Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2022

# Supplementary for

# Pre-zeolite framework super-MIEC anodes for high-rate lithium-ion batteries

Shitong Wang, Lijiang Zhao, Yanhao Dong, He Zhu, Yang Yang, Haowei Xu, Baoming Wang, Yakun Yuan, Yang Ren, Xiaojing Huang, Wei Quan, Yutong Li, Yimeng Huang, Charles M. Settens, Qi He, Yongwen Sun, Hua Wang, Zunqiu Xiao, Wenjun Liu, Xianghui Xiao, Riqiang Fu, Qiang Li, Yong S. Chu, Zhongtai Zhang, Qi Liu, Andrew M. Minor, Junying Zhang, Zilong Tang, and Ju Li

Correspondence to: dongyanhao@tsinghua.edu.cn (Y. Dong), zjy@buaa.edu.cn (J. Zhang), tzl@tsinghua.edu.cn (Z. Tang), liju@mit.edu (J. Li).

### This PDF file includes:

Methods Supplementary Figs. S1 to S24 Supplementary Tables S1 to S7 Supplementary References 1 to 83

### Methods

#### Materials synthesis

H-Nb<sub>2</sub>O<sub>5</sub> was synthesized by heat-treating Nb<sub>2</sub>O<sub>5</sub> (99.99% purity) at 1125 °C for 5 h. NPO was synthesized by mixing Nb<sub>2</sub>O<sub>5</sub> (99.99% purity) and P (99.8% purity) with the Nb: P molar ratio of 9:1.1 (10% access P was added to compensate for P loss during heat treatment), followed by heat treatment at 1100 °C for 20 h. TNO was synthesized by mixing Nb<sub>2</sub>O<sub>5</sub> (99.99% purity) and TiO<sub>2</sub> (99.8% purity) with the Nb: Ti molar ratio of 2:1, followed by heat treatment at 1125 °C for 5 h. NWO was synthesized by mixing Nb<sub>2</sub>O<sub>5</sub> (99.99 % purity) and WO<sub>3</sub> (99.99% purity) with the Nb: W molar ratio of 9:8, followed by high-temperature treatment at 1100 °C for 20 h. NWT944 and NWT926 were synthesized by mixing NbC (99.99 % purity) and TiO<sub>2</sub> (99.8 % purity) and WO<sub>3</sub> (99.99% purity) with Nb: W: Ti molar ratio of 9:4:4 and 9:2:6, respectively, followed by high-temperature treatment at 1100 °C for 10 h. To synthesize H-Nb<sub>2</sub>O<sub>5</sub>-B, Nb<sub>2</sub>O<sub>5</sub> (99.99% purity) powders were first cold-pressed into a pellet under 50 MPa and heat-treated at 1200 °C for 3 h. The heat-treated pellet was ground, mixed with ethanol, and ball-milled at 350 rpm for 6 h. After ball milling, the slurry was dried in a vacuum oven at 60 °C for 6 h, and then sieved by 150 and 600 meshes to obtain H-Nb<sub>2</sub>O<sub>5</sub>-B. A heating rate of 2 °C min<sup>-1</sup> and furnace cooling was used in all heat treatment processes.

#### Material characterizations

In-situ X-ray diffraction for CTE measurements: X-ray diffraction (XRD, Burke D8 ADVANCE; Cu  $K_{\alpha}$  radiation with wavelength  $\lambda$ =1.5418 Å) with a temperature control stage was used to characterize the phase and the temperature-dependent structural information. Temperature-dependent XRD measurements for H-Nb<sub>2</sub>O<sub>5</sub>, NPO, NTO, NWO, NWT926, Li<sub>0.2</sub>Nb<sub>2</sub>O<sub>5</sub>, and Li<sub>1.6</sub>Nb<sub>2</sub>O<sub>5</sub> were firstly conducted at 100 K, and then at higher temperatures from 150 K to 650 K with 50 K temperature interval, a ramping rate of 2 K min<sup>-1</sup>, and 10 min constant-temperature rest before measurement at each temperature. Profile fittings for H-Nb<sub>2</sub>O<sub>5</sub>, NPO, NTO, NWO, Li<sub>0.2</sub>Nb<sub>2</sub>O<sub>5</sub>, and Li<sub>1.6</sub>Nb<sub>2</sub>O<sub>5</sub> were conducted on the PANalytical X'Pert HighScore Plus<sup>1</sup> at the Center for Materials Science and Engineering, MIT. For NWT926 material, the temperature-dependent lattice parameters were extracted by using Fullprof software<sup>2</sup>. Rietveld refinement was carried out based on the monoclinic *C*2/*c* unit cell.

Synchrotron high energy XRD and PDF measurements: The high energy XRD and PDF data were collected using the 11-ID-C beamline at the Advanced Photon Source (APS) of Argonne National Laboratory (ANL), with the Xray wavelength of 0.1173 Å. Si (113) single crystal was used as a monochromator for an X-ray beam at 105.7 keV. In a typical data collection, the NWT926 powder sample (for high energy XRD measurement), H-Nb<sub>2</sub>O<sub>5</sub>, and  $Li_{0.1}Nb_2O_5$  powder samples (for PDF measurements) were loaded into a 3 mm capillary with a data acquisition time of 20 minutes. The background was extracted from the same empty capillary. A two-dimensional Perkin-Elmer detector was used to record the scattering patterns in transmission mode. Fit 2D software was applied to calibrate the scattering patterns with the CeO<sub>2</sub> standard sample and integrate the 2D patterns into 1D profiles<sup>3</sup>. The G(r) function was computed by Fourier transform of reduced structural function (F(Q), up to 17.6 Å<sup>-1</sup>) with PDFgetX2 software<sup>4</sup>. The Rietveld method was used to determine the crystal structure of NWT926 using Fullprof software<sup>2</sup>. A monoclinic C2/c unit cell was built to describe the XRD pattern. The pseudo-Voigt peak-shape function was used to fit the full width at half maximum (FWHM) with fitting parameters U, V, W, and Gaussian/Lorentz ratio. Due to the structural complexity of NWT926, not all the atomic information can be extracted. The atomic coordination values in Table S2, ESI<sup>†</sup> were inherited from the pristine NWO structure with undistorted octahedra, while the occupancies were calculated based on the stoichiometric ratio. The current structural model can describe the XRD pattern reasonably well. The resolution of the collected XRD data is insufficient to provide complete atomic information, and singlecrystal diffraction experiments need to be carried out to determine the exact structure of NWT926 in the future studies to fully resolve the structure.

*Morphology and structural characterizations:* A scanning electron microscope (SEM, MERLIN VP Compact) was used to characterize the morphology. A Ga-focused ion beam (Ga-FIB) system (FEI Helios G4) was used to lift out a thin TEM lamella from H-Nb<sub>2</sub>O<sub>5</sub> particles. The H-Nb<sub>2</sub>O<sub>5</sub> particles were protected by Pt deposition before lift-out. During the thinning process, the energy of the ion beam was reduced from 30 to 16, 8, 5, 2, 1 keV step by step. TEAM-1, a double aberration-corrected TEM operating at 300 kV at the national center for electron microscopy

(NCEM) in the Lawrence Berkeley National Laboratory, was used to collect atomic-resolution STEM-HAADF images. Image pairs with orthogonal scan directions were collected and a MATLAB code developed by Ophus et al.<sup>5</sup> was used to correct the nonlinear scan distortion. The 4D-STEM experiments were performed on an FEI Titan operating at 300 keV. A 10 µm condenser C2 aperture and a convergence angle of 0.12 mrad were chosen to form a nanosized electron beam with a full width half maximum (FWHM) of about 12 nm. The scan step size was 10 nm. The camera length was 480 mm. The py4DSTEM package<sup>6</sup> was used for the analysis of 4D-STEM data.

*Method of stacking fault mapping:* Conventional STEM-HAADF images cannot depict the location of SFs accurately due to the co-existence of multiple structural information. To better map the SFs/twins in the sample, a new method is developed. For regions with stacking faults (SFs), diffuse streaks between Bragg peaks will show up in the nanobeam electron diffraction (NBED) patterns. Because the streaks due to SFs tend to make the Bragg peaks more elliptical, the averaged aspect ratio (a/b, where a and b are the length of the long axis and length of the short axis, respectively) of Bragg peaks in an NBED pattern can be correlated to the relative density of SFs. When there are more SFs, a/b is smaller. While there are no SFs, a/b is close to 1. To calculate a/b, windows of 20 pixels by 20 pixels in size are chosen whose center overlaps with each Bragg peak. The standard deviation along the streak direction and perpendicular to the streak direction is calculated as a and b, respectively. py4DSTEM package<sup>6</sup> is used to find the location of each Bragg peak.

*Methods of displacement analysis:* The cross-sectional  $Li_{0.1}Nb_2O_5$  TEM specimen was prepared using a Thermo Fisher Helios 600 focused ion beam (FIB)/SEM microscope. The specimen was first coated with 10 nm carbon using Denton DV502A Evaporator to minimize the beam damage and charging effects. Additive protective layers were deposited by combining e-beam and ion-beam deposition in the FIB instrument, including an e-beam-deposited 100 nm Pt layer and an ion-beam-deposited 1 µm carbon layer. The sample was thinned step by step by lowering ion voltages from 30 kV to 2 kV and currents from 0.92 nA to 89 pA. The surface damage caused by FIB is further removed by argon ion milling using a Fischione 1051 TEM Mill at room temperature with a voltage of 100 V and angle of 7°. The high-resolution HAADF images are taken in a Thermo Fisher Themis Z-STEM at MIT with an acceleration voltage of 200 kV. The potential atom positions were obtained by identifying the local maxima of the HAADF image. After manual correction of the misidentified positions, a Gaussian function was used to fit a 5×5 pixels area around each local maxima, which generated a list of 2D coordinates of the atoms from the experimental image. Then, a unit cell was selected by identifying and averaging the smallest repeating unit of the atomic structure. A reference lattice was generated by periodically repeating the averaged unit cell in two in-plane directions of the image. Finally, the displacement vectors were calculated by comparing the experimental atomic coordinates with the reference lattice.

*Characterizations of H<sub>2</sub>O adsorption/desorption:* Thermogravimetric analysis (TGA) was carried out using NETZSCH-STA 449 F3 with a heating rate of 10 °C min<sup>-1</sup> under an air atmosphere. The powder samples were suspended in deionized H<sub>2</sub>O for 10 mins, then collected and dried at 60 °C for 5 h.

