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Supporting Information

Titanium Niobium Oxide $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ /Carbon Hybrid Electrodes Derived by Mechanochemically Synthesized Carbide for High-Performance Lithium-Ion Batteries

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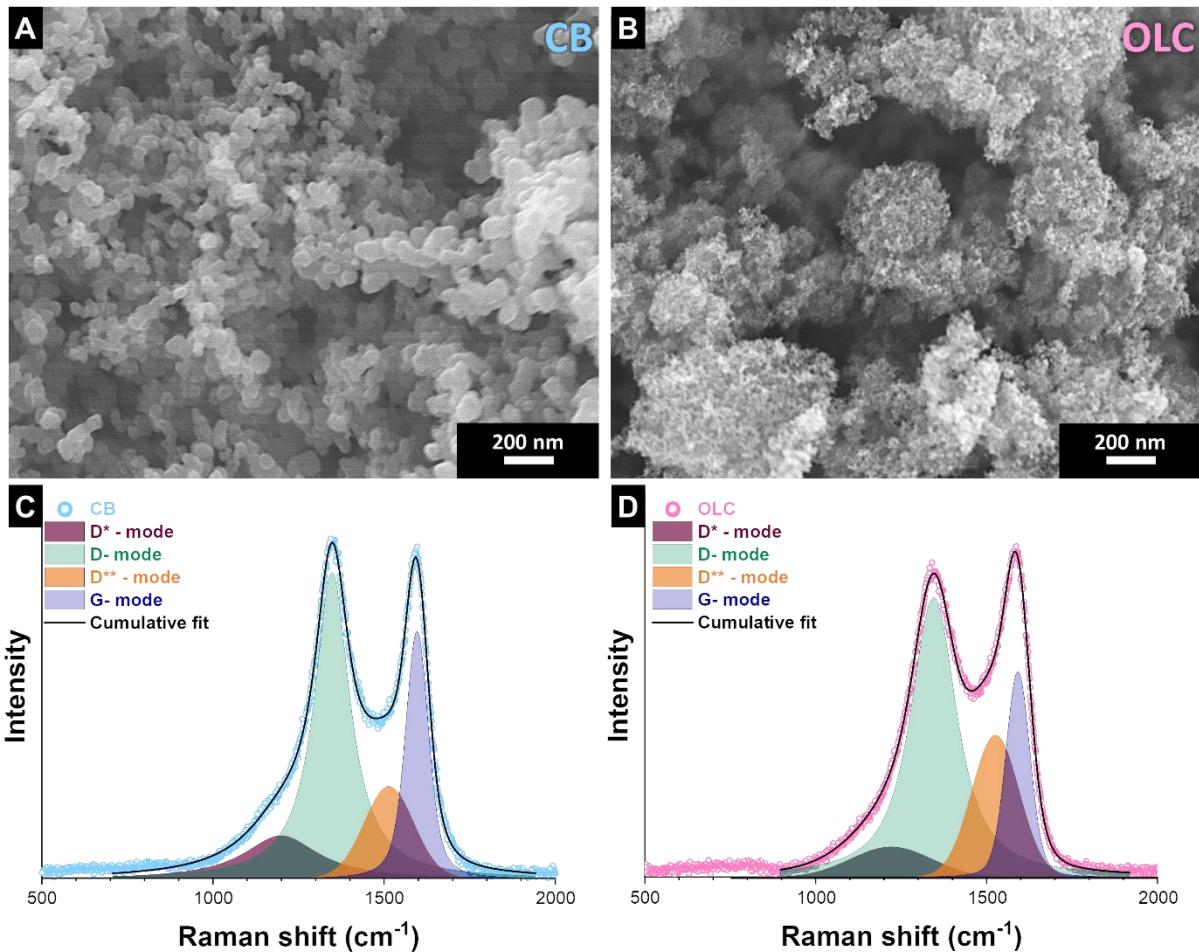


Fig. S1. (A-B) Scanning electron micrographs of (A) CB, and (B) OLC. Fitted Raman spectra of (C) CB, and (D) OLC.

