

Electronic Supplementary Information

for

**Facet-engineered NaNbO₃ cubes with exposed (101) plane for
enhanced lithium-ion storage**

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Experimental Section

Material Synthesis

All chemical reagents were used directly without any further pretreatment. Three kinds of NaNbO_3 samples exposed to different degrees of the (101) crystal plane were prepared via the typical hydrothermal method. First, 1.5 g of sodium hydroxide (NaOH) and 0.2 g of niobium pentachloride (NbCl_5) were dispersed in 30 mL of deionized water with stirring at room temperature for 1 hour. Subsequently, the suspension was transferred to an autoclave and reacted at 150 °C for 24 hours. After the reaction, the obtained sample was collected, washed with deionized water and ethanol, and dried in an oven at 60 °C. In this experiment, three kinds of NaNbO_3 (named NaNbO_3 -1, NaNbO_3 -3, NaNbO_3 -6) samples exposed to different degrees of the (101) crystal plane were obtained by controlling different stirring time (1h, 3h, 6h). Therefore, repeated the above experimental steps, but varied the stirring time to get other NaNbO_3 samples.

Material Characterization

The morphology and microstructure of the samples were observed by the scanning electron microscope (FE-SEM, JEOL, JSM-7800F) and the high-resolution transmission electron microscope (HRTEM, FEI Tecnai G² F30 S-Twin TEM operated at 300 kV). The composition and phase information of the samples were investigated by the powder X-ray diffractometer (XRD, German Bruker D8 with $\text{Cu K}\alpha$, $\lambda=1.54056 \text{ \AA}$), with the scanning range from $10^\circ \sim 80^\circ$ and the scanning rate with 5° min^{-1} .

Electrochemical Measurement

The 80 wt. % active material, 10 wt. % super conducting carbon black (SCCB,

Ketjenblack EC-600JD) and 10 wt. % polyvinylidene fluoride (PVDF) binder were mixed in a certain amount of N-Methyl pyrrolidone (NMP) to make the uniform slurry. Then, applied uniformly by a doctor-blade method the slurry onto the prepared coated carbon copper foil. Afterword, the working electrodes were dried in a vacuum oven at 60 °C for 12 hours. Finally, the CR2032 type coin cells were assembled in an argon-filled glove box. The lithium metal was used as the counter electrode. The porous polypropylene membrane (Celgard 2400) was used as the separator. The 1.0 mol L⁻¹ LiPF₆ in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 v/v/v) was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were recorded on the electrochemical workstation (Gamry Interface 1000E Potentiostat) and the galvanostatic charging and discharging were measured using a Land CT 2001A battery test system.

DFT calculations

All the electronic structure calculations were performed using plane-wave periodic density functional theory as implemented in the Vienna Ab-Initio Simulation Package (VASP).¹⁻² The PBE density functional combined with PAW pseudopotentials was used to describe electron-ion interactions. In order to more accurately estimate the non-bonded interaction between Li and the NaNbO₃, the dispersion corrected term was added into the PBE functional.³ Two typical slab models were constructed to explore the adsorptive strength and diffuse barriers of Li atom on NaNbO₃ surface (**Fig. S1**), namely, NaNbO₃(101) and NaNbO₃(141). As can be seen from it, both slab models consist of four layers and the compositions are both Na₁₈Nb₁₈O₄₈, which is the exactly an integral multiple of the

chemical formula. Hence, it is believed that the models can give reasonable results for the adsorptive strength and diffuse barriers of Li atom. In addition, to avoid the artificial interaction between adjacent surface, a 15 Å vacuum in *c*-axis was constructed. The surface Monkhorst–Pack meshes of 3×3×1 K-point sampling was used to describe the surface Brillouin zone of NaNbO₃(101), whereas the K-point sampling of NaNbO₃(141) was set to 1×3×1. For the structural relaxation, the first layer of both models was optimized and other three layers were fixed for both consideration of accuracy and computational cost. Besides, the energy cutoff of 400 eV for the plane-wave expansion of the PAW's and the Gaussian smearing method were adopted. For the diffusion barriers, the climbing image nudged-elastic band (CI-NEB) method with 5 intermediate images was utilized to search the transition states. The adsorptive energy (E_{ads}) was calculated as following formula:

$$E_{ads} = E_{com} - E_{slab} - E_{Li} \quad (1)$$

Where the E_{com} stands for the energy of complex formed by adsorption of Li, E_{slab} is the energy of the slab model, E_{Li} is the energy of single Li atom.