*Characterizations of chemical compositions and surface areas:* Because of the low volatility of Nb, Ti and W elements, the ratios of transition metal (TM) were determined by the ratios of the raw materials, and the ratio of TM/O was determined by balancing the valance (as the synthesis was conducted at oxidation environment, we assumed +5 for Nb, +6 for W, and +4 for Ti). Inductively coupled plasma mass spectroscopy (ICP-MS, iCP QC, Thermo Fisher Scientific) measurements were also conducted to confirm the ratios of TM. The specific surface area was measured by Autosorb-iQ2-MP (Quanta Chrome) and calculated following the Brunauer-Emmett-Teller (BET) method.

#### **Electrochemical measurements**

*Preparation of half cells:* To prepare the composite working electrodes, active materials, conductive carbon, and binder were mixed with a specific weight ratio to form a homogeneous slurry, spread on commercial Al foils (for H-Nb<sub>2</sub>O<sub>5</sub>, H-Nb<sub>2</sub>O<sub>5</sub>-B, NPO, NTO, NWO, NWT944, NWT926, Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LiCoO<sub>2</sub>, LiNi<sub>0.33</sub>Co<sub>0.33</sub>Mn<sub>0.33</sub>O<sub>2</sub>, LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and LiFePO<sub>4</sub>) or Cu foils (for meso-carbon microbeads), and dried at 110 °C in vacuum for 12 h. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LiCoO<sub>2</sub>, LiNi<sub>0.33</sub>Co<sub>0.33</sub>Mn<sub>0.33</sub>O<sub>2</sub>, LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and meso-carbon microbeads were obtained from commercial vendors, while others were home-synthesized. The slurries of H-Nb<sub>2</sub>O<sub>5</sub>, H-Nb<sub>2</sub>O<sub>5</sub>-B, NPO, NTO, NWO, NWT944, and NWT926 were prepared using water as the solvent, and

sodium carboxymethyl cellulose (CMC) and polymerized styrene-butadiene rubber (SBR) with a weight ratio of 1:1 as the binder. The slurries of Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, LiCoO<sub>2</sub>, and LiNi<sub>0.33</sub>Co<sub>0.33</sub>Mn<sub>0.33</sub>O<sub>2</sub>, LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>, LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and LiFePO<sub>4</sub> were prepared using N-methyl-2-pyrrolidone (NMP) as the solvent, and polyvinylidene fluoride (PVDF) as the binder. Mass loadings for the electrodes in half cells were controlled between  $1.0 \sim 3.0$  mg cm<sup>-2</sup>. 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) in a 1:1:1 volume ratio, and 1 M LiClO<sub>4</sub> dissolved in propylene carbonate (PC) was used as the electrolyte. The electrolyte volume in this experimental section is excess (~50 mL Ah<sup>-1</sup>). The Li metal used in half cells is 0.45 mm thick with the diameter of 18 mm. Microporous polypropylene films (Celgard 2500) were used as the separator. Cell assembly (CR2032 type) was carried out in an Ar glove box with oxygen and water contents below 1.0 ppm and 0.5 ppm, respectively. Charge/discharge tests and galvanostatic intermittent titration technique (GITT) were conducted at varied current densities using a LAND battery testing system (CT-2001A). Detailed information on electrode compositions, half-cell cycling window, and GITT measurements was listed in Table S7, ESI<sup>+</sup>.

**Preparation of lithiated samples for characterizations:**  $H-Nb_2O_5$  electrode (without the addition of binder and conductive carbon) was prepared by cold pressing under 20 MPa. Li|| $H-Nb_2O_5$  half-cells were assembled by using Li metal as the counter and reference electrode and 1.0 M LiPF<sub>6</sub> in EC: DMC: EMC as the electrolyte. The cells were discharged at 50 mA g<sup>-1</sup> to the set potentials: 2.0 V for Li<sub>0.1</sub>Nb<sub>2</sub>O<sub>5</sub>, 1.8 V for Li<sub>0.2</sub>Nb<sub>2</sub>O<sub>5</sub>, 1.3 V for Li<sub>1.6</sub>Nb<sub>2</sub>O<sub>5</sub>, respectively. Lithiated materials were obtained from disassembled cells, followed by washing (by DMC solvent) and drying repeated three times.

*Electronic conductivity measurements:* Testing cells for electronic conductivity measurements were assembled by sandwiching the lithiated materials between stainless steels as the two blocking electrodes (blocking to Li<sup>+</sup>), and cold-pressing under 20 MPa. The electronic resistance (*R*) for Nb<sub>2</sub>O<sub>5</sub> and Li<sub>0.1</sub>Nb<sub>2</sub>O<sub>5</sub> was measured by a direct current (DC) method. 50 mV DC voltage was applied to the cell, and the steady-state current was recorded after ~1 h where the current changed less than 1  $\mu$ A g<sup>-1</sup> per minute. The electronic conductivity ( $\sigma_e$ ) was calculated by the geometry of the pressed materials.

**Preparation of full cells:** H-Nb<sub>2</sub>O<sub>5</sub> vs. LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> and H-Nb<sub>2</sub>O<sub>5</sub> vs. LiFePO<sub>4</sub> coin-cell type full cells (CR2032 type) were assembled and tested. H-Nb<sub>2</sub>O<sub>5</sub> vs. LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> pouch-type full cells and H-Nb<sub>2</sub>O<sub>5</sub>-B vs. LiCoO<sub>2</sub> pouch-type full cells were also assembled and tested. Mass loading for the anodes in full cells was controlled between  $5.0 \sim 16.0 \text{ mg cm}^{-2}$ . Mass loading for the cathodes in full cells was controlled between  $7.0 \sim 14.0 \text{ mg cm}^{-2}$  to match with the optimized negative to positive capacity (*N/P*) ratio. More details are listed in Table S7, ESI<sup>†</sup>.

#### Model and simulation

*First-principles calculations*: Spin-polarized first-principles calculations were conducted on Vienna ab initio simulation package (VASP) using projector augmented-wave (PAW) method with Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)<sup>7-10</sup>. We used PAW potentials with 1 valence electron for Li, 13 valence electrons for Nb, 6 valence electrons for O, and plane-wave cutoff energy of 520 eV. Li storage in H-Nb<sub>2</sub>O<sub>5</sub> was simulated by adding 1 Li to the described sites in a  $1 \times 3 \times 1$  supercell containing 84 Nb and 210 O. Convergence was considered as reached when residue atomic forces were less than 0.05 eV Å<sup>-1</sup>. Li<sup>+</sup> migration was simulated in the same supercell, using the climbing image nudged elastic band (NEB) method<sup>11</sup>. The convergence of NEB calculations was set to be reached when the residual atomic forces were less than 0.1 eV Å<sup>-1</sup>. The Brillouin zone was sampled using the Monhorst-Pack scheme with a  $1 \times 1 \times 1$  k-point mesh. Atomic structures were visualized and plotted using VESTA<sup>12</sup>.

*RMC simulations:* Initial structural model for RMC simulations was generated using a  $3 \times 5 \times 13$  supercell of the perfect H-Nb<sub>2</sub>O<sub>5</sub> unit cell, containing 3780 Nb and 9450 O in total. For Li<sub>0.1</sub>Nb<sub>2</sub>O<sub>5</sub>, Li atoms were not included in RMC simulations because of the weak diffraction signal of Li. RMC simulations were conducted using the software RMCprofile<sup>13</sup>. The minimum distance windows of Nb...O, Nb...Nb, and O...O atom pairs were set as 1.9 Å, 2.8 Å, and 1.3 Å, respectively, while their maximum distance windows were 3.5 Å, 4.0 Å, and 2.5 Å, respectively.

## **Supplementary Figures**



**Fig. S1** (a) Atomic structure of block structure oxide  $H-Nb_2O_5$ . Tunnels marked as P1 to P14 within one unit cell. (b) Calculated migration barrier for Li<sup>+</sup> between two neighboring square-planar sites from one on the sidewall to the one in the *a*-*c* plane within the P6 tunnel.



**Fig. S2**  $H_2O$  adsorption/desorption study of (a)  $H-Nb_2O_5$ , (b) NPO, (c) NTO, (d) NWO, (e) NWT944, and (f) NWT926 by thermogravimetric analysis.



**Fig. S3** The correlation between thermal expansion and the average atomic volume for H-Nb<sub>2</sub>O<sub>5</sub>, NPO, NTO, NWO, NWT926, and the common oxides and fluorides reported in reference<sup>14</sup>.



**Fig. S4** (a $\sim$ c) XRD analysis of H-Nb<sub>2</sub>O<sub>5</sub> at 100 K, 150 K, 200 K, 250 K, 300 K, 350 K, 400 K, 450 K, 500 K, 550 K, 600 K, and 650 K. (d $\sim$ h) Primary-cell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S5** (a~c) XRD analysis of NPO at 200 K, 250 K, 300 K, 350 K, 400 K, 450 K, 500 K, 550 K, and 600 K. (d~g) Primary-cell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S6** (a $\sim$ c) XRD analysis of NTO at 300 K, 350 K, 400 K, 450 K, 500 K, 550 K, 600 K, and 650 K. (d $\sim$ h) Primary-cell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S7** (a $\sim$ c) XRD analysis of NWO at 100 K, 150 K, 200 K, 250 K, 300 K, 350 K, 400 K, 450 K, 500 K, and 550 K. (d $\sim$ g) Primary-cell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S8** (a<sup>~</sup>c) XRD analysis of NWT926 at 100 K, 150 K, 200 K, 250 K, 300 K, and 350 K. (d<sup>~</sup>h) Primarycell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S9** CTEs of 260 materials in the database of Table S2, ESI<sup>+</sup>. Inset: measured CTEs for H-Nb<sub>2</sub>O<sub>5</sub>, NPO, NTO, and NWO.



**Fig. S10** First five galvanostatic discharge/charge profiles together with Coulombic efficiencies of (a)  $H-Nb_2O_5$  and (d) NPO at 100 mA g<sup>-1</sup>. (c) The differential capacity (dQ/dV) plots of the  $H-Nb_2O_5$ . Rate capacities for (b)  $H-Nb_2O_5$  and (e) NPO at 200, 500, 1,000, 2,000, 4,000, 6,000, 8,000, 10,000, 12,000, and 16,000 mA g<sup>-1</sup>. From the dQ/dV plots of the  $H-Nb_2O_5$ , there is one pair of sharp reversible peaks at 1.69/1.65 V and two pairs of broad tiny peaks at 1.35/1.17 V and 2.05/2.01 V. The sharp reversible peaks at 1.69/1.65 V together with the broad tiny peaks at 2.05/2.01 V are associated with the redox reactions of  $Nb^{5+}/Nb^{4+}$ ; while the broad tiny peaks at 1.35/1.17 V are associated with the redox reactions of  $Nb^{4+}/Nb^{3+15}$ . For the Li storage mechanism, the sharp-peak regions around 1.69/1.65 V are assigned to two-phase reaction; while the broad-peak regions around 1.35/1.17 V and 2.05/2.01 V are assigned to solid-solution reaction<sup>16</sup>.