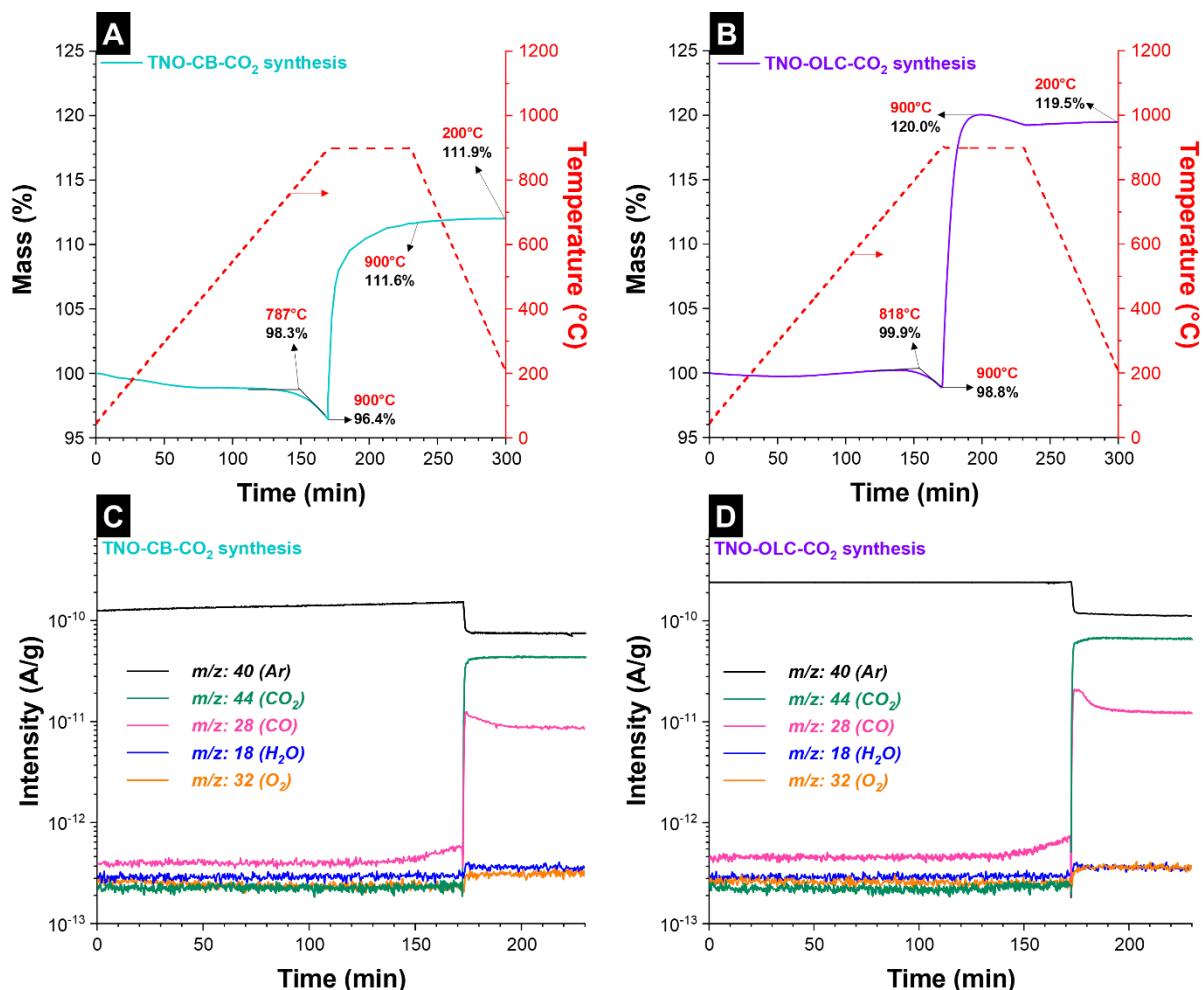


Fig. S2. (A-B) Thermograms of (A) TNO-CB-CO₂, and (B) TNO-OLC-CO₂ synthesis following the synthesis protocol of hybrid materials. The corresponding mass spectra of TGA-MS measurements of (C) TNO-CB-CO₂, and (D) TNO-OLC-CO₂ synthesis.

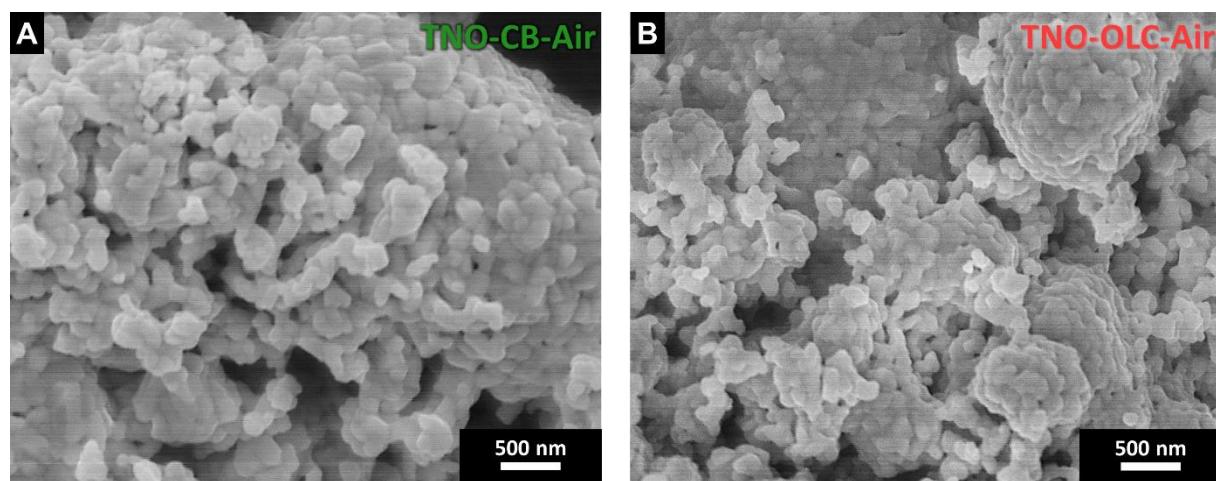


Fig. S3. (A-B) Scanning electron micrographs of (A) TNO-CB-Air, and (B) TNO-OLC-Air.