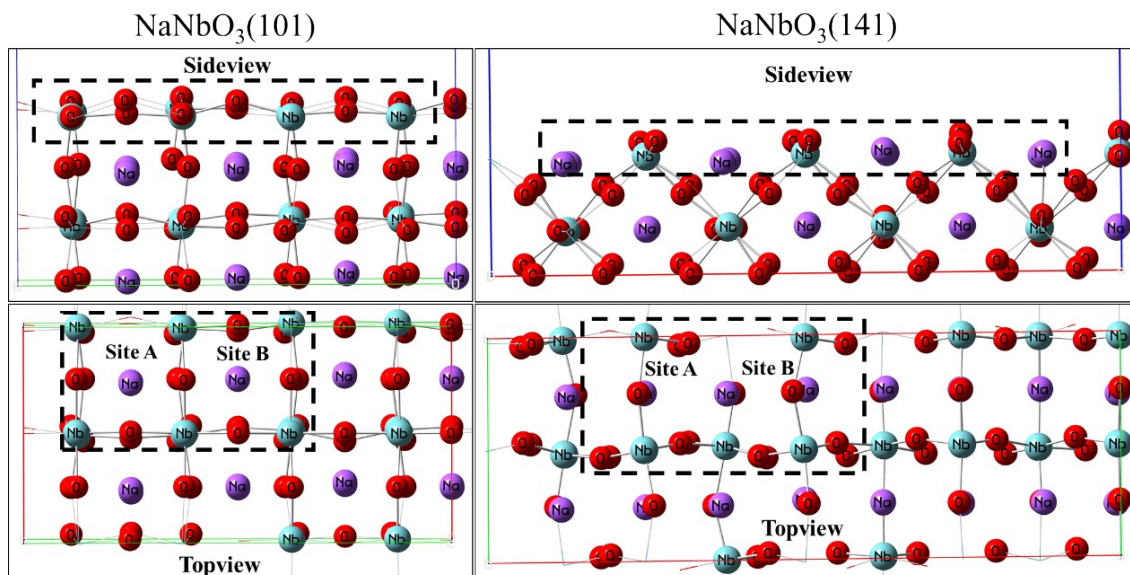


Fig. S1 Overview of the slab models for NaNbO₃ (101) and NaNbO₃ (141) surfaces. The first/second row illustrate the side view/top view of NaNbO₃ (101) and NaNbO₃ (141) surfaces.