**Fig. S11** First five galvanostatic discharge/charge profiles together with Coulombic efficiencies of (a) NTO and (c) NWO at 100 mA  $g^{-1}$ . Rate capacities for (b) NTO and (d) NWO at 200, 500, 1,000, 2,000, 4,000, 6,000, 8,000, 10,000, 12,000, and 16,000 mA  $g^{-1}$ .



**Fig. S12** First five galvanostatic discharge/charge profiles together with Coulombic efficiencies of (a) NWT944 and (c) NWT926 at 100 mA  $g^{-1}$ . Rate capacities for (b) NWT944 and (d) NWT926 at 200, 500, 1,000, 2,000, 4,000, 6,000, 8,000, 10,000, 12,000, and 16,000 mA  $g^{-1}$ .



**Fig. S13** GITT curves and calculated diffusion coefficients of lithium  $D_{Li}$  at 10~35 °C for (a, b) H-Nb<sub>2</sub>O<sub>5</sub>, (c, d) NPO, (e, f) NTO, (g, h) NWO by using 1.0 M LiPF<sub>6</sub> in EC: DMC: EMC as the electrolyte.



**Fig. S14** GITT curves and calculated diffusion coefficients of lithium  $D_{Li}$  at (a, b) 10~40 °C for LiCoO<sub>2</sub>, and (c, d) 20~50 °C for LiNi<sub>0.33</sub>Co<sub>0.33</sub>Mn<sub>0.33</sub>O<sub>2</sub> by using 1.0 M LiPF<sub>6</sub> in EC: DMC: EMC as the electrolyte.



**Fig. S15** GITT curves and calculated diffusion coefficients of lithium  $D_{Li}$  at 10<sup>~</sup>35 °C for (a, b) H-Nb<sub>2</sub>O<sub>5</sub>, (c, d) NPO, (e, f) NTO, (g, h) NWO by using 1.0 M LiClO<sub>4</sub> in PC as the electrolyte.



**Fig. S16** (a) First five galvanostatic discharge/charge profiles at 100 mA g<sup>-1</sup> together with Coulombic efficiencies. (b) Rate capacities at 200, 500, 1,000, 2,000, 4,000, 6,000, 8,000, 12,000, and 16,000 mA g<sup>-1</sup> after 200 cycles at 4,000 mA g<sup>-1</sup> for electrode activation. (c) XRD pattern and (d) particle distribution analysis for H-Nb<sub>2</sub>O<sub>5</sub>-B. Note that the high-rate capacity of H-Nb<sub>2</sub>O<sub>5</sub>-B is not as good as H-Nb<sub>2</sub>O<sub>5</sub>, because at high current densities (like >6000 mA g<sup>-1</sup>) H-Nb<sub>2</sub>O<sub>5</sub>-B has reached the limit of Li<sup>+</sup> transport as well as e<sup>-</sup> transport (low content of conductive carbon).



Fig. S17 The photos of Li metal (a) before and (b) after 7300 cycles of the NWT944 half-cell.



Fig. S18 Full cells performances using H-Nb<sub>2</sub>O<sub>5</sub> as the anode. (a) Galvanostatic discharge/charge profiles at 0.1, 0.25, 0.5, 1.0, 2.0, and 4.0 mA cm<sup>-2</sup> and (b) cycling performances at 4.0 mA cm<sup>-2</sup> of H-Nb<sub>2</sub>O<sub>5</sub> in full cells paired with LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cathode. Mass loadings of cathode: 13.6 mg cm<sup>-2</sup>. Mass loadings of anode: 5.5 mg cm<sup>-2</sup>. Negative to positive capacity (N/P) ratio: 0.83. (c) Rate performances and (d) cycling performances at 4.0 mA cm<sup>-2</sup> of H-Nb<sub>2</sub>O<sub>5</sub> in full cells paired with LiFePO<sub>4</sub> cathode. Mass loadings of cathode: 7.4 mg cm<sup>-2</sup>. Mass loadings of anode: 5.2 mg cm<sup>-2</sup>. N/P ratio: 1.03. All the specific capacities were calculated by the anodes. (e) Photo and (f) cycling performance of 0.5 Ah H-Nb<sub>2</sub>O<sub>5</sub> pouch-type full cells (paired with LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub> cathode) at 1 C. Mass loadings of cathode: 8.9 mg cm<sup>-2</sup>. Mass loadings of anode: 9.0 mg cm<sup>-2</sup>. N/P ratio: 1.0. (g) Photo and (h) cycling performance of H-Nb<sub>2</sub>O<sub>5</sub>-B pouch-type full cells (paired with LiCoO<sub>2</sub> cathode) at 1 C and 4 C. Mass loadings of cathode: 13.4 mg cm<sup>-2</sup>. Mass loadings of anode: 15.7 mg cm<sup>-2</sup>. N/P ratio: 1.0. The volumetric energy density of the pouch cell was calculated by using the following equation: (Cell capacity) × (Average voltage)/ [(Electrode area) × (Thickness of anode including active materials,

binder and carbon black)].



**Fig. S19** SEM images of the surface of  $H-Nb_2O_5$  electrodes (a) before and (b) after 1,000 cycles at 6,000 mA g<sup>-1</sup>, the surface of NPO electrodes (c) before and (d) after 1,000 cycles at 6,000 mA g<sup>-1</sup>, cross-sectional images of NPO electrodes (e) before and (f) after 1,000 cycles at 6,000 mA g<sup>-1</sup>, the surface of NWT944 electrodes (g) before and (h) after 7,300 cycles at 6,000 mA g<sup>-1</sup>.



Fig. S20 Stacking fault analysis by using high-resolution STEM-HAADF of H-Nb<sub>2</sub>O<sub>5</sub>.



**Fig. S21** (a) Pair distribution function (PDF) experimental data for  $Nb_2O_5$  as well as ideal data for the perfect  $Nb_2O_5$  crystal. The distribution of Nb and O displacements for (b)  $Nb_2O_5$  and (c)  $Li_{0.1}Nb_2O_5$  compared with the perfect  $Nb_2O_5$  crystal.



**Fig. S22** (a<sup> $\sim$ </sup>c) XRD analysis of Li<sub>0.2</sub>Nb<sub>2</sub>O<sub>5</sub> at 100 K, 150 K, and 200 K. (d<sup> $\sim$ </sup>h) Primary-cell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S23** (a<sup> $\sim$ </sup>c) XRD analysis of Li<sub>1.6</sub>Nb<sub>2</sub>O<sub>5</sub> at 100 K, 150 K, and 200 K. (d<sup> $\sim$ </sup>h) Primary-cell parameters as a function of temperature *T*, together with the calculated coefficient of linear thermal expansion.



**Fig. S24** The calculated pre-zeolite frameworks in the NbO<sub>2.5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> phase diagram. The colored area is associated with the Wadsley-Roth structures, with the anion-to-cation ratio from 2.33 to 2.80.

## **Supplementary Tables**

**Table S1** Electrochemical comparison table considering characterized particle size, specific surface area, electrode composition, electrode density, high-rate capacity, and cycling capacity retention among Nb<sub>2</sub>O<sub>5</sub>, H-Nb<sub>2</sub>O<sub>5</sub>-B, NPO, NWT944, NWT926, and representative Nb-based anodes with high-rate performances. The electrode compositions (mass ratio of active materials: conductive carbon: binder) are listed for references.

Materials	Character ized size (µm)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Electrode composition	Electrode density (mg cm <sup>-2</sup> )	High-rate capacity (mAh g <sup>-1</sup> )	Cycling capacity retention after cycles	Refs
H-Nb₂O₅	1~5	1.3	85:9:6	1.0~2.0	77 (16 A g <sup>-1</sup> )	100%, 1,000 cycles (6 A g <sup>-1</sup> )	This work
H-Nb₂O₅-B	20~50	0.8	92:4:4	2.0~3.0	61 (12 A g <sup>-1</sup> )	105%, 1,000 cycles (4 A g <sup>-1</sup> )	This work
NPO	1~3	1.1	90:4:6	1.0~2.0	62 (16 A g <sup>-1</sup> )	47%, 1,000 cycles (6 A g <sup>-1</sup> )	This work
NWT944	1~3	3.7	85:9:6	1.0~2.0	95 (16 A g <sup>-1</sup> )	56%, 15,000 cycles (6 A g <sup>-1</sup> )	This work
NWT926	1~2	4.0	85:9:6	1.0~2.0	92 (16 A g <sup>-1</sup> )	80%, 1,000 cycles (6 A g <sup>-1</sup> )	This work
Ag-coated nitridated $H-Nb_2O_5$	~1.0	N/A	80:10:10	1.5	88 (5 A g <sup>-1</sup> )	~80%, 1,000 cycles (3 A g <sup>-1</sup> )	17
$H-Nb_2O_5$ with defects	0.5~1.0	1.0	80:10:10	1.0~1.5	86 (16 A g <sup>-1</sup> )	~95%, 2,000 cycles (6 A g <sup>-1</sup> )	18
$KNb_6O_{15}F\text{-}wired\ Nb_2O_5$	0.1~1.0	N/A	70:20:10	~2.0	80 (20 C)	75%, 200 cycles (0.5 C)	19
$T-Nb_2O_5$ /carbide-derived carbon	~0.5	19	80:10:10	1.4	100 (10 A g <sup>-1</sup> )	72%, 500 cycles (0.1 A g <sup>-1</sup> )	20
Hollow and mesoporous $T\text{-}Nb_2O_5$	0.3	N/A	70:20:10	1.0~1.5	125 (50 C)	86%, 2,000 cycles (1 C)	21
$M-Nb_2O_5$ microspheres	~0.3	N/A	70:20:10	~3.6	122 (5 A g <sup>-1</sup> )	82%, 1,000 cycles (0.2 A g <sup>-1</sup> )	22
$T-Nb_2O_5$ nanotubes	0.2	39	80:10:10	0.7~1.1	99 (20 C)	~100%, 1,000 cycles (10 C)	23
$T-Nb_2O_5$ nanoflowers	0.1	N/A	80:10:10	1.2~2.0	130 (5 A g <sup>-1</sup> )	83%, 400 cycles (1 A g <sup>-1</sup> )	24
T-Nb <sub>2</sub> O <sub>5-x</sub>	0.05~0.1	N/A	70:20:10	2.0~4.0	107 (25 C)	~90%, 1,100 cycles (5 C)	25
3D T-Nb <sub>2</sub> O <sub>5</sub> microspheres	0.01~0.1	56.2	70:20:10	N/A	113 (3.2 A g <sup>-1</sup> )	86%, 1,000 cycles (0.8 A g <sup>-1</sup> )	26
$T-Nb_2O_5@C$ nanoparticles	<0.1	214.4	80:10:10	2.0	177 (6 A g <sup>-1</sup> )	87.9%, 2,000 cycles (2 A g <sup>-1</sup> )	27
$M-Nb_2O_5@$ graphene sheets	0.015~0.0 7	>100	85:10:5	N/A	509 C g <sup>-1</sup> (20 A g <sup>-1</sup> )	~88%, 2,000 cycles (1 A g <sup>-1</sup> )	28
Nanosheets Nb <sub>12</sub> O <sub>29</sub> microspheres	0.05	12.9	65:25:10	1.4	179 (20 C)	96.5%, 500 cycles (10 C)	29
Mesoporous T-Nb $_2O_5$ nanotubes	0.03	23.7	80:10:10	1.5	70 (5 A g <sup>-1</sup> )	~90%, 5,000 cycles (3 A g <sup>-1</sup> )	30
$T-Nb_2O_5$ quantum dots in carbon	0.005	268	80:10:10	~1.0	105 (5 A g <sup>-1</sup> )	70%, 1,000 cycles (1 A g <sup>-1</sup> )	31
$3D T-Nb_2O_5$ nanosheets@C	0.015	N/A	80:10:10	1.2	144 (5 A g <sup>-1</sup> )	95%, 1,000 cycles (2 A g <sup>-1</sup> )	32
3D holey-graphene $T-Nb_2O_5$	0.015	83	80:10:10	6.0	92 (50 C)	90%, 10,000 cycles (10 C)	33
T-Nb <sub>2</sub> O <sub>5</sub> nanowires/graphene	0.01	N/A	93.5:6.5:0	N/A	95 (5 A g <sup>-1</sup> )	~100%, 1,000 cycles (5 A g <sup>-1</sup> )	34