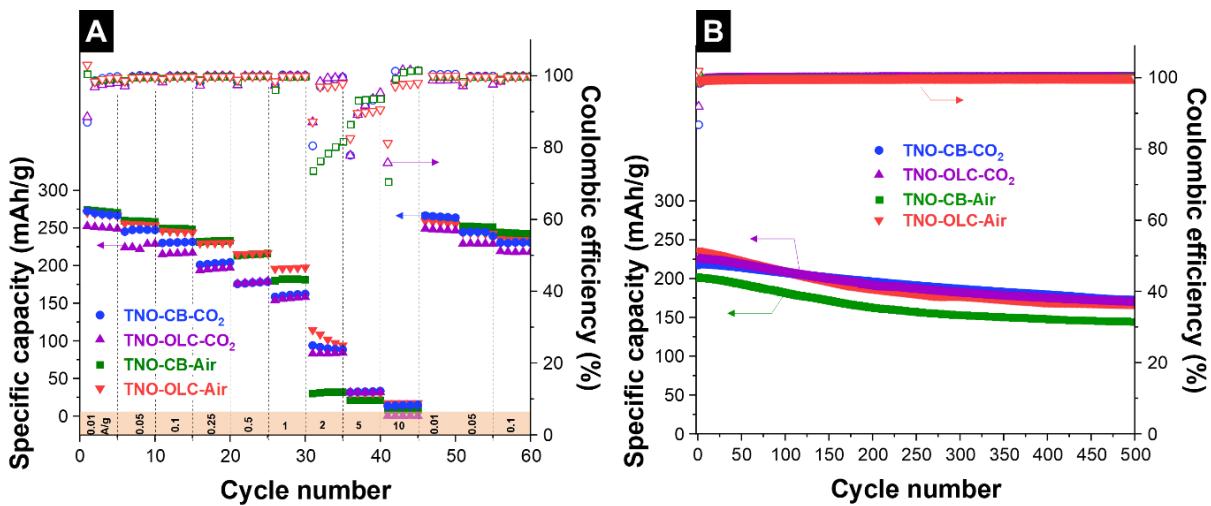


Fig. S4. (A) Rate handling performance of the hybrid and non-hybrid materials in the potential window of 1.0–2.5 V vs. Li/Li⁺. (B) Cyclic stability performance of the hybrid and non-hybrid materials in the potential window of 1.0–2.5 V vs. Li/Li⁺.

