Electronic Supplementary Information

Realizing single-phase reaction and K^+/vacancy disordering in P2-$K_{0.56}Na_{0.11}Li_{0.12}Ni_{0.22}Mn_{0.66}O_2$ by lithium substitution for potassium-ion batteries

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Experimental Section

Material synthesis

P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ (P2-NaNM) and P2-$Na_{0.85}Li_{0.12}Ni_{0.22}Mn_{0.66}O_2$ (P2-NaLNM) were synthesized by solid-state method. Stoichiometric amounts of Na_2CO_3 (99.9%; 2 wt% excess), Li_2CO_3 (99.9%,2 wt% excess), NiO (99%), Mn_2O_3 (98%) were ball-milled for eight hours and pelletized under 16 MPa. Then those pellets were sintered at 900°C in air for 24 hours and the obtained samples were kept in an argon-filled glovebox for further test. P2-KNaLNM was obtained through electrochemical ion-exchange of P2-NaLNM electrode.

Characterizations

The XRD of P2-NaNM and P2-NaLNM were obtained via Bruker D8 Advance with Cu Kα radiation (λ = 1.5418 Å) and *ex-situ* XRD of cycled electrodes and P2-KNaLNM were carried out under protection of Kapton film. Rietveld refinements were realized by using TOPAS software. The composition of KNaLNM was analyzed by inductively coupled plasma-atomic mass spectrometer (ICP-MS; NexION 350D). The morphology of each material was examined by scanning electron microscopy (SEM, HITACHI SU8200; GeminiSEM 500) and transmission electron microscopy (TEM, JOEL, JEM-2010; Talos F200X). X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALab Xi^+spectrometer (Thermo Fisher) to analyze the valence states of Mn and Ni element.

Electrochemical measurement

The slurry of 75 wt% active materials, 15 wt% Super P, and 10 wt% polyvinylidene fluoride (PVDF) were coated on Al foil and then vacuum-dried at 80 °C for 8 h to prepare working electrodes. The loading of active materials was about 1.5 mg cm^{-2}. Coin cells (CR2032) were assembled in an argon-filled glove-box with working electrode as cathode, porous glass fiber (GF/D) as separator and potassium as anode. The electrolyte was saturated $KClO_4$ in EC: DEC (1:1 by volume). The electrochemical tests were conducted on Land battery test instrument at 25 °C. Cyclic voltammetry (CV) tests were carried out using an electrochemical workstation (Autolab). The diffusion coefficient of K^+ was calculated through variable sweep speed CV according to Randles-Sevcik equation:

$$I_P = 2.69 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C_0$$

where I_p is the peak current, n is the number of electrons transferred, A is the area of the electrode,

D is the diffusion coefficient of K^+, v is the sweep speed and C_0 is the concentration of K^+ in the crystal.

For galvanostatic intermittent titration technique (GITT) test, the cell was charged for 30 min at 0.1 C and then rest for 10 h at an open circuit. The diffusion coefficient is calculated according to the following equation:

$$D = \frac{4}{\pi\tau}\left(\frac{mV_m}{MS}\right)^2\left(\frac{\triangle E_s}{\triangle E_\tau}\right)^2$$

where m, V_m and M are the mass, molar volume and molar mass of the active materials, τ is the testing time in each step, S is the electrode contact area, $\triangle E_s$ is the voltage change before and after the titration and $\triangle E_\tau$ is the voltage change during the titration.

DFT calculations

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP.5.4.4).[1] The exchange-correlation effects of electrons were addressed using Perdew-Burke-Ernzerhof (PBE) density functional of generalized-gradient approximation (GGA).[2] The valence electron orbitals of relevant atoms were treated with the projector augmented wave (PAW) method.[3] The climbing image nudged elastic band (CI-NEB) method was employed to calculate the migration energy profile for K^+ on each diffusion pathways.[4] All calculations were spin-polarized for structural relaxations. The kinetic energy cutoff value was set to 500 eV for plane wave expansion in reciprocal space. Due to the use of large supercells, the energy integration in the first Brillouin zone was conducted using a single k point at Γ-point. The convergence thresholds were set to 10^{-6} eV for total energy and 0.05 eV $Å^{-1}$ for the atomic force, respectively.