3D porous carbon nanowebs T- Nb₂O₅	~0.01	103	80:10:10	1.0	82 (10 A g <sup>-1</sup> )	88%, 70,000 cycles (1 A g <sup>-1</sup> )	35
TT-Nb <sub>2</sub> O <sub>5</sub> /CNT films	0.007	N/A	75:15:10	N/A	83 (2 A g <sup>-1</sup> )	66%, 1,000 cycles (5 A g <sup>-1</sup> )	36
T-Nb₂O₅/rGO	0.005	80	70:20:10	1.1~1.5	134 (25 C)	87%, 1,000 cycles (5 C)	37
PNb <sub>9</sub> O <sub>25</sub>	N/A	N/A	75:15:10	1.5	30 (60 C)	86%, 500 cycles (2 C)	38
PNb₀O₂₅ nanofiber	0.1~0.5 (dia.)	N/A	80:10:10	1.0~1.4	181 (6 C)	71%, 500 cycles (6 C)	39
Cu <sub>0.02</sub> Ti <sub>0.94</sub> Nb <sub>2.04</sub> O <sub>7</sub>	4.0	0.7	65:25:10	1.0	182 (10 C)	99%, 1,000 cycles (10 C)	40
Coarse-grained Mo <sub>x</sub> Ti <sub>1-x</sub> Nb <sub>2</sub> O <sub>7+y</sub>	1~2	1.1	90:5:5	1~2	158 (6 A g <sup>-1</sup> )	75%, 500 cycles (2 A g <sup>-1</sup> )	41
$TiNb_{24}O_{62}$ nanowires	0.3	8.3	80:10:10	1.0~1.5	177 (6 C)	92%, 900 cycles (10 C)	42
Porous TiNb <sub>2</sub> O <sub>7</sub> nanotubes	0.3	151	70:20:10	N/A	180 (100 C)	86%, 700 cycles (50 C)	43
1D TiNb <sub>2</sub> O <sub>7-x</sub> @C fibers	0.2	6.7	90:5:5	11	32 (6 C)	78%, 100 cycles (0.3 C)	44
TiNb <sub>2</sub> O <sub>7</sub> hollow nanofiber	0.2	N/A	80:10:10	1.5	200 (10 C)	81%, 900 cycles (10 C)	45
Porous TiNb <sub>2</sub> O <sub>7</sub> nanotubes	0.2	50.2	80:10:10	N/A	116 (30 C)	88%, 500 cycles (5 C)	46
Ti <sub>2</sub> Nb <sub>10</sub> O <sub>29</sub> @TiC/C	0.05~0.08	N/A	100:0:0	0.8	165 (100 C)	66%, 10,000 cycles (10 C)	47
N-doped graphene $TiNb_2O_{7-x}$	0.06	N/A	70:20:10	1.3~1.5	89 (100 C)	87%, 2,000 cycles (10 C)	48
3D/2D cross-linked Ti₂Nb₁₀O₂₂₋v@C	0.05	N/A	80:10:10	2.0	197 (20 C)	99%, 500 cycles (10 C)	49
$TiNb_2O_7$ microspheres	~0.05	19.8	85:15:5	N/A	142 (100 C)	90%, 1,000 cycles (5 C)	50
Porous Ti <sub>2</sub> Nb <sub>10</sub> O <sub>29</sub> microspheres	~0.05	19.4	70:20:10	N/A	193 (50 C)	~100%, 1,000 cycles (10 C)	51
TiO <sub>2</sub> /Nb <sub>2</sub> O <sub>5</sub> /TiNb <sub>2</sub> O <sub>7</sub>	0.05	25.4	60:25:15	N/A	185 (5 C)	95%, 1,800 cycles (5 C)	52
Microporous TiNb <sub>2</sub> O <sub>7</sub>	0.05	27	70:20:10	1.5	99 (100 C)	82%, 1,000 cycles (10 C)	53
2D Ti <sub>2</sub> Nb <sub>10</sub> O <sub>29</sub>	0.04~0.05	55	70:20:10	1.5	144 (40 C)	82%, 1,000 cycles (10 C)	54
Vertical graphene/TiNb <sub>2</sub> O <sub>7</sub> @S–C	0.02~0.04	N/A	100:0:0	0.9	181 (160 C)	78%, 5,000 cycles (10 C)	55
Porous Ti <sub>2</sub> Nb <sub>10</sub> O <sub>29</sub> microspheres	0.02~0.05	25.1	65:25:10	2.0	208 (20 C)	90%, 500 cycles (10 C)	56
Ti <sub>2</sub> Nb <sub>10</sub> O <sub>29-x</sub> @C	0.01~0.05	N/A	65:25:10	N/A	165 (40 C)	98%, 500 cycles (10 C)	57
Highly porous TiNb <sub>2</sub> O <sub>7</sub>	~0.02	48	75:15:10	1.5~2.0	160 (100 C)	84%, 1,000 cycles (5 C)	58
Cr <sup>3+</sup> -Ti <sub>2</sub> Nb <sub>10</sub> O <sub>29</sub> @ graphene@TiC-	0.01	N/A	100:0:0	2.0	220 (40 C)	91%, 500 cycles (10 C)	59
Mesostructured TiNb <sub>2</sub> O <sub>7</sub>	0.015	74	70:20:10	1.1~1.4	116 (50 C)	81%, 2,000 cycles (10 C)	60
Coarse-grained Nb <sub>18</sub> W <sub>16</sub> O <sub>93</sub>	5.0	N/A	80:10:10	2~3	72 (100 C)	95%, 750 cycles (20 C)	61
WNb <sub>12</sub> O <sub>33</sub> nanowires	0.2	N/A	80:10:10	1.5	146 (0.7 A g <sup>-1</sup> )	86%, 700 cycles (0.7 A g <sup>-1</sup> )	62
$W_3Nb_{14}O_{44}$ nanowires	0.4	N/A	80:10:10	N/A	138 (0.7 A g <sup>-1</sup> )	64%, 1,000 cycles (1 A g <sup>-1</sup> )	63
Coarse-grained FeNb <sub>11</sub> O <sub>29</sub>	0.2~20	0.2	65:25:10	1.4	145 (10 C)	93%, 200 cycles (10 C)	64

Coarse-grained Cr <sub>0.2</sub> Fe <sub>0.8</sub> Nb <sub>11</sub> O <sub>29</sub>	0.2~20	0.3	65:25:10	N/A	123 (10 C)	87%, 500 cycles (10 C)	65
Coarse-grained HfNb <sub>24</sub> O <sub>62</sub>	2~10	0.4	65:25:10	N/A	105 (10 C)	87%, 500 cycles (10 C)	66
Coarse-grained Cu <sub>2</sub> Nb <sub>34</sub> O <sub>87</sub>	1~10	0.8	65:25:10	N/A	184 (10 C)	89%, 1,000 cycles (10 C)	67
Coarse-grained AINb <sub>11</sub> O <sub>29</sub>	~1.0	3.0	89:7:4	8.0	163 (5 C)	80%, 450 cycles (0.5 C)	68
FeNb <sub>11</sub> O <sub>29</sub> @N	0.2~0.9	N/A	70:20:10	1.5~2.0	44 (100 C)	88%, 10,000 cycles (20 C)	69
$Zr_2Nb_{34}O_{87}$ nanofibers	0.1~0.3	18.4	65:25:10	1.0	86 (10 C)	99%, 1,000 cycles (5 C)	70
GaNb <sub>11</sub> O <sub>29</sub> nanowebs	0.25	10.3	65:25:10	N/A	175 (10 C)	87%, 1,000 cycles (10 C)	71
$Cu_2Nb_{34}O_{87}$ nanowires	0.25	N/A	80:10:10	N/A	233 (1.5 A g <sup>-1</sup> )	89%, 300 cycles (0.3 A g <sup>-1</sup> )	72
FeNb <sub>11</sub> O <sub>29</sub> nanotubes	0.2	N/A	80:10:10	N/A	54 (50 C)	75%, 2,000 cycles (1 C)	73
AINb <sub>11</sub> O <sub>29</sub> nanowires	0.16	9.7	65:25:10	1.4	131 (10 C)	93%, 500 cycles (10 C)	74
ZrNb <sub>14</sub> O <sub>37</sub> nanowires	0.12	N/A	80:10:10	2	168 (0.7 A g <sup>-1</sup> )	74%, 1,000 cycles (0.1 A g <sup>-1</sup> )	75
ZrNb <sub>24</sub> O <sub>62</sub> nanowires	0.05	34.9	65:25:10	1.4	182 (30 C)	90%, 1,500 cycles (10 C)	76
Porous MoNb <sub>12</sub> O <sub>33</sub> microspheres	0.1	13.1	65:25:10	1.0	138 (10 C)	96%, 1,000 cycles (5 C)	77
CrNb <sub>11</sub> O <sub>29</sub> nanorods	0.03~0.05	22.3	65:25:10	N/A	228 (10 C)	91%, 400 cycles (10 C)	78
Porous Al <sub>0.5</sub> Nb <sub>24.5</sub> O <sub>62</sub> microspheres	0.03~0.04	8.3	65:25:10	1.5	192 (10 C)	90%, 500 cycles (10 C)	79