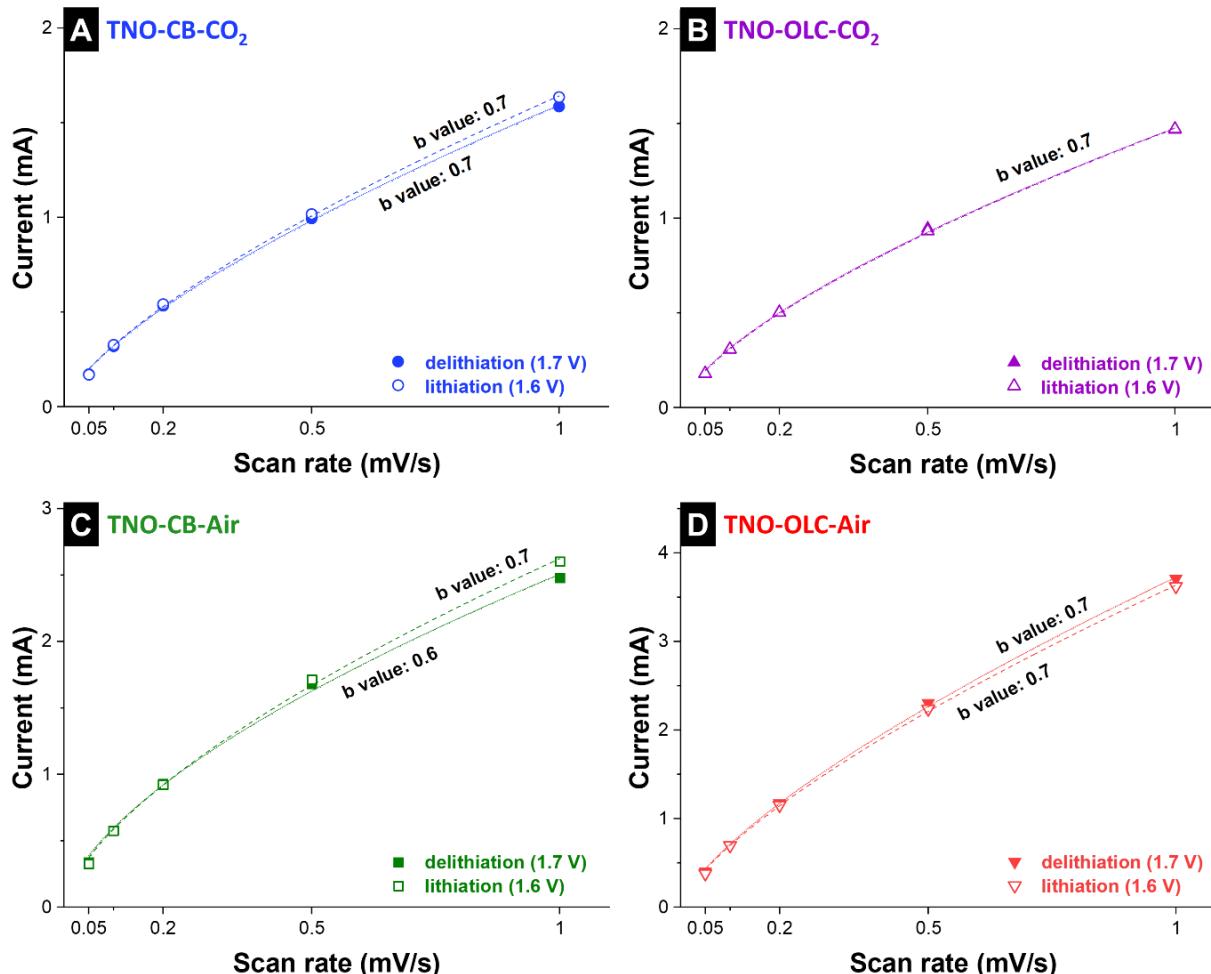


Fig. S5. Kinetic analysis of (A) TNO-CB-CO₂, (B) TNO-OLC-CO₂, (C) TNO-CB-Air, and (D) TNO-OLC-Air calculated from cyclic voltammograms at the different scan rates for the potential window of 1.0–2.5 V vs. Li/Li⁺.