The cathode materials investigated in this work all belong to the layered sodium transition metal oxides with a general formula $NaMO_2$, where M refers to a transition metal such as Ni, Mn and etc. The crystal structure of $NaMO_2$ consists of two distinct layers, i.e., the transition metal oxide layer and the Na layer. The modelling structures were built according to the experimental compositions P2-$K_{12}Li_2Ni_4Mn_{12}O_{36}$. In the structure, the Li, Ni, and Mn atoms occupying 2a Wyckoff sites were placed in the MO_6 layers. Meanwhile, all K atoms were allocated at 2b and 2d Wyckoff sites based on the experimentally determined occupies. Finally, the 3×3×1 supercell model of P2-$K_{12}Li_2Ni_4Mn_{12}O_{36}$, was obtained based on the original cell of P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ phase and the results of the Rietveld refinement results. It is worth noting that the irreversible K ordering during structure optimization will have some impact on the accuracy of the diffusion barrier calculation, so when calculating the migration energy profile, the 2b and 2d Wyckoff Na sites in the modelling structure was fully occupied by K, respectively.

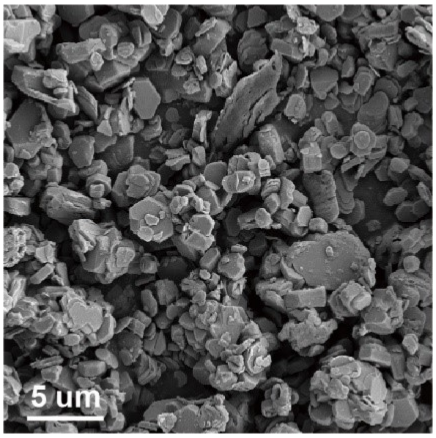

Fig. S1 SEM image of P2-NaNM.

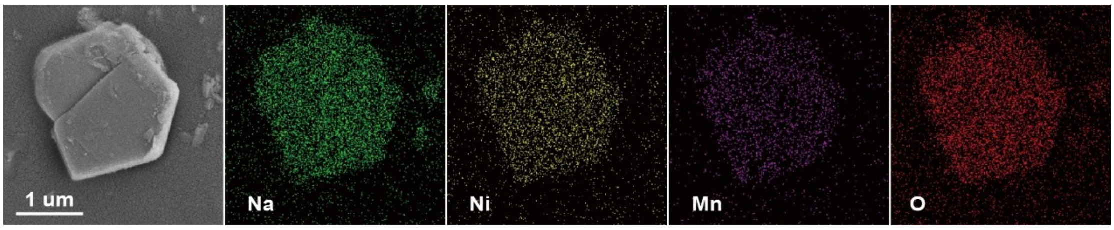

Fig. S2 EDS images of P2-NaNM.

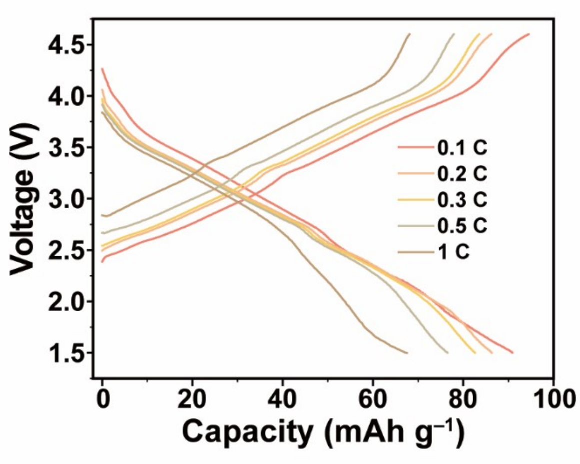

Fig. S3 Galvanostatic charge/discharge curves of P2-NaLNM at different rates in the voltage range of 1.5–4.6 V.