	Phase: Monoclinic								
Space Group: C2/c (No. 15). 162 atoms per unit cell									
cattice Parameters: α=31 439 Å b=3 866 Å c=20 901 Å α=90 000° β=112 990° ν=90 000° V=2338 516 Å <sup>3</sup>									
Atom	X	y	<u>z</u>	Occupancy					
Nb1	0.066	0.000	0.037	0.529					
W1	0.066	0.000	0.037	0.118					
Ti1	0.066	0.000	0.037	0.353					
Nb2	0.067	0.000	0.224	0.529					
W2	0.067	0.000	0.224	0.118					
Ti2	0.067	0.000	0.224	0.353					
Nb3	0.064	0.500	0.356	0.529					
W3	0.064	0.500	0.356	0.118					
Ti3	0.064	0.500	0.356	0.353					
Nb4	0.202	0.000	0.119	0.529					
W4	0.202	0.000	0.119	0.118					
Ti4	0.202	0.000	0.119	0.353					
Nb5	0.201	0.000	0.302	0.529					
W5	0.201	0.000	0.302	0.118					
Ti5	0.201	0.000	0.302	0.353					
Nb6	0.200	0.500	0.433	0.529					
W6	0.200	0.500	0.433	0.118					
Ti6	0.200	0.500	0.433	0.353					
01	0.000	0.000	0.000	0.986					
02	0.006	0.000	0.195	0.986					
03	0.068	0.000	0.136	0.986					
O4	0.071	0.000	0.333	0.986					
05	0.072	0.500	0.057	0.986					
O6	0.073	0.500	0.256	0.986					
07	0.067	0.500	0.446	0.986					
08	0.141	0.000	0.075	0.986					
09	0.140	0.000	0.270	0.986					
O10	0.141	0.500	0.406	0.986					
011	0.220	0.000	0.031	0.986					
012	0.208	0.000	0.220	0.986					
013	0.204	0.000	0.413	0.986					
014	0.223	0.500	0.134	0.986					
015	0.210	0.500	0.333	0.986					

**Table S2** Crystallographic information of NWT926.

No.	Materials	CTE	No.	Materials	СТЕ	No.	Materials	CTE
1	MgO·2PbO·WO <sub>3</sub>	-7.69	31	Na <sub>1.5</sub> Zr <sub>1.5</sub> Cr <sub>0.5</sub> (PO <sub>4</sub> ) <sub>3</sub>	0.50	61	Sr <sub>0.5</sub> Zr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	3.16
2	$ZrO_2 \cdot 2WO_3$	-7.20	32	GaNbO <sub>4</sub>	0.50	62	$SrO \cdot Al_2O_3 \cdot 2SiO_2$	3.20
3	NaTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	-5.50	33	2MgO·2Al <sub>2</sub> O <sub>3</sub> ·5SiO <sub>2</sub>	0.60	63	TiTa <sub>18</sub> O <sub>47</sub>	3.24
4	$Ta_2O_5 \cdot V_2O_5$	-4.13	34	2ZnO·GeO₂	0.67	64	ZnO·V <sub>2</sub> O <sub>5</sub>	3.33
5	$NaZr_2(PO_4)_3$	-4.00	35	SrO·ZrO <sub>2</sub>	0.75	65	Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	3.33
6	$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	-3.33	36	$U_3O_8$	0.80	66	$Ba_{0.5}Zr_2(PO_4)_3$	3.37
7	PbO·TiO <sub>2</sub>	-3.30	37	V <sub>2</sub> O <sub>5</sub>	0.87	67	RuO <sub>2</sub>	3.60
8	Na <sub>3/2</sub> Zr <sub>15/8</sub> (PO <sub>4</sub> ) <sub>3</sub>	-2.35	38	PNb <sub>9</sub> O <sub>25</sub>	0.97	68	CaO·HfO <sub>2</sub>	3.60
9	3PbO·P <sub>2</sub> O <sub>5</sub>	-2.33	39	Mo <sub>2</sub> O <sub>3</sub>	1.10	69	HfSiO <sub>4</sub>	3.60
10	Ca <sub>0.5</sub> Zr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> -NZP	-2.11	40	Sn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1.43	70	ZrSiO <sub>4</sub>	3.64
11	Ca <sub>0.5</sub> Zr <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> -CTP	-1.60	41	TiTa <sub>2</sub> O <sub>7</sub>	1.43	71	$Dy_2O_3 \cdot 2AI_2O_3$	3.66
12	AINb <sub>9</sub> O <sub>24</sub>	-1.40	42	$Nb_2O_5 \cdot V_2O_5$	1.50	72	HfO <sub>2</sub>	3.80
13	$Nb_{14}W_3O_{44}$	-1.27	43	$Nb_{11}Ta_2Ti_3O_{41}$	1.50	73	SnO <sub>2</sub>	3.80
14	GeNb <sub>18</sub> O <sub>47</sub>	-1.26	44	$BaNb_6O_{16}$	1.51	74	$K_2O\cdot Nb_2O_5$	3.80
15	Nb <sub>12</sub> WO <sub>33</sub>	-1.25	45	$TiO_2 \cdot Ta_2O_5$	1.57	75	$Zn_2SiO_4$	3.86
16	AINb <sub>11</sub> O <sub>29</sub>	-1.19	46	$Sr_2Nb_{10}O_{27}$	1.61	76	MgO·2TiO <sub>2</sub>	3.88
17	$ZrNb_{14}O_{37}$	-1.17	47	TiO	1.67	77	IrO <sub>2</sub>	3.89
18	$2Nb_2O_5 \cdot Ta_2O_5$	-0.83	48	Ta <sub>2</sub> O <sub>5</sub>	1.87	78	Ta <sub>2</sub> O <sub>5</sub>	3.92
19	$GaNb_{11}O_{29}$	-0.82	49	Nb <sub>3</sub> BO <sub>9</sub>	1.94	79	AINbO <sub>4</sub>	3.97
20	Nb <sub>2</sub> O <sub>5</sub>	-0.70	50	NbPO <sub>5</sub>	2.00	80	3MgO·Nb <sub>2</sub> O <sub>5</sub>	4.00
21	$Ta_2O_5 \cdot Nb_2O_5$	-0.53	51	$Mg_{0.5}Zr_2(PO_4)_3$	2.11	81	CaCO <sub>3</sub>	4.00
22	$LaNb_5O_{14}$	-0.43	52	K <sub>2</sub> Nb <sub>8</sub> O <sub>21</sub>	2.13	82	Ca <sub>0.25</sub> Na <sub>0.5</sub> Ti <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	4.00
23	3CaO·5Al <sub>2</sub> O <sub>3</sub>	-0.40	53	$Li_2Nb_{32}O_{81}$	2.16	83	$BaO \cdot Al_2O_3 \cdot 2SiO_2$	4.00
24	$Ti_2Nb_{10}O_{29}$	-0.31	54	Zn(PO <sub>3</sub> ) <sub>2</sub>	2.20	84	NbPO <sub>5</sub>	4.20
25	$2AI_2O_3 \cdot 5WO_3$	0.00	55	$AI_2O_3$ ·SiO <sub>2</sub>	2.25	85	TaPO₅	4.25
26	$Sr_2O_3 \cdot WO_3$	0.00	56	$2AI_2O_3$ ·SiO <sub>2</sub>	2.25	86	ZnO	4.30
27	NiNb <sub>14</sub> O <sub>36</sub>	0.15	57	$ZrO_2 \cdot TiO_2$	2.50	87	2PbO·P <sub>2</sub> O <sub>5</sub>	4.33
28	$2CaO \cdot MgO \cdot WO_3$	0.18	58	WO <sub>2</sub>	2.60	88	Y <sub>2</sub> SiO <sub>5</sub>	4.33
29	TiNb <sub>2</sub> O <sub>7</sub>	0.45	59	$3Al_2O_3 \cdot 2SiO_2$	2.63	89	$Ca_{0.5}ZrTi(PO_4)_3$	4.35
30	SiO <sub>2</sub> (Fused)	0.49	60	$Li_2O \cdot Ta_2O_5$	2.66	90	Mg(PO <sub>3</sub> ) <sub>2</sub>	4.35

