Supporting Information

Probing the pseudo-1-D ion diffusion in lithium titanium niobate anode for

Li-ion battery

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EXPERIMENTAL: SYNTHESIS AND CHARACTERIZATION

*Synthesis of KTiNbO*₅: KTiNbO₅ is synthesized by a sol-gel method reported elsewhere.³³ Briefly, 2.95 ml (0.01 mol) of titanium tetra-isopropoxide (TTIP) (Sigma-Aldrich) is dissolved in ~ 33 ml of ethylene glycol (EG) resulting a clear solution. 28.8 g (0.15 mol) of citric acid (CA) and 0.7455 g (0.01 mol) of KCl are added to this solution such that a transparent solution is formed. 2.7 g (0.01 mol) of niobium pentachloride (NbCl₅) (Sigma-Aldrich) is dissolve in ~ 60 ml of dried methanol (MeOH) separately. The Nb-salt alcohol solution is added to the Ti-solution and condensed to form a gel at 130 °C. The gel is pyrolyzed at 400 °C for 4 h to form a black powder precursor. This sample further on heating at 700 °C in air for 2 h leads to the formation of white colored KTiNbO₅.

Synthesis of $Li_xK_{1-x}TiNbO_5$ (*Li-Ti-niobate*): $Li_xK_{1-x}TiNbO_5$ is synthesized from the assynthesized KTiNbO₅ by an ion-exchange method. In a typical procedure, 100 mg of KTiNbO₅ is dispersed in aqueous solution (20 ml) of Li_2SO_4 followed by stirring under N₂ atmosphere at around 55- 60 °C for 3 days. To ensure the maximum ion-exchange, the concentration of Li_2SO_4 is taken 20 times mole excess of KTiNbO₅. The as-synthesized Li-Ti-niobate is separated by centrifugation at 8000 rpm followed by washing the precipitate with de-ionized water, ethanol and finally dried at 70 °C in vacuum.

The as-synthesized $Li_xK_{1-x}TiNbO_5$ particles is downsized (d-Li-Ti-niobate) by ball milling 100 mg of as-prepared LiTiNbO₅ in pulverisette 23 planetary ball miller with three balls of total weight 6 g. Carbon coated downsized $Li_xK_{1-x}TiNbO_5$ (cd-Li-Ti-niobate) sample is prepared by hydrothermal carbonization of glucose solution.

Instrumentation: Powder X-ray diffraction (PXRD) pattern of the synthesized samples are recorded in the 2 θ range of 5°-80° in nickel filtered Philips X'pert diffractometer using Cu K α radiation, ($\lambda = 1.5418$ Å). Raman spectra of the samples are collected on a LabRam HR system with 532 nm diode pump solid state LASER. The AXIS-Ultra, instrument of Kratos

using monochromatic AlKa radiation (225 W, 15 mA, 15 kV) is used to record the X-ray photo electron spectroscopy (XPS) data. Elemental analysis of the samples is carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) in Themo-iCAP 6000 series model ICP-OES spectrometer. KCl, Nb₂O₅, TiO₂, and LiCl are chosen as the standards for the respective elements present in the electrode sample, $Li_xK_{1-x}TiNbO_5$ respectively. The concentration of the cations are measured at the emission wavelength of 670 nm, 766.5 nm, 510 nm and 327 nm for Li⁺, K⁺, Nb⁵⁺and Ti⁴⁺ respectively. Thermogravimetric analysis (TGA) is performed using a Mettler Toledo thermogravimetric system from room temperature (30 °C) to 800 °C under oxygen atmosphere with a heating rate of 5 °C/min. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and the selected area electron diffraction (SAED) patterns are recorded on a FEI TecnaiTM F30 machine operating at 300 kV. Cyclic voltammogram (CH Instrument-CH608C) of Li-Ti-niobate has been carried out in the voltage range (0.01- 3.5) V at a scan rate of 0.25 mV/s in a Swagelok cell, where metallic Li acts as both reference and counter electrode. The galvanostatic charge/discharge cycling are performed on an Arbin Corp. (Model BT 2000), USA at different C-rates ($1C = 353 \text{ mA g}^{-1}$) in the voltage range of (0.2-2.75) V (versus Li⁺ /Li). To study the kinetics of lithium diffusion inside the electrode material, galvanostatic intermittent titration technique (GITT) is performed on Arbin Instrument. For GITT the testing cells are first galvanostatically discharged and charged for one cycle to avoid the contribution of extra lithium storage during SEI formation. From the subsequent cycle the cells are discharged for 30 min at C/25 current rate and kept at rest for 5 h to reach its equilibrium potential. This protocol is repeated until the lower cut-off voltage is reached. The same protocol is followed in the charging process and the cells are charged until the upper cut-off voltage is reached.

