Supporting Information

Reversible Electrochemical Lithium Cycling in a Vanadium(IV) and Niobium(V)-based Wadsley-Roth Phase

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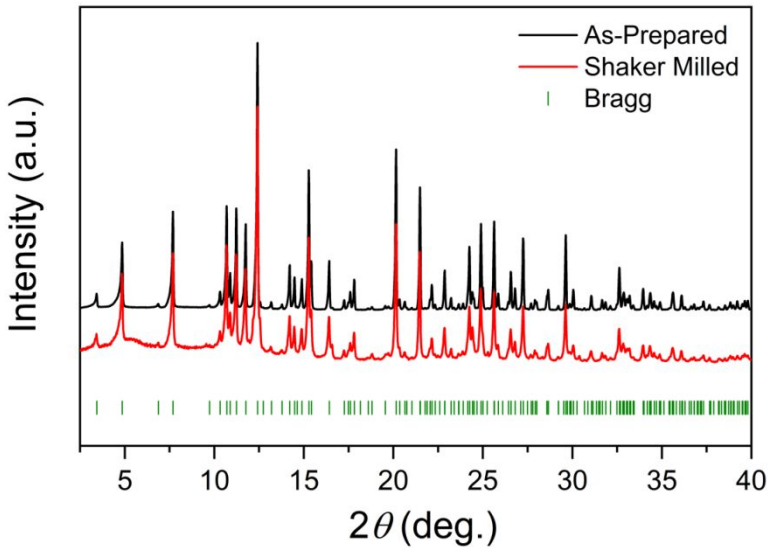
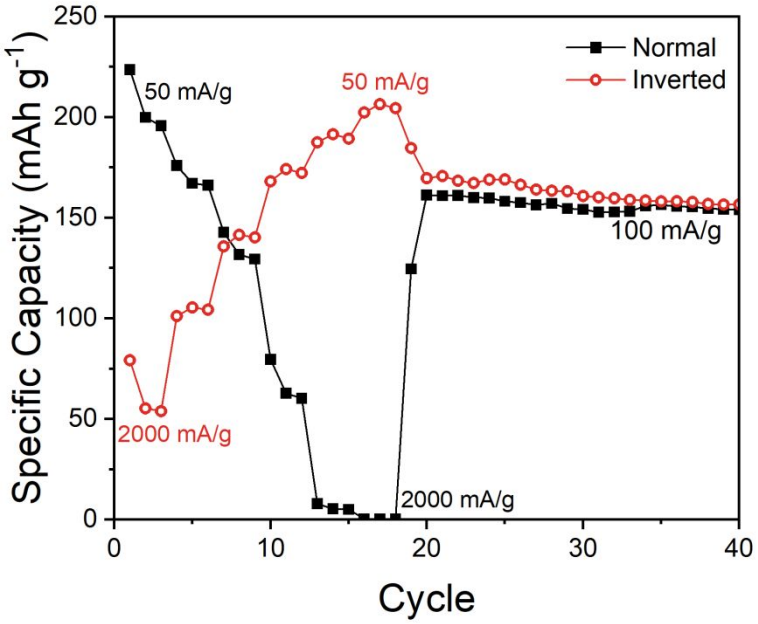
Supplementary Figure S1 – XRD comparison of as-prepared and shaker-milled $V_7Nb_6O_{29}$



