diffraction (XRD) patterns were obtained using a Panalytical X'pert Pro Diffractometer (Panalytical, Netherlands) equipped with a Cu K α radiation source ($\lambda 1 = 1.54056$ Å, $\lambda 2 = 1.54439$ Å) over a 2 θ range of 10-70°. In situ XRD analysis utilized a specialized Swagelok cell with an aluminum foil window. Scanning electron microscopy (SEM3100-CIQTEK) were used for morphological characterization. High angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) were performed on a JEM-ARM300F2.

Electrochemical tests. For the half-cell assembly, the working electrode was prepared as follows: First, a blend consisting of 70% active material, 20% Super P carbon, and 10% PVDF binder was mixed in N-Methyl-2-pyrrolidone (NMP). Then, this blend was coated onto aluminum foil. The coated aluminum foil was dried under vacuum at 80°C overnight. Subsequently, it was cut into circular pieces with a diameter of 10 mm, and the actual active material loading on these circular pieces was 2 - 3 mg cm⁻². CR2032 coin cells were assembled in an argon-filled glove box using a glass fiber separator. A sodium foil was used as the counter electrode, and the electrolyte was a 1

M NaClO₄ solution in propylene carbonate (PC) with an additional 5% fluoroethylene carbonate (FEC) as an additive. The battery was charged and discharged using a Neware testing system (CT-4008, Shenzhen, China), (1C=200mAh·g⁻¹ in 1.5-4.5V). Cyclic voltammetry (CV) measurements were conducted using a Princeton Instruments testing system. Galvanostatic intermittent titration technique (GITT) was used to measure equilibrium potentials with a 10 mA g⁻¹ pulse for 30 minutes, followed by 2 hour rest periods between pulses.

Sodium ion diffusion coefficient calculation based on GITT test.

The diffusion coefficient of Na⁺ can be determined by applying the Fick's second law of diffusion, and the equation is:

$$D_{Na^+} = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B A}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

Where $M_{\rm B}$, $V_{\rm m}$, $m_{\rm B}$, A, ΔEs and ΔEi are molecular weight, molar volume, mass, geometric area, the change of quasi-equilibrium potential and battery voltage, respectively.



Fig. S1 Powder XRD patterns of NMO and NLMTO.



Fig. S2 Rietveld-refined XRD pattern of NMO.



Fig. S3 SEM image of NMO.



Fig. S4 SEM image of NLMTO.



Fig. S5 Full XPS spectrum of NLMTO.



Fig. S6 (a) Mn 2p, (b) O 1s, (c) Ti 2p, and (d) Na 1s XPS spectrum of NLMTO.



Fig.S7 Electrochemical performances. GCD curves versus specific energy at 0.1C: (a) NMO and (b) NLMTO.



Fig. S8 The dQ/dV curves for the first three cycle at 0.1C: (a) NMO, and (b) NLMTO.



Fig.S9 Rate performance at different rates and cycle performance of NMO at 1C.



Fig. S10 Cyclic voltammetry curve of NLMTO at 0.1 mV s⁻¹.



Fig. S11 (a) Cyclic voltammetry curves at different scan rates of NLMTO cathode, and (b) The *b*-values analysis based on the relationship between $\log i$ and $\log v$.



Fig.S12 The corresponding intensity contour maps of the characteristic diffraction peaks in the *in-situ* XRD within the voltage range of 1.5-4.5 V.



Fig. S13 The *in-situ* XRD patterns of NLMTO at different states, including the pristine state, charged to 4.5 V and discharged to 1.5 V, were selected from the *in-situ* data.



Fig.S14 Comparisons of phase transition ratio with reported literatures. S1-5

Sample pace group		NLMTO P6 ₃ /mmc
b (Å)	2.8935(9)	
c (Å)	11.1347(3)	
χ^2	1.36	
R _p (%)	5.66	
R _{wp} (%)	7.64	

 Table S1 Lattice parameters of NLMTO refined with XRD data.

Sample pace group		NMO P6 ₃ /mmc
b (Å)	2.8760(6)	
c (Å)	11.1533(4)	
χ ²	1.35	
R _p (%)	5.62	
R _{wp} (%)	7.50	

 Table S2 Lattice parameters of NMO refined with XRD data.

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