**Table S3** Linear CTE (unit:  $10^{-6} \text{ K}^{-1}$ ) of 260 materials<sup>80-83</sup>.

No.	Materials	CTE	No.	Materials	CTE	No.	Materials	СТЕ
91	3PbO·Fe <sub>2</sub> O <sub>3</sub> ·WO <sub>3</sub>	4.38	121	MgO·Cr <sub>2</sub> O <sub>3</sub>	6.20	151	TiO <sub>2</sub>	7.50
92	GeO <sub>2</sub> (Rutile)	4.50	122	BeO	6.30	152	MgCO <sub>3</sub>	7.63
93	$CaAl_2(SiO_4)_2$	4.50	123	$Er_2O_3$	6.30	153	8PbO·P <sub>2</sub> O <sub>5</sub>	7.67
94	$CaO \cdot 6Al_2O_3$	4.53	124	$Ca_{0.25}Na_{0.5}Zr_2(PO_4)_3$	6.30	154	ThO <sub>2</sub>	7.70
95	$CaO \cdot Al_2O_3 \cdot SiO_2$	4.53	125	BaO·TiO <sub>2</sub>	6.30	155	3CaO·2SiO <sub>2</sub>	7.72
96	$ZrO_2 \cdot Cr_2O_3$	4.62	126	3PbO·2Ta <sub>2</sub> O <sub>5</sub>	6.50	156	Pr <sub>2</sub> O <sub>3</sub>	7.80
97	$CaO \cdot Al_2O_3$	4.70	127	$Gd_2O_3$	6.60	157	FeCO <sub>3</sub>	7.83
98	PbO·Al <sub>2</sub> O <sub>3</sub>	4.88	128	Sc <sub>2</sub> O <sub>3</sub>	6.60	158	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	7.90
99	$Na_2O\cdot Nb_2O_5$	4.97	129	BaO·ZrO <sub>2</sub>	6.67	159	$CaO \cdot ZrO_2$	7.90
100	2PbO·GeO₂	5.00	130	PbO·P <sub>2</sub> O <sub>5</sub>	6.67	160	Fe <sub>3</sub> O <sub>4</sub>	8.00
101	Ca <sub>0.5</sub> Ti <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub> -CTP	5.10	131	ThO₂·SiO₂	6.67	161	PuO <sub>2</sub>	8.10
102	VO <sub>2</sub>	5.22	132	3CaO·Al <sub>2</sub> O <sub>3</sub>	6.80	162	$AI_2O_3$ ·Ti $O_2$	8.10
103	$Na_3Cr_2(PO_4)_3$	5.30	133	4MgO·Nb <sub>2</sub> O <sub>5</sub>	6.80	163	4PbO·SiO <sub>2</sub>	8.10
104	$5CaO \cdot 3Al_2O_3$	5.30	134	CaO·MgO·2SiO <sub>2</sub>	6.80	164	$K_2O.7GeO_2$	8.24
105	2MgO·Nb <sub>2</sub> O <sub>5</sub>	5.33	135	2MgO·TiO <sub>2</sub>	6.89	165	$2ZnO \cdot V_2O_5$	8.33
106	Al <sub>2</sub> O <sub>3</sub>	5.40	136	$In_2O_3$	6.90	166	BaO·SnO <sub>2</sub>	8.34
107	$Lu_2O_3$	5.50	137	$Tm_2O_3$	7.00	167	MnO <sub>2</sub>	8.40
108	SrO∙HfO₂	5.50	138	MgO·Al <sub>2</sub> O <sub>3</sub>	7.00	168	NiO·TiO <sub>2</sub>	8.58
109	NiCO <sub>3</sub>	5.51	139	3PbO·2P <sub>2</sub> O <sub>5</sub>	7.00	169	MgSiO <sub>3</sub>	8.60
110	PbO·SiO <sub>2</sub>	5.71	140	MnSiO <sub>3</sub>	7.00	170	6HfO <sub>2</sub> ·Ta <sub>2</sub> O <sub>5</sub>	8.62
111	$Li_2Si_2O_5$	5.71	141	Li(Li <sub>0.1</sub> Mn <sub>1.9</sub> )O <sub>4</sub>	7.00	171	Cr <sub>2</sub> O <sub>3</sub>	8.80
112	$NiO \cdot Al_2O_3$	5.79	142	Ho <sub>2</sub> O <sub>3</sub>	7.10	172	Eu <sub>2</sub> O <sub>3</sub>	8.80
113	$Cr_2O_3 \cdot V_2O_5$	5.79	143	PbO·WO <sub>3</sub>	7.10	173	ZrO <sub>2</sub>	8.80
114	Mn <sub>2</sub> O <sub>3</sub>	5.80	144	BaO·TiO <sub>2</sub>	7.14	174	$MgO \cdot Fe_2O_3$	8.80
115	$K_2O \cdot Ta_2O_5$	5.80	145	$Dy_2O_3 \cdot Nb_2O_5$	7.25	175	$Zr_5Nb_2O_{15}$	8.94
116	Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	5.80	146	Y <sub>2</sub> O <sub>3</sub>	7.30	176	Ti <sub>2</sub> O <sub>3</sub>	9.00
117	$Zn_2P_2O_7$	5.93	147	BaO·4TiO <sub>2</sub>	7.40	177	$2CaO \cdot Fe_2O_3$	9.00
118	2MgO·4SiO <sub>2</sub>	6.00	148	3K <sub>2</sub> O·11GeO <sub>2</sub>	7.42	178	$CdO \cdot ZrO_2$	9.00
119	Yb <sub>2</sub> O <sub>3</sub>	6.10	149	Dy <sub>2</sub> O <sub>3</sub>	7.50	179	2FeO·SiO <sub>2</sub>	9.00
120	MgO·Nb <sub>2</sub> O <sub>5</sub>	6.13	150	SrO	7.50	180	CaO·FeO·SiO <sub>2</sub>	9.00

**Table S3** Linear CTE (unit:  $10^{-6} \text{ K}^{-1}$ ) of 260 materials (continued).

No.	Materials	СТЕ	No.	Materials	СТЕ	No.	Materials	СТЕ
181	$Mg_2SiO_4$	9.00	211	La <sub>2</sub> O <sub>3</sub>	10.80	241	Na <sub>2</sub> SO <sub>4</sub>	15.10
182	$MnO \cdot Al_2O_3$	9.13	212	CaO·MoO₃	10.90	242	PbO·Ta <sub>2</sub> O <sub>5</sub>	16.10
183	ZnO·Al <sub>2</sub> O <sub>3</sub>	9.20	213	CaO·MgO·SiO <sub>2</sub>	10.90	243	WO <sub>3</sub>	16.40
184	PbO·ZrO <sub>2</sub>	9.20	214	$Nd_2O_3$	11.00	244	BaO	17.80
185	$Sm_2O_3$	9.24	215	$Li_2O\cdot Nb_2O_5$	11.10	245	$NH_4H_2AsO_4$	18.20
186	GeO <sub>2</sub> (Quartz)	9.30	216	CaO	11.20	246	$Li_2O\cdot Na_2O\cdot 2P_2O_5$	20.00
187	MnCO <sub>3</sub>	9.30	217	MgO·2FeO	11.20	247	Ba(NO <sub>3</sub> ) <sub>2</sub>	20.80
188	UO <sub>2</sub>	9.40	218	$CaO \cdot Fe_2O_3$	11.40	248	$Gd_2O_3$ ·3MoO <sub>3</sub>	21.00
189	2PbO·Ta <sub>2</sub> O <sub>5</sub>	9.40	219	$2BaO \cdot SrO \cdot WO_3$	11.50	249	$Na_2O \cdot WO_3$	21.10
190	CaO·SiO <sub>2</sub>	9.40	220	PrO <sub>1.83</sub> (Pr <sub>6</sub> O <sub>11</sub> )	11.58	250	Li <sub>2</sub> SO <sub>4</sub>	21.60
191	CeO <sub>2</sub>	9.50	221	CaO·WO <sub>3</sub>	11.80	251	Na <sub>2</sub> O·La <sub>2</sub> O <sub>3</sub> ·4MoO <sub>3</sub>	21.70
192	3CaO·SiO <sub>2</sub>	9.50	222	FeO	12.00	252	Na <sub>2</sub> CaSiO <sub>4</sub>	21.70
193	Ni <sub>2</sub> SiO <sub>4</sub>	9.50	223	5PbO·GeO <sub>2</sub> ·P <sub>2</sub> O <sub>5</sub>	12.00	253	5PbO·B <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>	21.90
194	2CaO·MgO·2SiO <sub>2</sub>	9.60	224	CoO	12.20	254	$NaD_3(SeO_3)_2$	22.00
195	Co <sub>2</sub> SiO <sub>4</sub>	9.60	225	LiFePO <sub>4</sub>	12.20	255	KD <sub>2</sub> AsO <sub>4</sub>	25.60
196	CoO·TiO <sub>2</sub>	9.63	226	LiTi <sub>2</sub> (PO <sub>4</sub> ) <sub>3</sub>	12.20	256	La <sub>0.6</sub> Li <sub>0.2</sub> TiO <sub>3</sub>	26.60
197	$2BaO \cdot CaO \cdot WO_3$	9.72	227	KH <sub>2</sub> PO <sub>4</sub>	12.30	257	RbD <sub>2</sub> AsO <sub>4</sub>	26.60
198	Fe <sub>2</sub> O <sub>3</sub>	9.90	228	AIPO <sub>4</sub>	12.50	258	$KH_3(SeO_3)_2$	28.10
199	$3ZnO \cdot V_2O_5$	10.00	229	LiNi <sub>0.33</sub> Mn <sub>0.33</sub> Co <sub>0.33</sub> O <sub>2</sub>	12.50	259	RbH <sub>2</sub> AsO <sub>4</sub>	29.60
200	2FeO·2SiO <sub>2</sub>	10.00	230	MnO	12.70	260	$NaH_3(SeO_3)_2$	30.00
201	SrO·MoO <sub>3</sub>	10.10	231	2CaO·SiO <sub>2</sub>	12.80			
202	NiO	10.20	232	NaAlSiO <sub>4</sub>	13.00			
203	CoCO <sub>3</sub>	10.20	233	$Li_7La_3Zr_2O_{12}$	13.00			
204	SiO <sub>2</sub> (Crystalline)	10.30	234	LiCoO <sub>2</sub>	13.00			
205	SrO·TiO <sub>2</sub>	10.30	235	CdO	13.20			
206	YNbO <sub>4</sub>	10.40	236	EuO	13.50			
207	MgO	10.50	237	$K_2O \cdot 2GeO_2$	13.60			
208	VPO <sub>5</sub>	10.50	238	CsAl(SiO <sub>3</sub> ) <sub>2</sub>	13.60			
209	2PbO·SiO <sub>2</sub>	10.50	239	Li <sub>4</sub> SiO <sub>4</sub>	15.00			
210	5PbO·2P <sub>2</sub> O <sub>5</sub>	10.67	240	Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	15.00			

**Table S3** Linear CTE (unit:  $10^{-6} \text{ K}^{-1}$ ) of 260 materials (continued).

Materials	Characterized particle size (µm)	Electrode density (g cm <sup>-3</sup> )	Initial Coulombic efficiency (%)
H-Nb₂O₅	1~5	3.1	96.1
H-Nb <sub>2</sub> O <sub>5</sub> -B	20~50	3.7	97.0
NPO	1~3	3.3	97.2
ΤΝΟ	~1	2.7	97.3
NWO	2~10	3.8	94.8
NWT944	1~3	3.2	96.5
NWT926	1~2	3.3	96.0
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	0.8~3.0	2.5	97.0
Meso-carbon microbeads	16~19	2.0	88.5

**Table S4** Particle sizes and electrode densities of  $H-Nb_2O_5$ ,  $H-Nb_2O_5-B$ , NPO, NTO, NWO, NWT944, NWT926,  $Li_4Ti_5O_{12}$ , and meso-carbon microbeads.

**Table S5** Comparison of the electrochemical properties among  $H-Nb_2O_5$ ,  $H-Nb_2O_5$ -B, NPO, NTO, NWO, NWT944, NWT926. Capacity measured at 200 mA g<sup>-1</sup>, rate retention defined as the ratio of capacity at 6,000 mA g<sup>-1</sup> (12 mA cm<sup>-2</sup>) to capacity at 200 mA g<sup>-1</sup>, voltage defined as average discharge voltage at 200 mA g<sup>-1</sup>, gravimetric and volumetric energy density defined as the anode side (including active material, conductive carbon, and binder) in the full cells using LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> as the cathode, and cyclability defined as capacity retention after 1,000 cycles at 12 mA cm<sup>-2</sup> (~60 C).