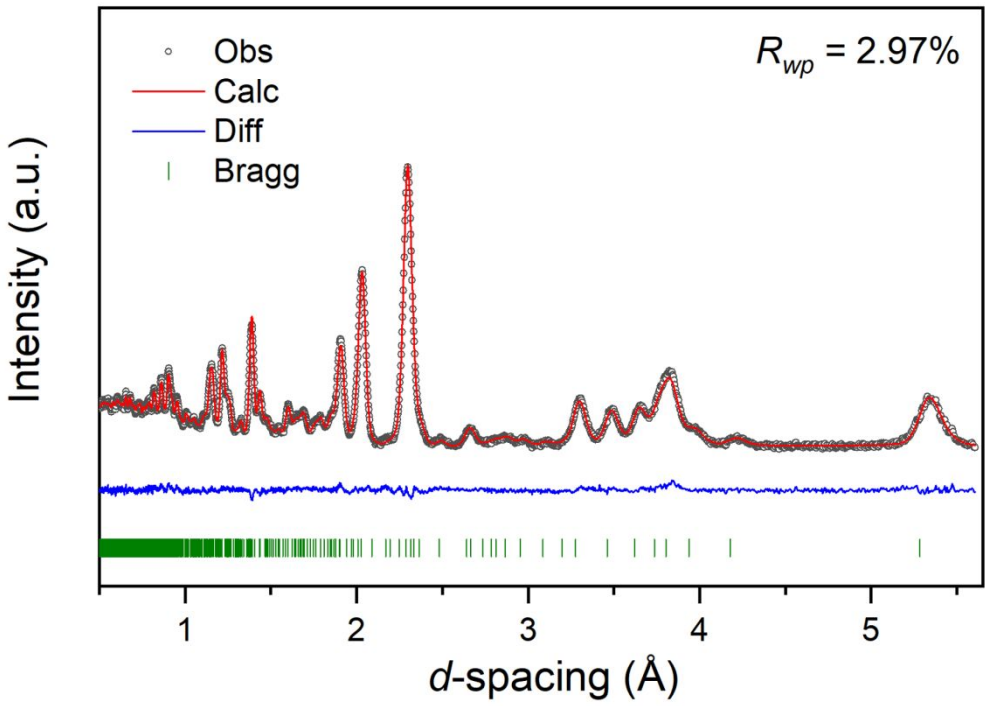
Minimal peak broadening is observed in the shaker-milled sample and is consistent with decreased particle size. Furthermore, increased background noise is observed due to the presence of carbon black that was added to improve electrical conductivity for electrochemical measurements.

Supplementary Figure S2 – Single-cell rate capability data

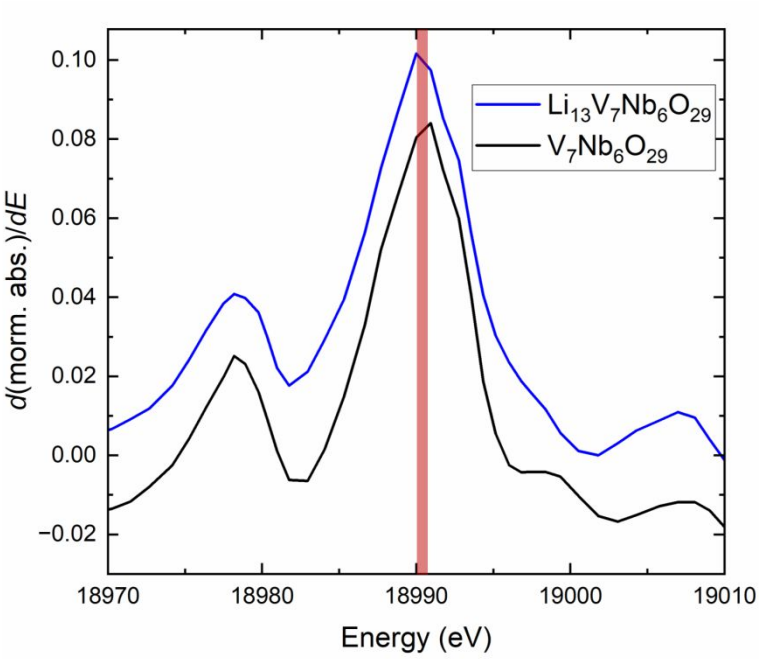


Single-cell rate data of $V_7Nb_6O_{29}$. 3 cycles were performed at each rate using both a "normal" (black) and "inverted" (red) cycling protocol. The "normal" protocol began at 50 mA/g and then increased the rate in ascending order to 100, 200, 500, 1000, and 2000 mA/g before returning to 100 mA/g for extended cycling. The "inverted" protocol began at 2000 mA/g and then decreased the rate in descending order to 1000, 500, 200, 100, and 50 mA/g before returning to 100 mA/g for extended cycling. The capacity extracted at low rates (50 and 100 mA/g) is nearly identical for both protocols. However, the capacity extracted during the "inverted" protocol is significantly higher than what is extracted from the "normal" protocol. Since the "normal rate" protocol data is also significantly lower than the observed capacities from Figures 3c and d in the main text, it is likely that the less stable cycling at low rates likely causes impedance buildup that significantly compromises the subsequent high-rate cycles.

Supplementary Figure S3 – Refinement of TOF powder neutron diffraction data on $V_7Nb_6O_{29}$ collected on NOMAD at room temperature.



Supplementary Figure S4 – Differentiated Nb K-edge absorption data comparison of pristine $V_7Nb_6O_{29}$ and $Li_{13}V_7Nb_6O_{29}$ (1.0 V).