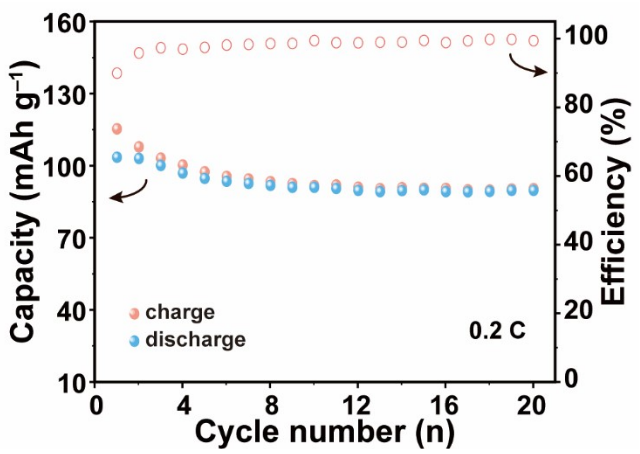

Fig. S4 Cycling performance of P2-NaLNM with higher mass loading (2.5 mg cm^{-2}) in the voltage range of 1.5–4.6 V.

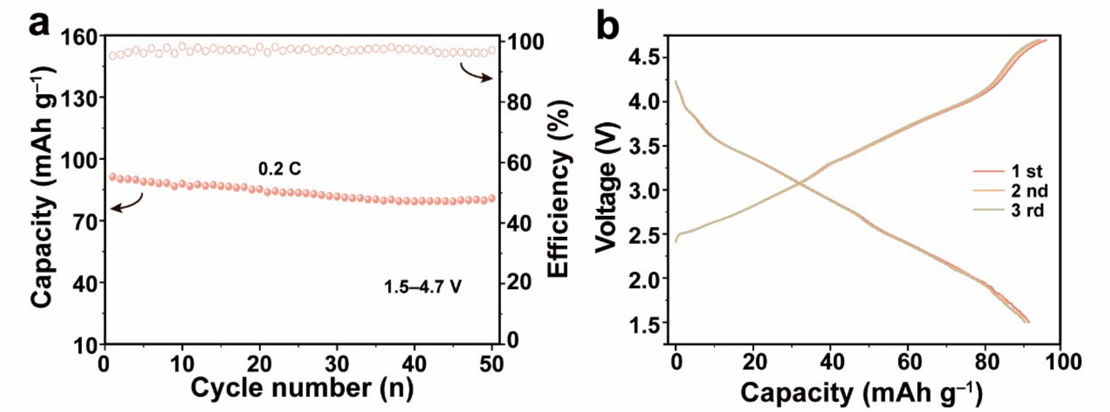

Fig. S5 (a) Cycling performance and (b) Galvanostatic charge/discharge curves of P2-KNaLNM at 0.2 C in the voltage range of 1.5–4.7 V.

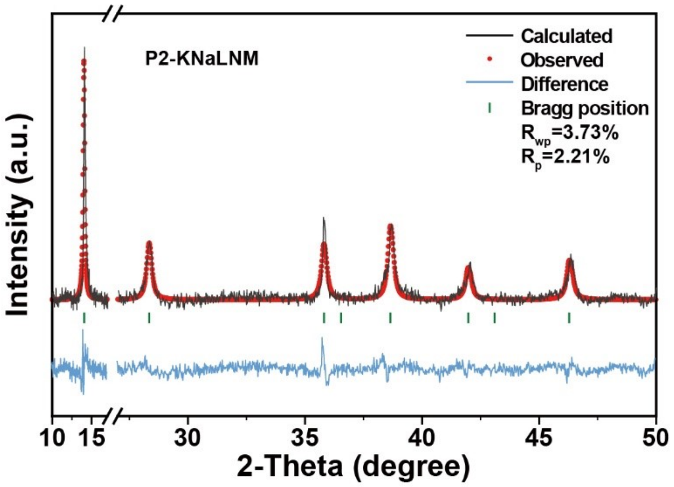

Fig. S6 XRD and Rietveld refinement of P2-KNaLNM obtained after the electrochemical ion-exchange.

