Supporting information for

Electrochemical Lithium Intercalation in monoclinic $Nb_{12}O_{29}$

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Experimental

Synthesis of $Nb_{12}O_{29}$

Depending on the synthesis temperature, $Nb_{12}O_{29}$ can form two polymorphs with monoclinic and orthorhombic symmetry, respectively.[S1,S2] They have the same basic structural unit, *i.e.* columns of 4×3×∞ corner-shared $NbO_{6/2}$ octahedra, but exhibit different arrangements of these columns. Since phase-pure orthorhombic $Nb_{12}O_{29}$ is difficult to obtain and it is less conductive than the monoclinic phase,[S2] we focus on the monoclinic $Nb_{12}O_{29}$ in this paper.

Monoclinic $Nb_{12}O_{29}$ samples were prepared from a stoichiometric mixture of H-Nb_2O_5 and Nb metal. H-Nb_2O_5 was first obtained by firing the commercially available Nb_2O_5 at 1100 °C for 24 h in air. The mixture of H-Nb_2O_5 and Nb metal was thoroughly ground in an agate mortar and then cold-pressed into pellets of ca. 3 mm in diameter under a 20 T loading force. These pellets were wrapped in molybdenum foil and heated at 1200 °C for 60 h in a vacuum furnace with pressures below 10^{-6} Torr. The details about preparation and characterizations of samples can be referred to the literature. [S2]

The $Nb_{12}O_{29}$ material was coated with carbon by dispersing the ground powder into a sucrose aqueous solution; the amount of carbon was about 5 wt.% of $Nb_{12}O_{29}$. The powder was calcined at 700 ^oC for 10 h in high vacuum with pressure below 10^{-6} Torr.

Characterization of materials

Powder x-ray diffraction (XRD) data were collected in the 2θ range 10 – 90° with a step size of 0.02° and a dwell time 10 s on a Philips X'pert difrractometer with Bragg-Brentano geometry and Cu Kα radiation (λ = 1.54056 Å). The XRD pattern was refined with the Rietveld method and the FullProf program.[S3] The sample morphology was examined with a scanning electron microscope (SEM, JEOL JSM-5610). Thermogravimetric analysis (TGA) on a *ca*. 30 mg powder sample was performed with a Perkin-Elmer Series 7 Thermal Analyzer at a heating rate of 1 ^{o}C min^{-1} from 20 ^{o}C to 850 ^{o}C in air. Before *ex-situ* XRD measurement, the reacted electrode was taken out from the cell in a glove box and washed by anhydrous DMC. The electrode sheet was pasted on a sample holder and covered by a layer of Mylar film.

Electrode fabrication and electrochemical tests

The electrodes were fabricated by mixing 75 wt.% $Nb_{12}O_{29}$ powder with 20 wt.% acetylene black as a current conductor, and 5 wt.% polytetrafluoroethylene (PTFE) as a binder. The mixture was rolled into thin sheets and punched into circular disks 7.8 mm in diameter as electrodes. The typical electrode mass and thickness were 5-10 mg and 0.03-0.08 mm, respectively. Electrochemical performances were evaluated with a standard CR 2032 coin cell assembled in an argon-filled glove box. Lithium-metal foil was used as the counter and reference electrodes. 1 M $LiPF_6$ in 1:1 ethylene carbonate (EC) and diethyl carbonate (DEC) was used as the electrolyte. The sealed cells were aged for 12 h before discharge/charge to ensure full absorption of the electrolyte into the electrode. Galvanostatic cycling studies were carried out with a battery-testing system (Arbin BTS-2043).

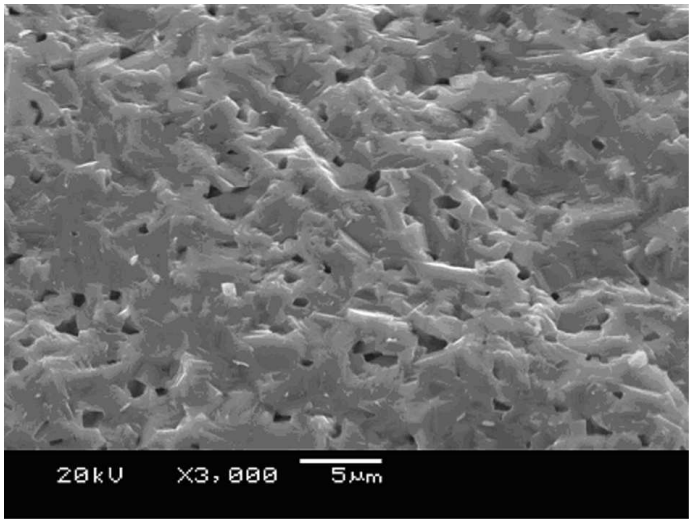

Figure S1. SEM image of the as-obtained $Nb_{12}O_{29}$ sample.