The Nb K-edge shift from $V_7Nb_6O_{29}$ (pristine) to $Li_{13}V_7Nb_6O_{29}$ (1.0 V) is quantified by taking the first derivative of the normalized absorption with respect to the energy. The shift in the maximum of the differential absorption is ~0.71 eV and is taken as the value of the edge shift.

Supplementary Table S1 – Crystallographic data of $V_7Nb_6O_{29}$ as obtained from Rietveld refinement of single-wavelength NPD collected on ECHIDNA at room temperature.

Source	**Chemical Formula**	**Formula Weight (g/mol)**	**Temperature**	**Wavelength (Å)**	**Crystal System**	**Space Group No.**
Neutron constant wavelength	$V_7Nb_6O_{29}$	1378.01	Room Temperature	1.6220(5)	Tetragonal	83
Space Group	***a* (Å)**	***c* (Å)**	***V* (Å^3)**	R_p #	R_{wp} *	**GOF♦**
P4/m	11.8108(6)	3.80170(19)	530.32(8)	2.55%	3.27%	2.11
d-space range (Å)	**Z**					
0.82 – 30.98	1					
Atom	**Site**	***x***	***y***	***z***	U_{iso} (Å^2)	**Occupancy**
O1	4*k*	0.75015(29)	0.5577(4)	0.5	0.0022(6)	1
O2	4*j*	0.81890(35)	0.69533(32)	0	0.0051(9)	1
O3	4*j*	0.85555(31)	0.46390(32)	0	0.0058(10)	1
O4	4*k*	0.03150(32)	0.39523(35)	0.5	0.0072(9)	1
O5	4*j*	0.5864(4)	0.6355(4)	0	0.0056(6)	1
O6	4*k*	0.9358(4)	0.84402(27)	0.5	0.0068(8)	1
O7	4*k*	0.8106(4)	0.29751(31)	0.5	0.0047(6)	1
O8	1*a*	0	0	0	0.0034(15)	1
Nb1	4*k*	0.87669(28)	0.43179(28)	0.5	0.0032(6)	0.871(8)
V1	4*k*	0.87669(28)	0.43179(28)	0.5	0.0032(6)	0.129(8)
Nb2	4*k*	0.8497(5)	0.7271(4)	0.5	0.0032(6)	0.630(7)
V2	4*k*	0.8497(5)	0.7271(4)	0.5	0.0032(6)	0.370(7)
V3	4*j*	0.70667	0.56748	0	0.0032(6)	1
V4	2*g*	0	0	0.4229	0.0032(6)	0.5

- Residual of least squares

* - Weighted residual

♦ - Goodness of Fit

Supplementary Table S2 – Crystallographic data of $Li_{13}V_7Nb_6O_{29}$ as obtained from Rietveld refinement of TOF NPD collected on NOMAD at room temperature.

Source	Chemical Formula	Formula Weight (g/mol)	Temperature	Z	Crystal System	Space Group No.
TOF Neutron	$V_7Nb_6O_{29}$	1378.01	Room Temperature	1	Tetragonal	83
Space Group	***a* (Å)**	***c* (Å)**	***V* (Å^3)**	R_{wp}*	**GOF♦**	**d-space range (Å)**
P4/m	12.05974(19)	4.00884(7)	583.19(2)	2.21%	4.04	0.2 – 6.5
Atom	**Site**	***x***	***y***	***z***	U_{iso} (Å^2)	**Occupancy**
O1	4*k*	0.7431(2)	0.5638(2)	0.5	0.0032(4)	1
O2	4*j*	0.8173(3)	0.7074(3)	0	0.0142(8)	1
O3	4*j*	0.8723(2)	0.4706(3)	0	0.0029(4)	1
O4	4*k*	0.0314(3)	0.3737(3)	0.5	0.010(0.7)	1
O5	4*j*	0.5864(3)	0.6412(3)	0	0.0041(4)	1
O6	4*k*	0.9141(4)	0.8564(4)	0.5	0.0171(8)	1
O7	4*k*	0.7990(3)	0.3160(3)	0.5	0.012(0.8)	1
O8	1*a*	0	0	0	0.043(4)	1
Nb1	4*k*	0.8968(2)	0.4674(3)	0.5	0.0042(4)	0.86
V1	4*k*	0.8968(2)	0.4674(3)	0.5	0.4540018	0.14
Nb2	4*k*	0.8299(4)	0.7321(3)	0.5	0.011(0.7)	0.64
V2	4*k*	0.8299(4)	0.7321(3)	0.5	0.4976649	0.36
V3	4*j*	0.7066	0.56749	0	0.3894941	1
V4	2*g*	0	0	0.42279	0.3995216	0.5
Li1	1c	0.5	0.5	1	0.0170(7)	0.99(7)
Li2	4k	0.5872(14)	0.6575(15)	0.5	0.0170(7)	0.68(2)
Li3	4k	0.7675(19)	0.9369(16)	0.5	0.0170(7)	0.58(2)
Li4	4j	0.9356(17)	0.850(2)	1	0.0170(7)	0.464(16)
Li5	4j	0.952(2)	0.622(3)	1	0.0170(7)	0.32(3)
Li6	4j	0.7919(10)	0.3242(11)	1	0.0170(7)	0.95(5)