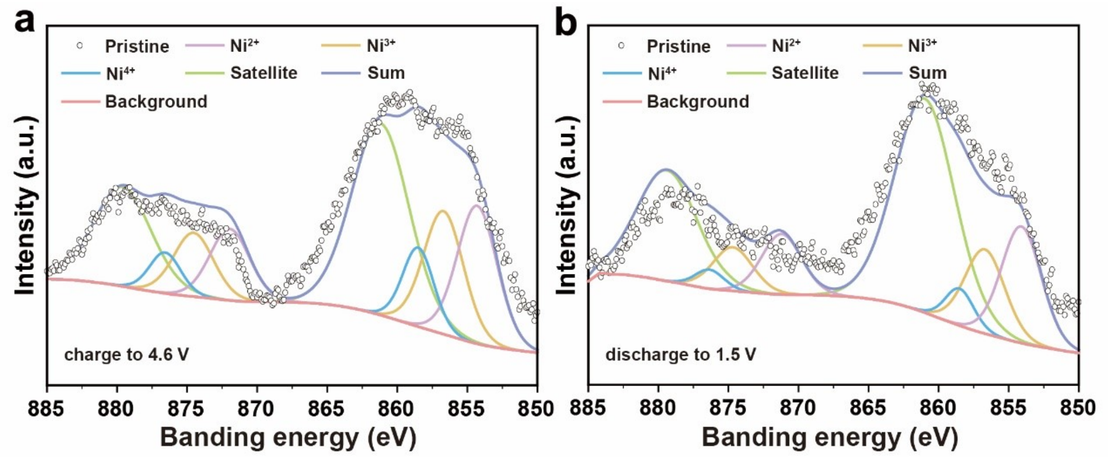

Fig. S7 XPS spectra of Ni 2p for P2-KNaLNM at different charge/discharge states.

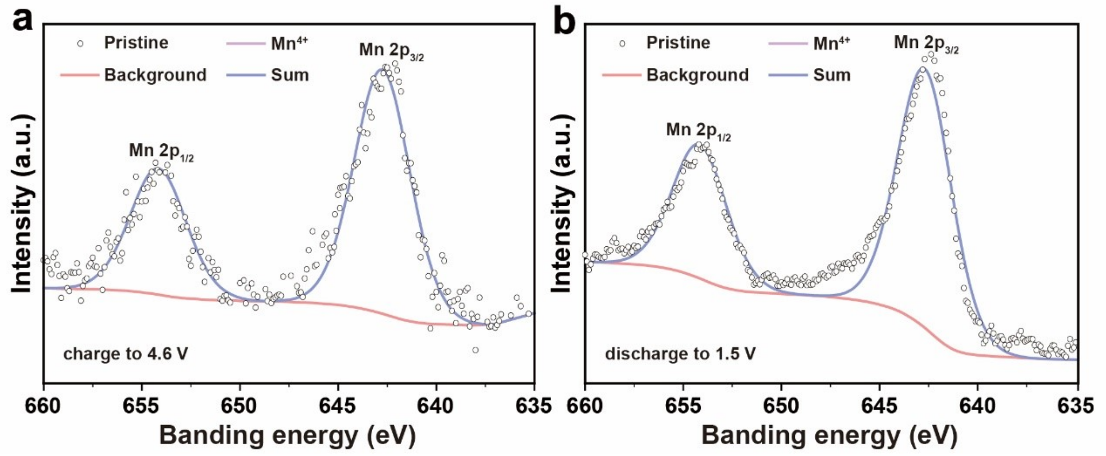

Fig. S8 XPS spectra of Mn 2p for P2-KNaLNM at different charge/discharge states.

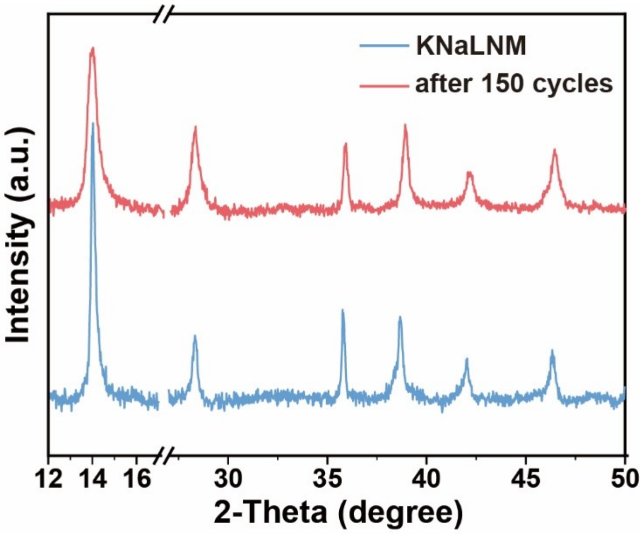

Fig. S9 XRD patterns of the pristine P2-KNaLNM and the electrode after 150 cycles at 0.2 C.