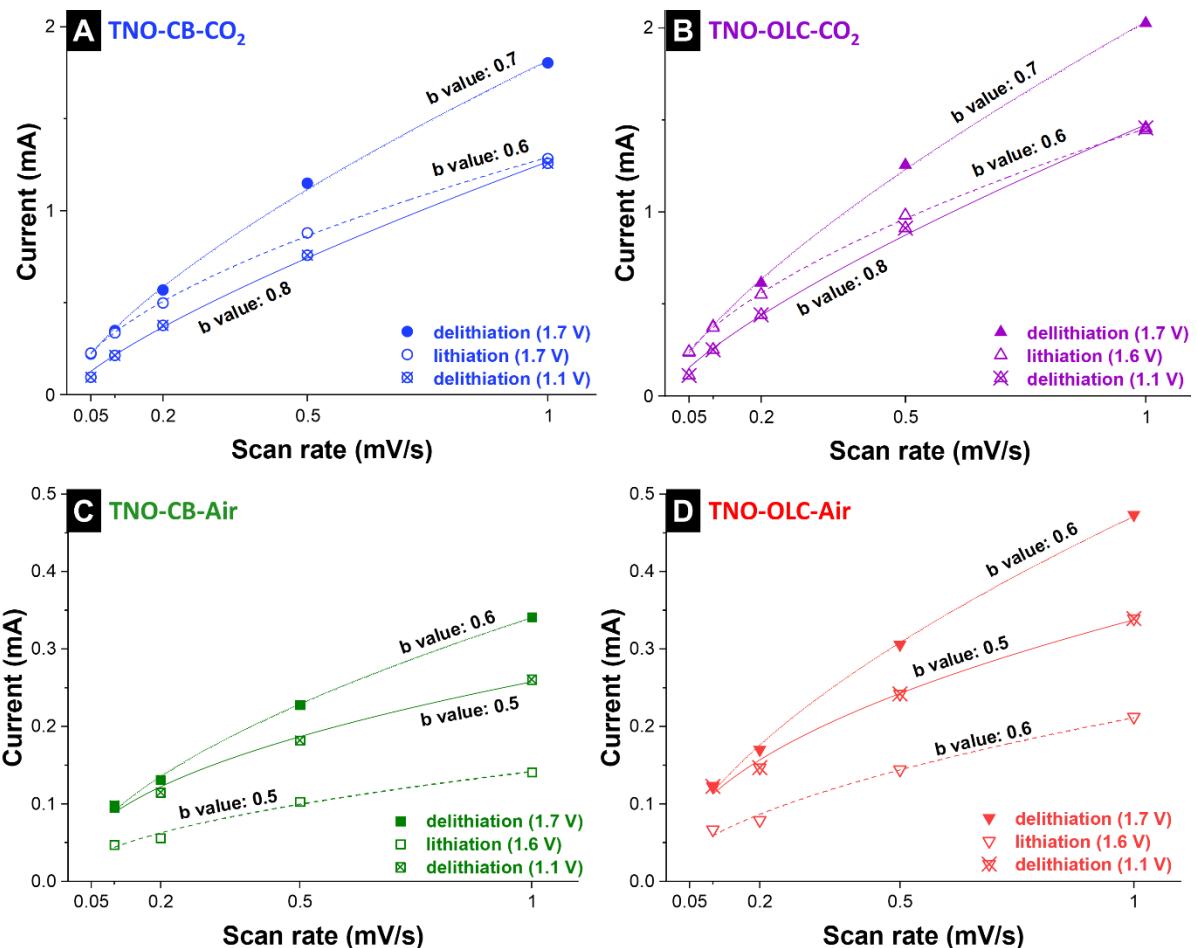


Fig. S6. Kinetic analysis of (A) TNO-CB-CO₂, (B) TNO-OLC-CO₂, (C) TNO-CB-Air, and (D) TNO-OLC-Air calculated from cyclic voltammograms at the different scan rates for the potential window of 0.05–2.5 V vs. Li/Li⁺.

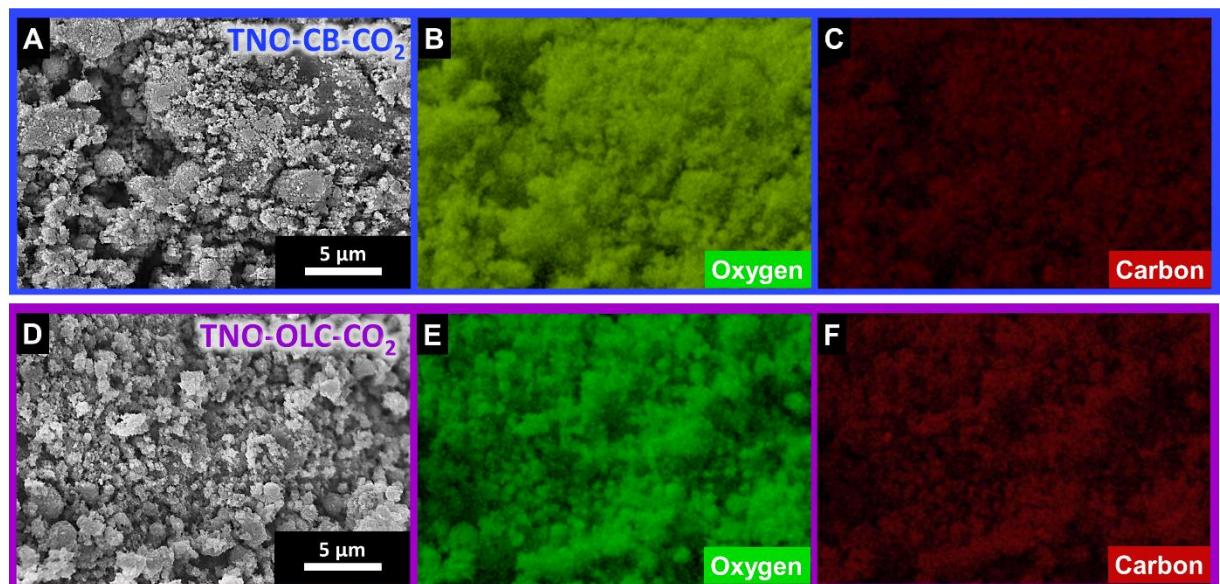


Fig. S7. (A-C) Analysis of the TNO-CB-CO₂ electrode: (A) Scanning electron micrographs, and (B-C) elemental mapping by EDX. (D-F) Analysis of the TNO-OLC-CO₂ electrode: (D) Scanning electron micrographs, and (E-F) elemental mapping by EDX.

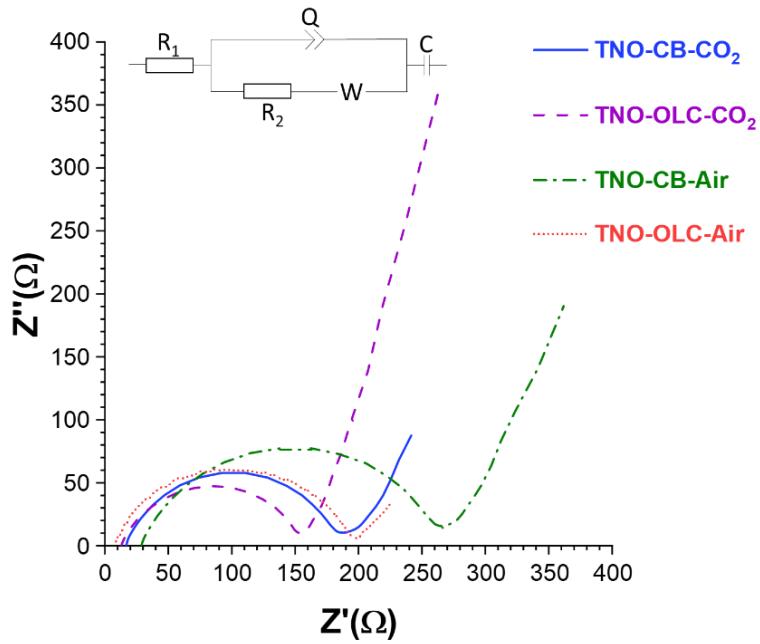


Fig. S8. Nyquist plot of hybrid and non-hybrid materials. The inset displays the equivalent circuit used for fitting of the electrochemical impedance spectra.

