

Supporting Information

Mo-doped TiNb_2O_7 anode for lithium-ion batteries with high rate capability due to charge redistribution

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Experimental

Synthesis: TNO (TiNb_2O_7) and Mo-TNO ($\text{Ti}_{0.95}\text{Mo}_{0.05}\text{Nb}_2\text{O}_7$) were synthesized by a conventional sol-gel method. Starting reagents $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (with a 1:2 and 0.95:2 molar ratio, respectively) were dissolved in ethanol and acetic acid with vigorous stirring for 5 h. After stirring, the solution was oven-dried overnight. The obtained powder was mixed with MoO_3 using a ball-mill and the ground powders were heat-treated at 1000 °C for 5 h in air.

Characterization: The phase compositions and crystal structures of the synthesized powders were characterized by XRD between 10 and 90° (2θ) using a D8 Discover with a 45 kV acceleration voltage and 0.650 mA tube current. Scanning electron microscope (SEM) images were obtained using a HITACHI S-4100 with an acceleration voltage of 5 kV. The electronic conductivities and mobilities were measured using a Hall effect measurement system (HMS 5000, Ecopia) using the van der Pauw method (i.e., four-point probe measurement) with sample powders pressed into pellets at a 10 ton pressure. The XPS spectra were recorded on a PHI 5000 VersaProbe system using a monochromated Al $K\alpha$ X-ray beam. Charge correction was performed using the C 1s peak (284.6 eV) as the reference; a Shirley background subtraction was applied to all XPS data. All peaks were fitted with a Gaussian–Lorentzian function to deconvolute overlapping peaks. The spin polarized PDOS calculations were performed using the CASTEP code.¹ The occupied states of the electrons were calculated using the Perdew-Wang 1991 (PW91) functional, based on the generalized gradient approximation (GGA).² To improve the GGA approach, the intra-atomic Coulomb interaction was modified through the LDA+U formalism, and the smearing factor was set to 0.02 eV. The supercell with two unit cells arranged along the b-direction (120 atoms) is employed in our calculations. 12 Ti atoms, 24 Nb atoms, and 84 O atoms were employed in the calculation for TNO. One of the

Ti atoms situated in 4i site was substituted with Mo atom in the calculation for Mo-TNO (11 Ti atoms, 1 Mo atom, 24 Nb atoms, and 84 O atoms).

Battery Tests: The sample electrodes were prepared with the active material, acetylene black, and polyvinyl difluoride (PVDF), mixed at a weight ratio of 70:20:10. The slurry was coated on a Cu foil and vacuum-dried at 75 °C for 24 h. A microporous polyethylene membrane was used as a separator, and 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 v/v) was used as the electrolyte. The coin cells (CR2032) were assembled with a Li foil on a Cu mesh as the counter and reference electrode in a glove-box filled with Ar gas. The charge and discharge tests were carried out on a standard battery cycler (WonATech) at different C-rates in the potential range of 1.0–3.0 V (vs Li⁺/Li). Full cell tests were performed with the LiMn₂O₄ (Sigma Aldrich) cathode in the potential range of 1.6–2.8 V at various C-rates (1C is assumed as 150 mAh/g as previously reported).³ The diffusion coefficients of the Li ions in all samples were measured using a galvanostatic intermittent titration technique (GITT).⁴ EIS measurements were also carried out using the VMP3 (Biologic science instruments) over the half cells. The frequency range was 100 MHz to 1 Hz with an amplitude of 10 mV.

References

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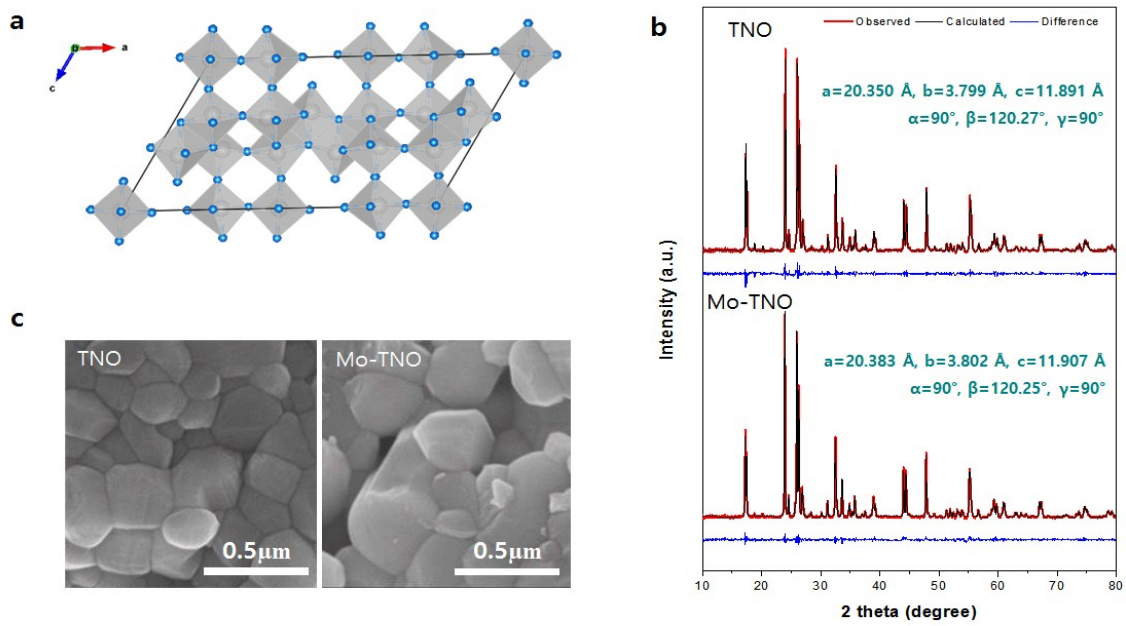