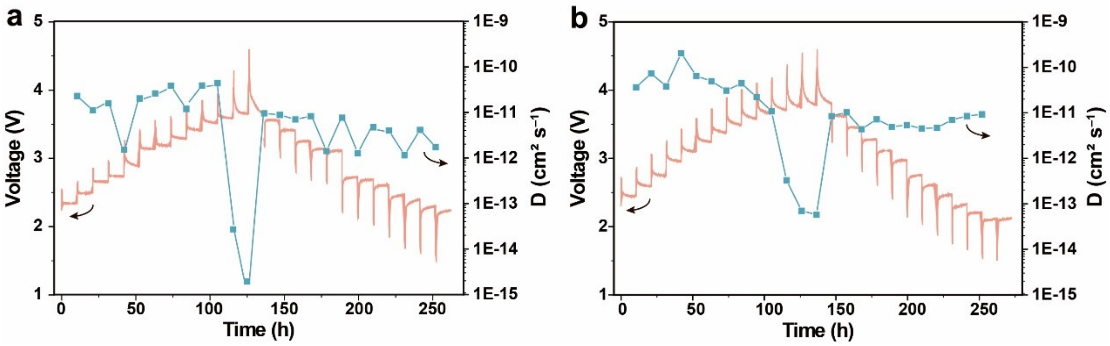

Fig. S10 GITT curves of (a) P2-NaNM and (b) P2-KNaLNM after electrochemical ion-exchange.

Table S1 Crystallographic parameters of P2-NaNM refined by the Rietveld method.

Site	**x**	**y**	**z**	**Occ.**
Na_f	0	0	1/4	0.314
Na_e	1/3	2/3	1/4	0.536
Ni	0	0	0	0.34
Mn	0	0	0	0.66
O	2/3	1/3	0.096	1
	a=2.887(3) Å	c=11.166(2) Å	V=80.759(1) $Å^3$	

Table S2 Crystallographic parameters of P2-NaLNM refined by the Rietveld method.

Site	**x**	**y**	**z**	**Occ.**
Na_f	0	0	1/4	0.2728
Na_e	1/3	2/3	1/4	0.2772
Li	0	0	0	0.12
Ni	0	0	0	0.22
Mn	0	0	0	0.66
O	2/3	1/3	0.09175	1
	a=2.890(3) Å	c=11.022(2) Å	V=79.781(1) $Å^3$	

Table S3 Crystallographic parameters of P2-KNaLNM refined by the Rietveld method.

Site	x	y	z	Occ.
K_f	0	0	1/4	0.1582
K_e	1/3	2/3	1/4	0.4018
Na_f	0	0	1/4	0.05
Na_e	1/3	2/3	1/4	0.06
Li	0	0	0	0.12
Ni	0	0	0	0.22
Mn	0	0	0	0.66
O	2/3	1/3	0.0707	1
	a=2.8928(3) Å	c=12.58(2) Å	V=91.1711(1) $Å^3$	

Table S4 ICP-MS results for different cycled electrode.

Different cycled electrode	**Measured atomic ratio**			
	Na	**K**	**Ni**	**Mn**
First	0.34	0.43	0.22	0.64
Tenth	0.11	0.56	0.22	0.66

Reference:

1 G. Kresse and J. Furthmüller, *Phys Rev B*, 1996, **54**, 11169-11186.

2 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

3 P. E. Blöchl, *Phys Rev B*, 1994, **50**, 17953-17979.

4 G. Henkelman, B. P. Uberuaga and H. Jónsson, *J Chem Phys*, 2000, **113**, 9901-9904.