Electrochemical cell assembly: The electrochemical studies of the materials are intensively tested in SwagelokTM cells with lithium foil (Aldrich, thickness = 0.75 mm) as a counter and reference electrode, AGM (absorptive glass mat) as separator and 1 M LiPF₆ in 1:1 volume ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte. For casting, slurry is prepared with the electro-active material, acetylene carbon black (Alfa Aesar) and polyvinylidene fluoride (PVDF, Kynarflex) in a weight ratio of 80:10:10 in cyclopentanone. This is then cast on a battery grade clean copper foil and dried overnight at atmospheric temperature. All cell assemblies are done at 25 °C in a glove box (MBraun) under argon atmosphere (H₂O < 0.5 ppm, O₂ < 0.5 ppm).

Details of theoretical calculations: To ascertain and probe possible preferential direction of the Li⁺-ion diffusion, the density functional theory (DFT) based calculations are performed. The calculations are performed using the VASP (Vienna *ab-initio* Simulation Package) program based on the projector-augmented wave (PAW)^{34, 35} formalism in order to obtain the minimum energy configuration structure. Since the experimentally obtained composition for Li-Ti-niobate is obtained as $Li_{0.55}K_{0.45}TiNbO_5$ (vide infra), for the theoretical calculations a 50% exchange structure i.e. Li_{0.5}K_{0.5}TiNbO₅ is taken. The crystal structure of Li_{0.5}K_{0.5}TiNbO₅ (corresponding lattice parameters: a = 13.12 Å, b = 11.43 Å, c = 18.33 Å and $\alpha = 86.07^{\circ}$, $\beta =$ 88.65° and $\gamma = 90.30^{\circ}$) has been created using Special Quasi Random Structure (SQS) approach embedded USPEX code.³⁶ The Perdew-Burke-Ernzerhof (PBE) type of generalized gradient approximation (GGA)³⁷ has been employed as the exchange-correlation functional. A 500 eV energy cut off for the plane wave basis set and gamma point sampling for the Brillouin zone has been considered for structural minimization with 0.01eV/Å as the force convergence criteria. Lithium diffusion is investigated in the crystal structure of Li_{0.5}K_{0.5}TiNbO₅ with a 2x3x1 supercell containing 240 atoms. The climbing image nudged elastic band method (cNEB)³⁸ framework was employed to derive the activation energy of each considered Li⁺ migration pathway with a sufficient number of images. The diffusion coefficient for each pathway is, then, evaluated as $D = d^2 v_0 \exp\left(-\frac{E_a}{k_b T}\right)$ where *d* is the average hop distance, v_0 is the attempt frequency, E_a is the activation energy, k_b is the Boltzmann constant and *T* is the temperature.

Table-S1: Comparison of 2θ and *d*-spacing value of (00l) peaks of KTiNbO₅ and Li-Tiniobate.

	KTiNbO ₅		Li-Ti-niobate		Difference in	
	20	d value/Å	20	d value/Å	20	d value/Å
(002)	9.5	9.2	9.3	9.5	0.2	0.2
(004)	19.2	4.6	18.8	4.7	0.4	0.1



Fig. S1. ICP-OES results for elemental compositions of Li-Ti-niobate



Fig. S2 Indexing of FFT pattern of HRTEM image shown in Figure 3d



Fig. S3 Equilibrium potential versus Vt plot



Fig. S4 (a), (b) and (c) are the HRTEM images showing lattice fringes (the FFT patterns are shown as inset of the respective image) of Li-Ti-niobate. (d), (e) and (f) are the images (inverse FFT patterns) generated by extracting only the (002), (200) and (020) planes respectively from the FFT patterns in (a), (b) and (c) respectively. Insets in (d-f) represent patterns that are masked to obtain the respective inverse FFT patterns.



Fig. S5 A zoomed-in view of cyclic voltammogram of Li-Ti-Niobate. Peaks at 2.4 V and 2.65 V correspond to the Nb⁵⁺ | Nb⁴⁺ and Nb⁴⁺ | Nb⁵⁺ redox processes.



Fig. S6 (a-d) are the derivative plot of cathodic scan of (1-4) cycles respectively. The vertical line at around 0.65 V indicates the formation of Ti^{2+} over the cycles



Fig. S7 GITT curve of Li-Ti-niobate versus Li+|Li electrode in the voltage range 1-3V



Fig. S8 TEM image of (a) d- Li-Ti-niobate and (b) cd-Li-Ti-niobate.



Fig. S9 Capacity vs cycle no. plot of d- Li-Ti-niobate (without carbon coating) in the voltage range 0.2-2.75 V at C/10 current.



Fig. S10 Coulombic efficiency of Li-Ti-niobate in two different voltage range and downsized carbon coated Li-Ti-niobate.