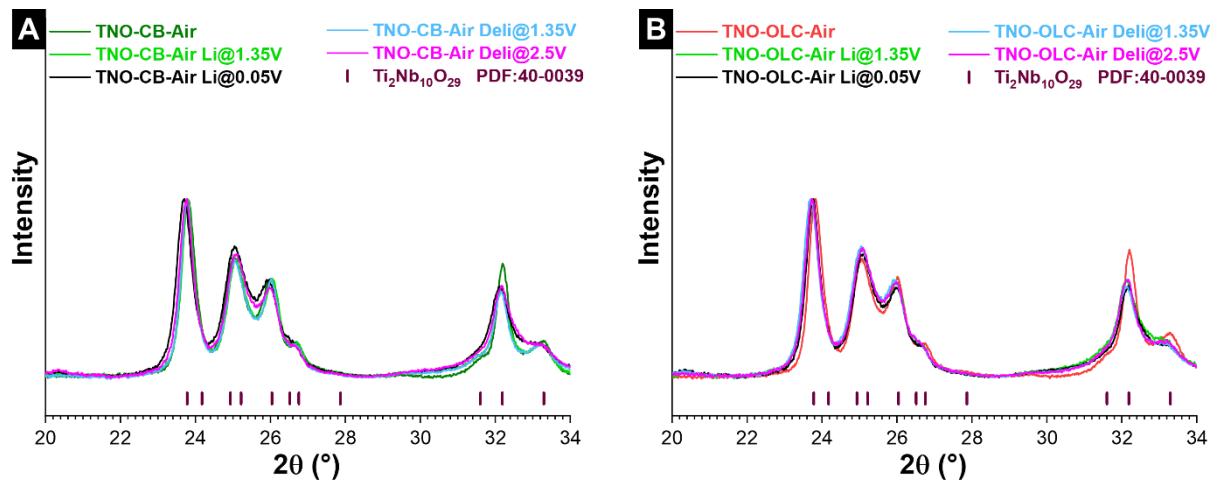


Fig. S9. X-ray diffraction patterns of (A) TNO-CB-Air, and (B) TNO-OLC-Air electrodes at the different lithiated/delithiated states (denoted as “Li” and “Deli”).

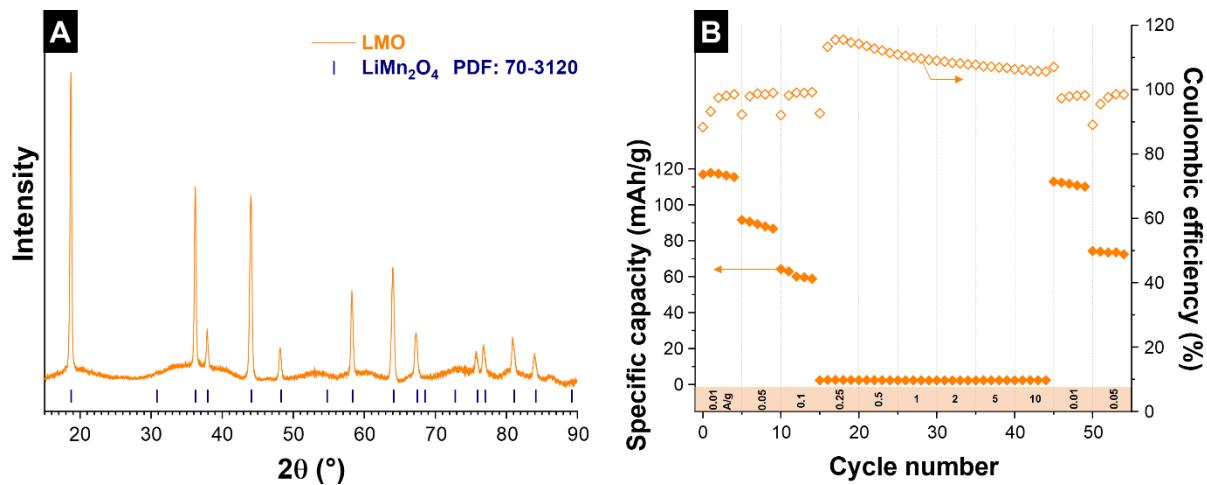


Fig. S10. (A) X-ray diffractogram of LiMn₂O₄ (LMO) with the reported Bragg positions from PDF 70-3120. (B) Rate handling performance of LMO.