* - Weighted Residual

♦ - Goodness of Fit

Supplementary Table S3 – Crystallographic data of $V_7Nb_6O_{29}$ as obtained from Rietveld refinement of TOF NPD collected on NOMAD at room temperature.

Source	**Chemical Formula**	**Formula Weight (g/mol)**	**Temperature**	**Z**	**Crystal System**	**Space Group No.**
TOF Neutron	$V_7Nb_6O_{29}$	1378.01	Room Temperature	1	Tetragonal	83
Space Group	***a* (Å)**	***c* (Å)**	***V* (Å^3)**	**R_{wp}***	**GOF♦**	**d-space range (Å)**
P4/m	11.8140(2)	3.80277(6)	530.76(2)	2.97%	2.86	0.2 – 6.5
Atom	**Site**	***x***	***y***	***z***	**U_{iso} (Å^2)**	**Occupancy**
O1	4*k*	0.74927(19)	0.5592(2)	0.5	0.0066(4)	1
O2	4*j*	0.8194(2)	0.69633(18)	0	0.0057(4)	1
O3	4*j*	0.85702(18)	0.46384(18)	0	0.0063(4)	1
O4	4*k*	1.03268(18)	0.3939(2)	0.5	0.0067(4)	1
O5	4*j*	0.5847(2)	0.6358(2)	0	0.0076(4)	1
O6	4*k*	0.9378(2)	0.84517(18)	0.5	0.0095(4)	1
O7	4*k*	0.8091(2)	0.2978(2)	0.5	0.010(0.4)	1
O8	1*a*	0	0	0	0.011(0.9)	1
Nb1	4*k*	0.87775(16)	0.43388(16)	0.5	0.0027(4)	0.774(6)
V1	4*k*	0.87775(16)	0.43388(16)	0.5	0.450054	0.226(6)
Nb2	4*k*	0.8501(2)	0.7274(2)	0.5	0.0046(5)	0.609(5)
V2	4*k*	0.8501(2)	0.7274(2)	0.5	0.4919011	0.391(5)
V3	4*j*	0.70667	0.56748	0	0.3774137	1
V4	2*g*	0	0	0.4229	0.3884676	0.5

* - Weighted Residual

♦ - Goodness of Fit

Supplementary Table S4 – Refinement results of the NPDF data using the random structural model.

Space Group	P4/m
***a* (Å)**	11.792
***c* (Å)**	3.79749
Scale Factor	0.501751
δ_1	1.19509
R_w	12.6%
Nb1 Site Occupancy	0.8467
V1 Site Occupancy	0.1533
Nb2 Site Occupancy	0.6208
V2 Site Occupancy	0.3792
O U_{iso} (Å^2)	0.008666
Nb and V U_{iso} (Å^2)	0.005281

Supplementary Table S5 – Li sites used for DFT band structure calculations.

Atom	*x*	*y*	*z*
Li1	0.5	0.5	1
Li2	0.614600	0.678900	0.5
Li3	0.678900	0.385360	0.5
Li4	0.385360	0.321080	0.5
Li5	0.321080	0.614600	0.5
Li6	0.772700	0.937400	0.5
Li7	0.937400	0.227300	0.5
Li8	0.062600	0.772700	0.5
Li9	0.227300	0.062600	0.5
Li10	0.923560	0.846200	1
Li11	0.153800	0.923560	1
Li12	0.076440	0.153800	1
Li13	0.846200	0.076440	1

For DFT calculations, symmetry was removed from the $Li_{13}V_7Nb_6O_{29}$ structure resulting in a P1 unit cell. This causes all Li sites to be 1a sites.