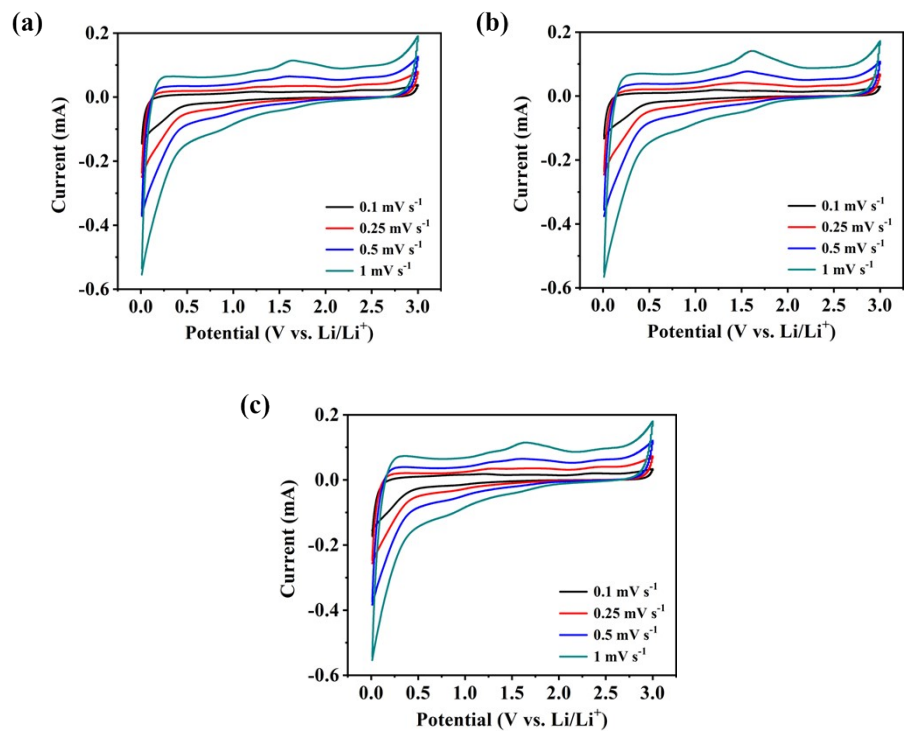


Fig. S2 CV curves from 0.1 mV s⁻¹ to 1 mV s⁻¹ of (a) 1 μm NaNbO₃ cube, (b) 3 μm NaNbO₃ cube, and (c) 6 μm NaNbO₃ cube.

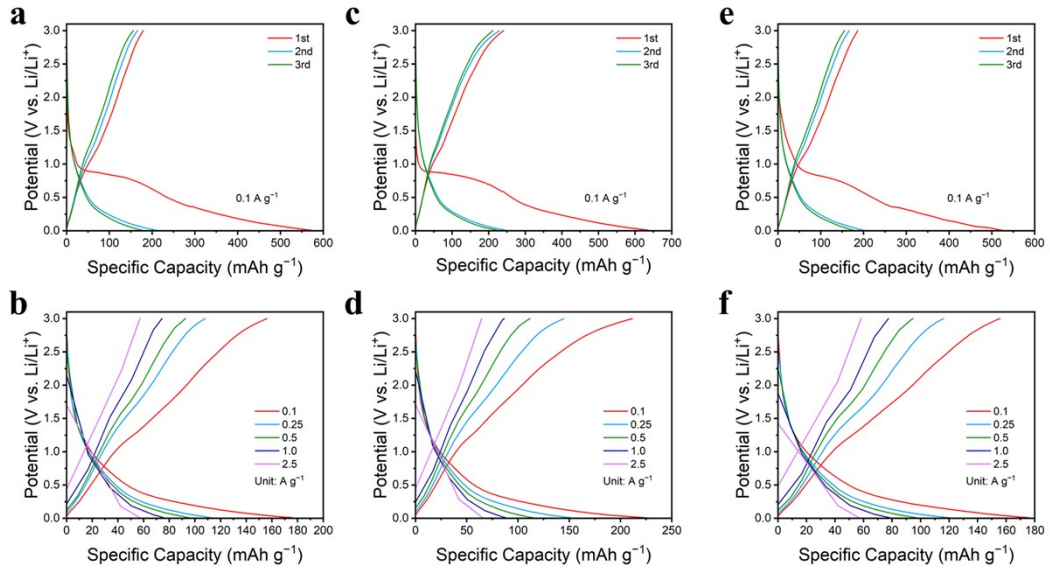


Fig. S3 Galvanostatic charge/discharge curves of (a, b) 1 μm (c, d) 3 μm, and (e, f) 6 μm NaNbO₃ cube at a low current density and the various current densities.

Table S1. The numerical values of R_b , R_{ct} , σ_{Li} and D_{Li} of the $NaNbO_3$ cubes of different sizes.

Samples (Li-ion)	R_b (Ohm)	R_{ct} (Ohm)	σ_{Li} (Ohm s ⁻¹)	D_{Li} (cm ² s ⁻¹)
1 μ m $NaNbO_3$	2.76	82.23	60.06	1.96*10 ⁻¹¹
3 μ m $NaNbO_3$	1.02	66.92	25.99	1.05*10 ⁻¹⁰
6 μ m $NaNbO_3$	0.99	56.96	10.13	6.9*10 ⁻¹⁰

Reference

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2. G. Kresse and J. Furthmüller, *Phys. Rev. B - Condens. Matter.*, 1996, **54**, 11169.
3. S. Grimme, A. Hansen, J. G. Brandenburg and C. Bannwarth, *Chem. Rev.*, 2016, **116**, 5105.