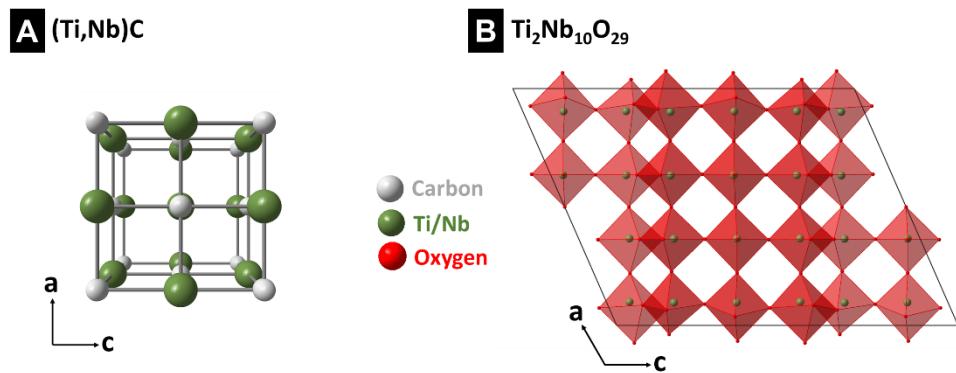


Fig. S11. Structural illustrations of the crystal lattice of (A) titanium niobium carbide (Ti,Nb)C, and (B) Ti₂Nb₁₀O₂₉.

Table S1. Rietveld refinement results of TNC-CB and TNC-OLC.

Sample	Phase	Space group	Lattice parameter (Å)	Volume (Å ³)	Domain size (nm)	Amount (mass%)	R _{wp} (%)
TNC-CB	(Ti,Nb)C	<i>Fm</i> $\bar{3}m$	$a = 4.43(4)$	87.09(4)	19.7(4)	98	2.3
	WC	<i>P</i> $\bar{6}m2$	$a = 2.90(3)$ $c = 2.85(3)$	20.82(3)	>200	2	
TNC-OLC	(Ti,Nb)C	<i>Fm</i> $\bar{3}m$	$a = 4.43(4)$	88.12(4)	15.3(4)	98	2.5
	WC	<i>P</i> $\bar{6}m2$	$a = 2.90(6)$ $c = 2.85(6)$	20.76(6)	>200	2	

Table S2. Le Bail analysis results of the analysis of X-ray diffraction patterns of TNO-CB-CO₂, TNO-OLC-CO₂, TNO-CB-Air, and TNO-OLC-Air.

Sample	Phase	Space group	Lattice parameter (Å)	Interaxial angle (°)	Volume (Å ³)	Domain size (nm)	R _{wp} (%)
TNO-CB-CO ₂	Ti ₂ Nb ₁₀ O ₂₉	A12/ <i>m1</i>	$a = 15.64$ $b = 3.82$ $c = 20.52$	$\beta = 113.4$	1124.1	55	3.4
TNO-OLC-CO ₂	Ti ₂ Nb ₁₀ O ₂₉	A12/ <i>m1</i>	$a = 15.62$ $b = 3.81$ $c = 20.52$	$\beta = 113.4$	1122.4	63	3.7
TNO-CB-Air	Ti ₂ Nb ₁₀ O ₂₉	A12/ <i>m1</i>	$a = 15.71$ $b = 3.85$ $c = 20.61$	$\beta = 113.4$	1145.3	56	3.5
TNO-OLC-Air	Ti ₂ Nb ₁₀ O ₂₉	A12/ <i>m1</i>	$a = 15.71$ $b = 3.85$ $c = 20.62$	$\beta = 113.4$	1146.0	88	3.6

Table S3. Electrochemical performance comparison of titanium niobium oxides ($TiNb_2O_7$, and $Ti_2Nb_{10}O_{29}$). CNTs: carbon nanotubes. CF: carbon fiber. rGO: reduced graphene oxide. CNFs: carbon nanofibers. CC: carbon cloth. DEC: diethylene carbonate. DMC: dimethyl carbonate. EC: ethylene carbonate. EMC: ethyl methyl carbonate. PC: propylene carbonate. MSR: Mechanically-induced self-sustaining reaction.