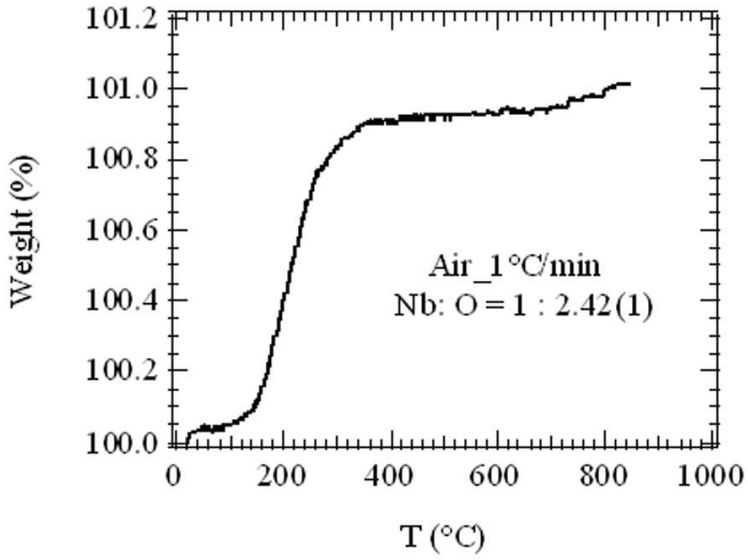

Figure S2. TGA data of $Nb_{12}O_{29}$ measured in air up to 850°C.

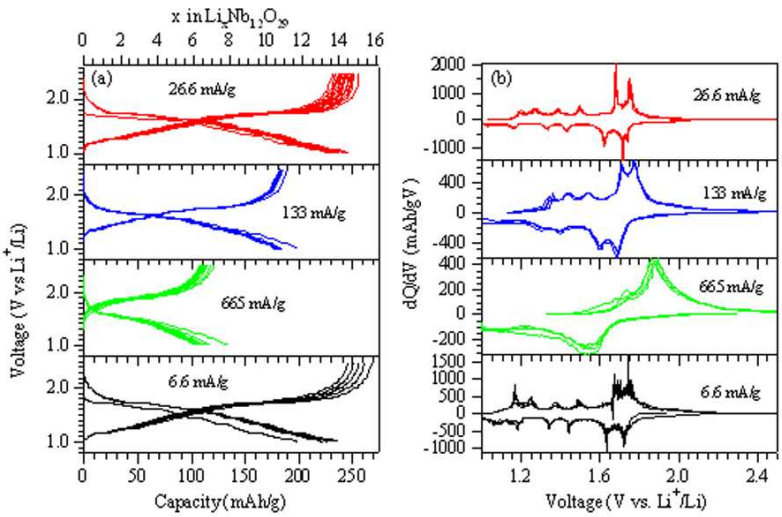

Figure S3. (a) Charge-discharge curves of monoclinic $Nb_{12}O_{29}$ with carbon coating for the first 20 cycles between 2.5 and 1.0 V cycled at different current rates from 26.6 to 133, and 665 mA/g, and then back to 6.6 mA/g; (b) Differential capacity plots derived from the charge-discharge curves of the 1st, 5th, 10th and 20th cycles at corresponding currents.

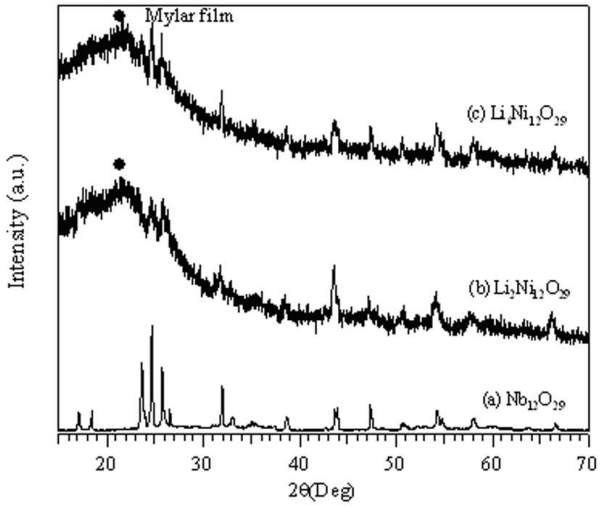

Figure S4. *Ex-situ* XRD patterns of $Nb_{12}O_{29}$: (a) before discharge, (b) discharge to 1.75 V, and (c) discharge to 1.6 V during the 5th cycle at 6.6 mA/g.

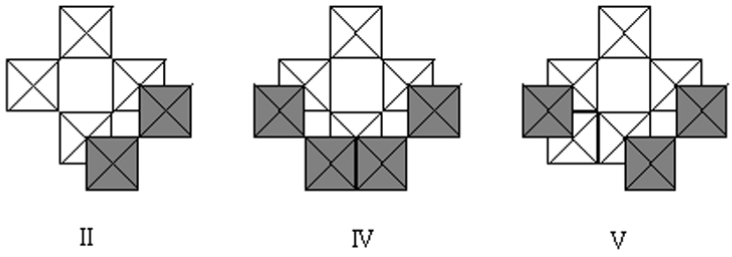

Figure S5. Cavity types of available sites present in monoclinic $Nb_{12}O_{29}$ described by Cava *et al*. [S4]

Reference

(S1) Andersen, E. N.; Klimezuk, T.; Miller, V. L.; Zandbergen, H. W.; Cava, R. J. *Phys. Rev. B* **2005**, *72*, 033413.

(S2) Cheng, J.-G.; Zhou, J.-S.; Goodenough, J. B.; Zhou, H. D.; Wiebe, C. R.; Takami, T.; Fujii, T. *Phys. Rev. B* **2009**, *80*, 134428.

(S3) Rodríguez-Carvajal, J. *Physica B* **1993**, *192*, 55.

(S4) Cava, R. J.; Murphy, D. W.; Zahurak, S. M. *J. Electrochem. Soc.* **1983**, *130*, 2345.