Materials	Capacity at 200 mA g <sup>-1</sup> (mAh g <sup>-1</sup> )	Rate retention at 12 mA cm <sup>-2</sup> (%)	Voltage (V vs. Li*/Li)	Gravimetric energy density at 12 mA cm <sup>-2</sup> (Wh kg <sup>-1</sup> )	Volumetric energy density at 12 mA cm <sup>-2</sup> (Wh L <sup>-1</sup> )	Capacity retention after 1000 cycles at 12 mA cm <sup>-2</sup> (%)
H-Nb₂O₅	192.2	60.4	1.54	364	1,128	99.7
H-Nb <sub>2</sub> O <sub>5</sub> -B	215.9	54.3	1.60	360	1,333	104.6
NPO	209.9	69.4	1.53	470	1,550	46.8
ΝΤΟ	236.3	60.1	1.50	465	1,256	69.0
NWO	180.2	69.6	1.68	394	1,499	36.1
NWT944	204.2	67.4	1.62	422	1,350	88.7
NWT926	187.1	59.0	1.57	343	1,133	79.5

**Table S6** Comparison of diffusion coefficient at 390 K, calculated activation energy and pre-A factor for the  $Li_xNb_{16}W_5O_{55}$  (x = 6.3, 8.4) and  $Li_xNb_{18}W_{16}O_{93}$  (x = 3.4, 6.8, 10.2) in reference<sup>61</sup>.

Materials	Diffusion coefficient at 390 K (m <sup>2</sup> s <sup>-1</sup> )	Activation energy (meV)	Pre-A factor
Li <sub>6.3</sub> Nb <sub>16</sub> W <sub>5</sub> O <sub>55</sub>	4.1×10 <sup>-13</sup>	54.2	2.2×10 <sup>-5</sup>
Li <sub>8.4</sub> Nb <sub>16</sub> W <sub>5</sub> O <sub>55</sub>	5.6×10 <sup>-13</sup>	56.6	2.5×10 <sup>-5</sup>
$\rm Li_{3.4}Nb_{18}W_{16}O_{93}$	1.5×10 <sup>-12</sup>	101.5	1.5×10 <sup>-4</sup>
Li <sub>6.8</sub> Nb <sub>18</sub> W <sub>16</sub> O <sub>93</sub>	1.1×10 <sup>-12</sup>	139.5	3.9×10 <sup>-4</sup>
$\rm Li_{10.2}Nb_{18}W_{16}O_{93}$	1.7×10 <sup>-12</sup>	126.2	3.4×10 <sup>-4</sup>

**Table S7** Details of electrochemical measurements for  $H-Nb_2O_5$ ,  $H-Nb_2O_5-B$ , NPO, NTO, NWO, NWT944, NWT926,  $Li_4Ti_5O_{12}$ , meso-carbon microbeads,  $LiCoO_2$ , and  $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ ,  $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ ,  $LiNi_{0.5}Mn_{1.5}O_4$ , and  $LiFePO_4$ . The listed electrode compositions are the mass ratio of active materials: conductive carbon: binder.

Materials	Electrode composition	Active material loading (mg cm <sup>-2</sup> )	Half-cell cycling window (vs. Li <sup>+</sup> /Li)	GITT titration time (mins)	GITT relaxation time (mins)
H-Nb <sub>2</sub> O <sub>5</sub>	85:9:6	1.0~2.0 5.0~11.0 (full cells)	1.0~2.5	50	900
H-Nb <sub>2</sub> O <sub>5</sub> -B	92:4:4	2.0°3.0 2.0~16.0 (different mass loading analysis) 15.0~16.0 (full cells)	1.0~2.5	50	900
NPO	90:4:6	1.0~2.0	1.0~2.5	50	900
TNO	90:4:6	1.0~2.0	1.0~2.5	60	900
NWO	85:7.5:7.5	1.0~2.0	1.0~3.0	50	900
NWT944	85:9:6	1.0~2.0	1.0~3.0	50	900
NWT926	85:9:6	1.0~2.0	1.0~3.0	50	900
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	85:7.5:7.5	1.0~2.0	1.0~2.5	/	/
Meso-carbon microbeads	90:5:5	1.0~2.0	0.01~2.5	/	/
LiCoO <sub>2</sub>	90:5:5	1.0~2.0 13.0~14.0 (full cells)	3.1~4.4	25	480
LiNi <sub>0.33</sub> Co <sub>0.33</sub> Mn <sub>0.33</sub> O <sub>2</sub>	90:5:5	1.0~2.0	3.1~4.4	50	900
LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub>	85:7.5:7.5	8.0~10.0 (full cells)	3.1~4.4	/	/
LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>	85:7.5:7.5	1.0~2.0 13.0~14.0 (full cells)	3.4~4.9	/	/
LiFePO <sub>4</sub>	85:7.5:7.5	1.0~2.0 7.0~8.0 (full cells)	2.0~4.3	/	/

### **Supplementary References**

- 1. T. Degen, M. Sadki, E. Bron, U. König and G. Nénert, Powder Diffr., 2014, 29, 13-18.
- J. Rodriguez-Carvajal, Satellite meeting on powder diffraction of the XV congress of the IUCr, Toulouse, France, 1990, 127.
- 3. A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann, High Press. Res., 1996, 14, 235-248.
- 4. X. Qiu, J. W. Thompson and S. J. Billinge, J. Appl. Crystallogr., 2004, 37, 678-678.
- 5. C. Ophus, J. Ciston and C. T. Nelson, Ultramicroscopy, 2016, 162, 1-9.
- B. H. Savitzky, S. E. Zeltmann, L. A. Hughes, H. G. Brown, S. Zhao, P. M. Pelz, T. C. Pekin, E. S. Barnard, J. Donohue,
   L. Rangel DaCosta, E. Kennedy, Y. Xie, M. T. Janish, M. M. Schneider, P. Herring, C. Gopal, A. Anapolsky, R. Dhall, K.
   C. Bustillo, P. Ercius, M. C. Scott, J. Ciston, A. M. Minor and C. Ophus, *Microsc. Microanal.*, 2021, 27, 712-743.
- 7. G. Kresse and D. Joubert, Phys. Rev. B, 1999, 59, 1758.
- 8. G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15-50.
- 9. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 10. G. Kresse and J. Furthmüller, Phys. Rev. B, 1996, 54, 11169.
- 11. G. Henkelman, B. P. Uberuaga and H. Jónsson, J. Chem. Phys., 2000, 113, 9901-9904.
- 12. K. Momma and F. Izumi, J. Appl. Crystallogr., 2011, 44, 1272-1276.
- 13. M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin and Q. Hui, J. Phys. Condens. Matter., 2007, 19, 335218.
- 14. Q. Gao, J. Wang, A. Sanson, Q. Sun, E. Liang, X. Xing and J. Chen, J. Am. Chem. Soc., 2020, 142, 6935-6939.
- 15. R. Li, Y. Qin, X. Liu, L. Yang, C. Lin, R. Xia, S. Lin, Y. Chen and J. Li, *Electrochim. Acta*, 2018, 266, 202-211.
- 16. Z. Song, H. Li, W. Liu, H. Zhang, J. Yan, Y. Tang, J. Huang, H. Zhang and X. Li, Adv. Mater., 2020, 32, 2001001.
- 17. J. Y. Cheong, C. Kim, J. W. Jung, K. R. Yoon, S. H. Cho, D. Y. Youn, H. Y. Jang and I. D. Kim, *Small*, 2017, **13**, 1603610.
- T. Li, G. Nam, K. Liu, J.-H. Wang, B. Zhao, Y. Ding, L. Soule, M. Avdeev, Z. Luo, W. Zhang, T. Yuan, P. Jing, M. G. Kim, Y. Song and M. Liu, *Energy Environ. Sci.*, 2022, **15**, 254-264.
- 19. D. Cao, Z. Yao, J. Liu, J. Zhang and C. Li, *Energy Storage Mater.*, 2018, **11**, 152-160.
- Ö. Budak, M. Geißler, D. Becker, A. Kruth, A. Quade, R. Haberkorn, G. Kickelbick, B. J. M. Etzold and V. Presser, ACS Appl. Mater. Interfaces, 2020, 3, 4275-4285.
- 21. Y. G. Sun, J. Y. Piao, L. L. Hu, D. S. Bin, X. J. Lin, S. Y. Duan, A. M. Cao and L. J. Wan, *J. Am. Chem. Soc.*, 2018, 140, 9070-9073.
- 22. Z. Hu, Q. He, Z. Liu, X. Liu, M. Qin, B. Wen, W. Shi, Y. Zhao, Q. Li and L. Mai, Sci. Bull., 2020, 65, 1154-1162.
- 23. N. Li, X. Lan, L. Wang, Y. Jiang, S. Guo, Y. Li and X. Hu, ACS Appl. Mater. Interfaces, 2021, 13, 16445-16453.
- 24. F. Su, J. Qin, P. Das, F. Zhou and Z.-S. Wu, Energy Environ. Sci., 2021, 14, 2269-2277.
- 25. Y. Zheng, Z. Yao, Z. Shadike, M. Lei, J. Liu and C. Li, Adv. Funct. Mater., 2021, 32, 2107060.
- 26. Z. Chen, H. Li, X. Lu, L. Wu, J. Jiang, S. Jiang, J. Wang, H. Dou and X. Zhang, *ChemElectroChem*, 2018, **5**, 1516-1524.
- 27. J. Meng, Q. He, L. Xu, X. Zhang, F. Liu, X. Wang, Q. Li, X. Xu, G. Zhang, C. Niu, Z. Xiao, Z. Liu, Z. Zhu, Y. Zhao and L. Mai, Adv. Energy Mater., 2019, 9, 1802695.
- 28. L. Kong, X. Cao, J. Wang, W. Qiao, L. Ling and D. Long, J. Power Sources, 2016, 309, 42-49.
- 29. R. Li, X. Zhu, Q. Fu, G. Liang, Y. Chen, L. Luo, M. Dong, Q. Shao, C. Lin, R. Wei and Z. Guo, *Chem. Commun.*, 2019, **55**, 2493-2496.
- 30. J. Y. Cheong, J.-W. Jung, D.-Y. Youn, C. Kim, S. Yu, S.-H. Cho, K. R. Yoon and I.-D. Kim, J. Power Sources, 2017,

360, 434-442.