Materials	Synthesis	Capacity at a low rate (mAh/g, A/g)	Capacity at a high rate (mAh/g, A/g)	Voltage range (V vs. Li/Li ⁺)	Capacity retention (%, cycle number)	Electrolyte	Reference
$TiNb_2O_7$ /graphene hybrid	Solvothermal method	300, 0.03	150, 1.5	1.0-3.0	67, 300	1 M LiPF ₆ in EC:DMC	[1]
Nano- $TiNb_2O_7$ /CNTs	Direct hydrolysis method	300, 0.03	150, 4.5	0.8-3.0	97, 100	1 M LiPF ₆ in EC:DMC:DEC	[2]
$TiNb_2O_7$ /C nanoporous microspheres	Spray-drying method	393, 0.1	120, 3.6	1.0-2.6	75, 300	1 M LiPF ₆ in EC:DEC	[3]
CF/ $TiNb_2O_7$	Solvothermal method	250, 0.25	175, 1.75	1.0-2.5	88, 1000	1 M LiPF ₆ in EC:DMC	[4]
rGO- $TiNb_2O_7$ microsphere	Solvothermal method	225, 0.23	25, 2.5	1.0-3.0	61, 500	1 M LiPF ₆ in EC:EMC	[5]
$Ti_2Nb_{10}O_{29}$ /C composite	Solid-state reaction	296, 0.25	150, 4.5	1.0-2.5	87, 100	1 M LiPF ₆ in EC:DMC	[6]
$Ti_2Nb_{10}O_{29}$ /rGO	Solid-state reaction, ball-milling	250, 0.03	100, 1	1.0-2.5	77, 50	1 M LiPF ₆ in EC:DMC	[7]
$Ti_2Nb_{10}O_{29}$ /carbon onion nanohybrid	Sol-gel method	290, 0.01	169, 2	1.0-2.8	76, 800	1 M LiPF ₆ in EC:DMC	[8]
$Ti_2Nb_{10}O_{29}$ /carbon hybrid fiber	Electrospinning	260, 0.025	180, 5	0.8-3.0	60, 500	1 M LiPF ₆ in EC:DMC	[9]
$Ti_2Nb_{10}O_{29}$ /C microsphere	Solvothermal method	276, 0.27	215, 6.4	1.0-2.5	89, 200	1 M LiPF ₆ in EC:EMC:DEC	[10]
CNFs/ $Ti_2Nb_{10}O_{29}$ /CC	Electrophoretic deposition, solvothermal method	300, 0.03	200, 12	1.0-2.5	80, 1000	1 M LiPF ₆ in EC:DEC	[11]
TNO-CB-CO₂	MSR, CO₂ oxidation	272, 0.01	157, 1	1.0-2.5	82, 500	1 M LiPF ₆ in EC:DMC	This work
TNO-OLC-CO₂	MSR, CO₂ oxidation	304, 0.01	155, 1	0.05-2.5	70, 500	1 M LiPF ₆ in EC:DMC	This work
		253, 0.01	151, 1	1.0-2.5	76, 500		
		350, 0.01	144, 1	0.05-2.5	67, 500	1 M LiPF ₆ in EC:DMC	This work

Table S4. Results of the R_1 , and R_2 obtained by fitting the data from **Fig. S8**.

Material	R_1 (Ω)	R_2 (Ω)
TNO-CB-CO ₂	16.2	168.8
TNO-OLC-CO ₂	12.7	138.7
TNO-CB-Air	28.2	234.4
TNO-OLC-Air	7.3	184.4

References

- [1] A. G. Ashish, P. Arunkumar, B. Babu, P. Manikandan, S. Sarang, M. M. Shaijumon, *Electrochim. Acta* **2015**, *176*, 285-292.
- [2] C. Lin, L. Hu, C. Cheng, K. Sun, X. Guo, Q. Shao, J. Li, N. Wang, Z. Guo, *Electrochim. Acta* **2018**, *260*, 65-72.
- [3] G. Zhu, Q. Li, Y. Zhao, R. Che, *ACS Appl. Mater. Interfaces* **2017**, *9*, 41258-41264.
- [4] S. Shen, S. Deng, Y. Zhong, J. Wu, X. Wang, X. Xia, J. Tu, *Chin. Chem. Lett.* **2017**, *28*, 2219-2222.
- [5] H. Noh, W. Choi, *J. Electrochem. Soc.* **2016**, *163*, A1042-A1049.
- [6] G. Liu, B. Jin, R. Zhang, K. Bao, H. Xie, J. Guo, M. Wei, Q. Jiang, *Int. J. Hydrogen Energy* **2016**, *41*, 14807-14812.
- [7] W. L. Wang, B.-Y. Oh, J.-Y. Park, H. Ki, J. Jang, G.-Y. Lee, H.-B. Gu, M.-H. Ham, *J. Power Sources* **2015**, *300*, 272-278.
- [8] H. Shim, E. Lim, S. Fleischmann, A. Quade, A. Tolosa, V. Presser, *Sustainable Energy Fuels* **2019**, *3*, 1776-1789.
- [9] A. Tolosa, S. Fleischmann, I. Grobelsek, A. Quade, E. Lim, V. Presser, *ChemSusChem* **2018**, *11*, 159-170.
- [10] X. Liu, H. Wang, S. Zhang, G. Liu, H. Xie, J. Ma, *Electrochim. Acta* **2018**, *292*, 759-768.
- [11] Y. Tang, S. Deng, S. Shi, L. Wu, G. Wang, G. Pan, S. Lin, X. Xia, *Electrochim. Acta* **2020**, *332*, 135433.