Figure S1. (a) TNO unit cell, (b) XRD patterns (observed: red lines, calculated: black lines, difference: blue lines), and Rietveld refinement profiles of the TNO and Mo-TNO, and (c) SEM images of the TNO and Mo-TNO.

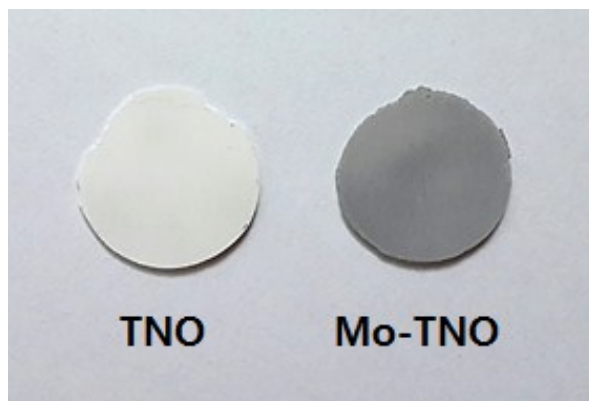


Figure S2. Sample colour of TNO and Mo-TNO

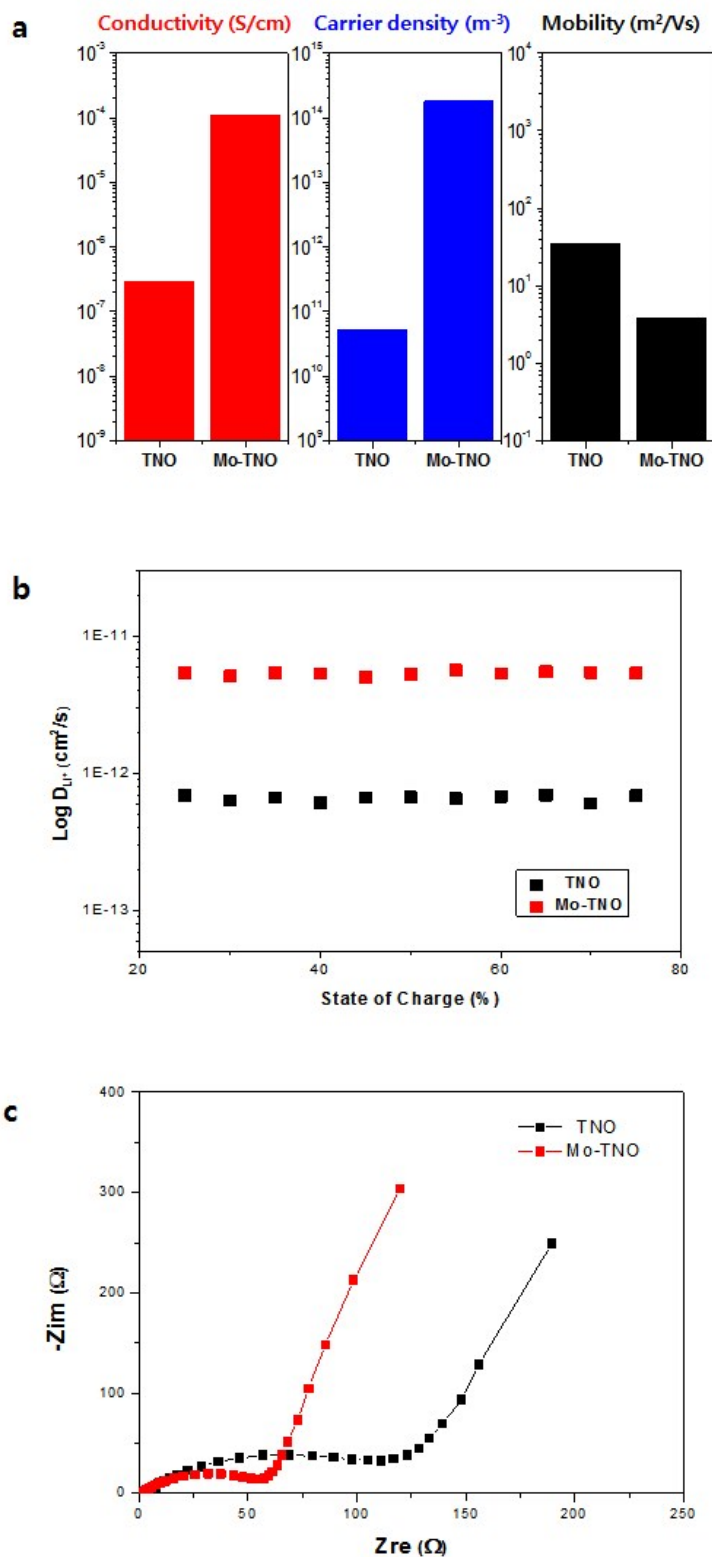


Figure S3. (a) Electronic conductivity (red bars), carrier density (blue bars), and mobility (black bars) of TNO and Mo-TNO. (b) Diffusion coefficients of TNO (black squares) and