- 31. S. Liu, J. Zhou, Z. Cai, G. Fang, Y. Cai, A. Pan and S. Liang, J. Mater. Chem. A, 2016, 4, 17838-17847.
- 32. Y. Li, Y. Wang, G. Cui, T. Zhu, J. Zhang, C. Yu, J. Cui, J. Wu, H. H. Tan, Y. Zhang and Y. Wu, ACS Appl. Energy *Mater.*, 2020, **3**, 12037-12045.
- 33. H. Sun, L. Mei, J. Liang, Z. Zhao, C. Lee, H. Fei, M. Ding, J. Lau, M. Li, C. Wang, X. Xu, G. Hao, B. Papandrea, I. Shakir, B. Dunn, Y. Huang and X. Duan, *Science*, 2017, **356**, 599-604.
- 34. H. Song, J. Fu, K. Ding, C. Huang, K. Wu, X. Zhang, B. Gao, K. Huo, X. Peng and P. K. Chu, *J. Power Sources*, 2016, 328, 599-606.
- 35. M. Y. Song, N. R. Kim, H. J. Yoon, S. Y. Cho, H. J. Jin and Y. S. Yun, ACS Appl. Mater. Interfaces, 2017, 9, 2267-2274.
- 36. J. Kang, H. Zhang, Z. Zhan, Y. Li, M. Ling and X. Gao, ACS Appl. Mater. Interfaces, 2020, 3, 11841-11847.
- 37. X. Han, P. A. Russo, C. Triolo, S. Santangelo, N. Goubard Bretesché and N. Pinna, *ChemElectroChem*, 2020, 7, 1689-1698.
- M. B. Preefer, M. Saber, Q. Wei, N. H. Bashian, J. D. Bocarsly, W. Zhang, G. Lee, J. Milam-Guerrero, E. S. Howard, R. C. Vincent, B. C. Melot, A. Van der Ven, R. Seshadri and B. S. Dunn, *Chem. Mater.*, 2020, **32**, 4553-4563.
- H. Yu, J. Zhang, M. Xia, C. Deng, X. Zhang, R. Zheng, S. Chen, J. Shu and Z.-B. Wang, J. Materiomics, 2020, 6, 781-787.
- 40. C. Yang, C. Lin, S. Lin, Y. Chen and J. Li, J. Power Sources, 2016, 328, 336-344.
- 41. L. Zhao, S. Wang, Y. Dong, W. Quan, F. Han, Y. Huang, Y. Li, X. Liu, M. Li, Z. Zhang, J. Zhang, Z. Tang and J. Li, *Energy Storage Mater.*, 2021, **34**, 574-581.
- 42. H. Yu, X. Cheng, H. Zhu, R. Zheng, T. Liu, J. Zhang, M. Shui, Y. Xie and J. Shu, Nano Energy, 2018, 54, 227-237.
- 43. H. Park, D. H. Shin, T. Song, W. I. Park and U. Paik, J. Mater. Chem. A, 2017, 5, 6958-6965.
- 44. T. Tian, L. L. Lu, Y. C. Yin, F. Li, T. W. Zhang, Y. H. Song, Y. H. Tan and H. B. Yao, *Adv. Funct. Mater.*, 2020, **31**, 2007419.
- 45. H. Yu, H. Lan, L. Yan, S. Qian, X. Cheng, H. Zhu, N. Long, M. Shui and J. Shu, Nano Energy, 2017, 38, 109-117.
- 46. H. Li, L. Shen, J. Wang, S. Fang, Y. Zhang, H. Dou and X. Zhang, J. Mater. Chem. A, 2015, 3, 16785-16790.
- 47. Z. Yao, X. Xia, S. Zhang, C.-a. Zhou, G. Pan, Q. Xiong, Y. Wang, X. Wang and J. Tu, *Energy Storage Mater.*, 2020, **25**, 555-562.
- 48. Y. Yang, J. Huang, Z. Cao, Z. Lv, D. Wu, Z. Wen, W. Meng, J. Zeng, C. C. Li and J. Zhao, *Adv Sci (Weinh)*, 2022, **9**, e2104530.
- S. Deng, H. Zhu, G. Wang, M. Luo, S. Shen, C. Ai, L. Yang, S. Lin, Q. Zhang, L. Gu, B. Liu, Y. Zhang, Q. Liu, G. Pan,
   Q. Xiong, X. Wang, X. Xia and J. Tu, *Nat. Commun.*, 2020, **11**, 132.
- 50. H. Park, H. B. Wu, T. Song, X. W. David Lou and U. Paik, Adv. Energy Mater., 2015, 5, 1401945.
- 51. S. Lou, X. Cheng, J. Gao, Q. Li, L. Wang, Y. Cao, Y. Ma, P. Zuo, Y. Gao, C. Du, H. Huo and G. Yin, *Energy Storage Mater.*, 2018, **11**, 57-66.
- 52. G. Wang, Z. Wen, L. Du, Y.-E. Yang, S. Li, J. Sun and S. Ji, J. Power Sources, 2017, 367, 106-115.
- 53. S. Lou, X. Cheng, Y. Zhao, A. Lushington, J. Gao, Q. Li, P. Zuo, B. Wang, Y. Gao, Y. Ma, C. Du, G. Yin and X. Sun, *Nano Energy*, 2017, **34**, 15-25.
- 54. S. Shen, S. Zhang, S. Deng, G. Pan, Y. Wang, Q. Liu, X. Wang, X. Xia and J. Tu, *J. Mater. Chem. A*, 2019, **7**, 22958-22966.
- 55. S. Shen, W. Guo, D. Xie, Y. Wang, S. Deng, Y. Zhong, X. Wang, X. Xia and J. Tu, *J. Mater. Chem. A*, 2018, **6**, 20195-20204.

- 56. X. Xia, S. Deng, S. Feng, J. Wu and J. Tu, J. Mater. Chem. A, 2017, 5, 21134-21139.
- 57. S. Deng, Y. Zhang, D. Xie, L. Yang, G. Wang, X. Zheng, J. Zhu, X. Wang, Y. Yu, G. Pan, X. Xia and J. Tu, *Nano Energy*, 2019, **58**, 355-364.
- 58. B. Guo, X. Yu, X.-G. Sun, M. Chi, Z.-A. Qiao, J. Liu, Y.-S. Hu, X.-Q. Yang, J. B. Goodenough and S. Dai, *Energy Environ. Sci.*, 2014, **7**, 2220-2226.
- S. Deng, H. Zhu, B. Liu, L. Yang, X. Wang, S. Shen, Y. Zhang, J. Wang, C. Ai, Y. Ren, Q. Liu, S. Lin, Y. Lu, G. Pan, J. Wu, X. Xia and J. Tu, *Adv. Funct. Mater.*, 2020, **30**, 2002665.
- 60. C. Jo, Y. Kim, J. Hwang, J. Shim, J. Chun and J. Lee, Chem. Mater., 2014, 26, 3508-3514.
- 61. K. J. Griffith, K. M. Wiaderek, G. Cibin, L. E. Marbella and C. P. Grey, Nature, 2018, 559, 556-563.
- 62. L. Yan, H. Lan, H. Yu, S. Qian, X. Cheng, N. Long, R. Zhang, M. Shui and J. Shu, J. Mater. Chem. A, 2017, 5, 8972-8980.
- 63. L. Yan, J. Shu, C. Li, X. Cheng, H. Zhu, H. Yu, C. Zhang, Y. Zheng, Y. Xie and Z. Guo, *Energy Storage Mater.*, 2019, 16, 535-544.
- 64. X. Lou, C. Lin, Q. Luo, J. Zhao, B. Wang, J. Li, Q. Shao, X. Guo, N. Wang and Z. Guo, *ChemElectroChem*, 2017, 4, 3171-3180.
- K. Lou, Z. Xu, Z. Luo, C. Lin, C. Yang, H. Zhao, P. Zheng, J. Li, N. Wang, Y. Chen and H. Wu, *Electrochim. Acta*, 2017, 245, 482-488.
- Q. Fu, H. Cao, G. Liang, L. Luo, Y. Chen, V. Murugadoss, S. Wu, T. Ding, C. Lin and Z. Guo, *Chem. Commun.*, 2019, 56, 619-622.
- 67. L. Yang, X. Zhu, X. Li, X. Zhao, K. Pei, W. You, X. Li, Y. Chen, C. Lin and R. Che, Adv. Energy Mater., 2019, 9.
- 68. M. W. Logan, D. Zhang, B. Tan and K. Gerasopoulos, J. Mater. Chem. A, 2021, 9, 11228-11240.
- 69. Y. Yang, H. Zhu, F. Yang, F. Yang, D. Chen, Z. Wen, D. Wu, M. Ye, Y. Zhang, J. Zhao, Q. Liu, X. Lu, M. Gu, C. C. Li and W. He, *Nano Lett.*, 2021, 21, 9675-9683.
- 70. X. Zhu, H. Cao, R. Li, Q. Fu, G. Liang, Y. Chen, L. Luo, C. Lin and X. S. Zhao, *J. Mater. Chem. A*, 2019, **7**, 25537-25547.
- 71. X. Lou, Q. Fu, J. Xu, X. Liu, C. Lin, J. Han, Y. Luo, Y. Chen, X. Fan and J. Li, ACS Appl. Nano Mater, 2017, 1, 183-190.
- 72. X. Cai, H. Yan, R. Zheng, H. Yu, Z. Yang, X. Zhang, M. Xia, W. Chen, Y. Cui and J. Shu, *Inorg. Chem. Front.*, 2021, **8**, 444-451.
- 73. R. Zheng, S. Qian, X. Cheng, H. Yu, N. Peng, T. Liu, J. Zhang, M. Xia, H. Zhu and J. Shu, *Nano Energy*, 2019, **58**, 399-409.
- 74. X. Lou, R. Li, X. Zhu, L. Luo, Y. Chen, C. Lin, H. Li and X. S. Zhao, ACS Appl. Mater. Interfaces, 2019, 11, 6089-6096.
- 75. Y. Li, R. Zheng, H. Yu, X. Cheng, T. Liu, N. Peng, J. Zhang, M. Shui and J. Shu, ACS Appl. Mater. Interfaces, 2019, **11**, 22429-22438.
- 76. C. Yang, Y. Zhang, F. Lv, C. Lin, Y. Liu, K. Wang, J. Feng, X. Wang, Y. Chen and J. Li, *J. Mater. Chem. A*, 2017, **5**, 22297-22304.
- 77. X. Zhu, J. Xu, Y. Luo, Q. Fu, G. Liang, L. Luo, Y. Chen, C. Lin and X. S. Zhao, J. Mater. Chem. A, 2019, 7, 6522-6532.
- 78. Q. Fu, X. Liu, J. Hou, Y. Pu, C. Lin, L. Yang, X. Zhu, L. Hu, S. Lin, L. Luo and Y. Chen, *J. Power Sources*, 2018, **397**, 231-239.
- 79. Q. Fu, R. Li, X. Zhu, G. Liang, L. Luo, Y. Chen, C. Lin and X. S. Zhao, J. Mater. Chem. A, 2019, 7, 19862-19871.
- 80. A. A. Hubaud, D. J. Schroeder, B. J. Ingram, J. S. Okasinski and J. T. Vaughey, J. Alloys Compd., 2015, 644, 804-807.
- N. Anantharamulu, K. Koteswara Rao, G. Rambabu, B. Vijaya Kumar, V. Radha and M. Vithal, *J. Mater. Sci.*, 2011, 46, 2821-2837.

82. E. J. Cheng, K. Hong, N. J. Taylor, H. Choe, J. Wolfenstine and J. Sakamoto, *J. Eur. Ceram. Soc.*, 2017, **37**, 3213-3217.
83. Y. Touloukian, R. Kirby, R. Taylor and T. Lee, *New York*, 1970, 89.