Mo-TNO (red squares). (c) Nyquist plots of TNO (black squares) and Mo-TNO (red squares) over the frequency range 100 MHz to 0.01 Hz.

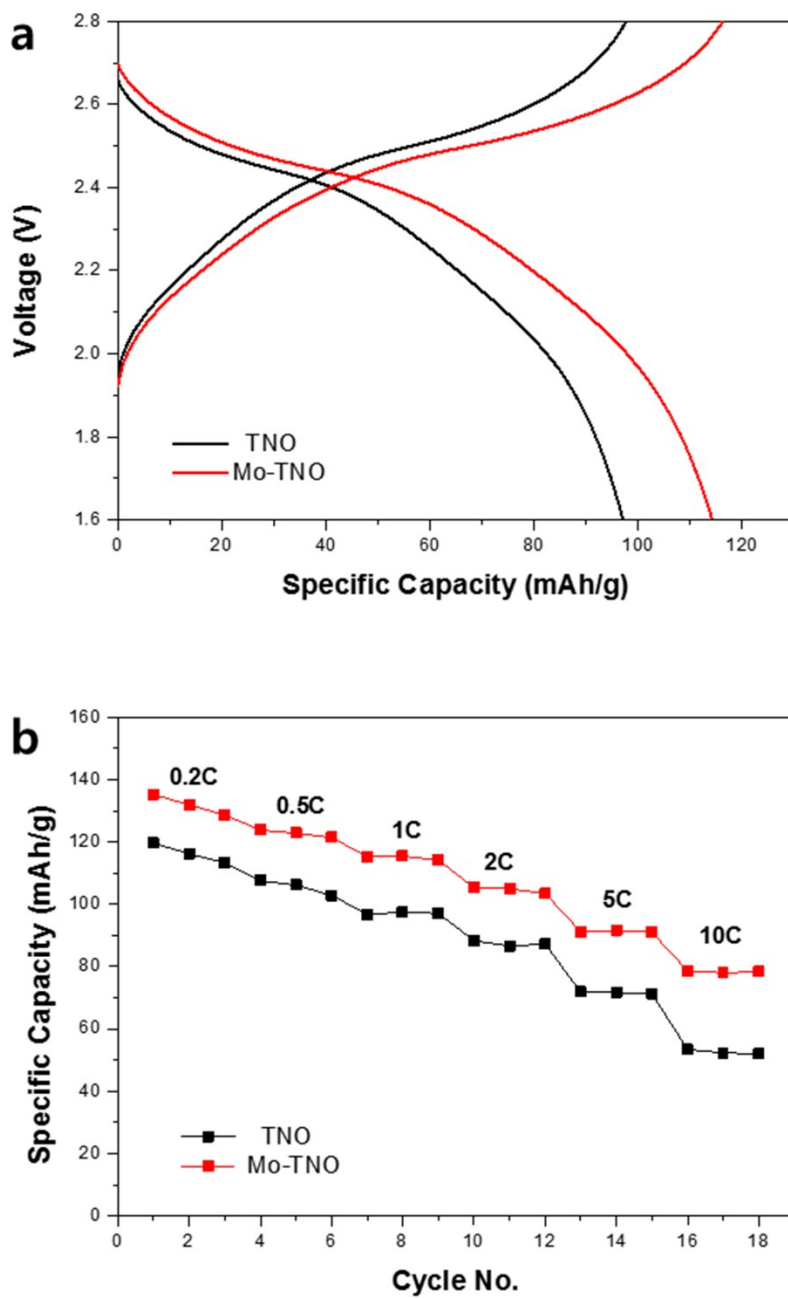


Figure S4. (a) Representative galvanostatic charge-discharge curves at 1C and (b) rate capabilities of full-cells.

Table S1. Lattice Parameters obtained by Rietveld Refinement

Sample	TNO	Mo-TNO
a / Å	20.350(0)	20.383(0)
b / Å	3.799(0)	3.802(1)
c / Å	11.891(1)	11.907(0)
α / °	90	90
β / °	120.27(1)	120.25(0)
γ / °	90	90
R_{wp} / %	6.68	6.50
GOF	1.5	1.4