Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Rapid and Durable Electrochemical Storage Behavior Enabled by $V_4Nb_{18}O_{55}$ Beaded Nanofibers: A Joint Theoretical and Experimental Study

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Electrode preparation and cell assembly

For electrochemical investigation, the working electrodes were manufactured by dispersing the mixture, which was composed of active material, carbon black conductive additive and polyvinyldifluoride binder in a weight ratio of 8:1:1, into N-methyl pyrrolidinone and then pasting on a copper-foil current collector. The electrodes were dried at 100 ^{o}C for 12 hours in vacuum. By using the as-prepared working electrode as cathode, lithium metal as anode, Whatman glass fiber as separator and 1 mol L^{-1} $LiPF_6$ dissolved in a 1:1 (v/v) mixture of ethylene carbonate and dimethyl carbonate as electrolyte, CR2032-type coin cells were assembled in Ar-filled glove box for the electrochemical studies. For full cell, $V_4Nb_{18}O_{55}$ was used as the active material of anode, and $LiMn_2O_4$ was used as the active material of as cathode. The mass ratio of $V_4Nb_{18}O_{55}$ (0.1 g) to $LiMn_2O_4$ (0.18g) was 1:1.8.

Determination of diffusion coefficient

$$\mathrm{i}_p = (2.69 \times 10^5)\mathrm{n}^{3/2}\mathrm{A}D_{Li^+}^{1/2}C_{Li^+}v^{1/2} \quad (1)$$

In the equation (1), n is the transferred number of electrons in the electrochemical reaction, and A means electrode surface area, C_{Li}^{+} donates the concentration of lithium ions in the anode.

$$D = \frac{\mathrm{R}^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad (2)$$

In equation (2), the parameters A, C, and n are the same as those in equation (1). Except for Warburg factors, other parameters also have fixed values, such as R for gas constant, T for absolute temperature and F for Faraday constant.

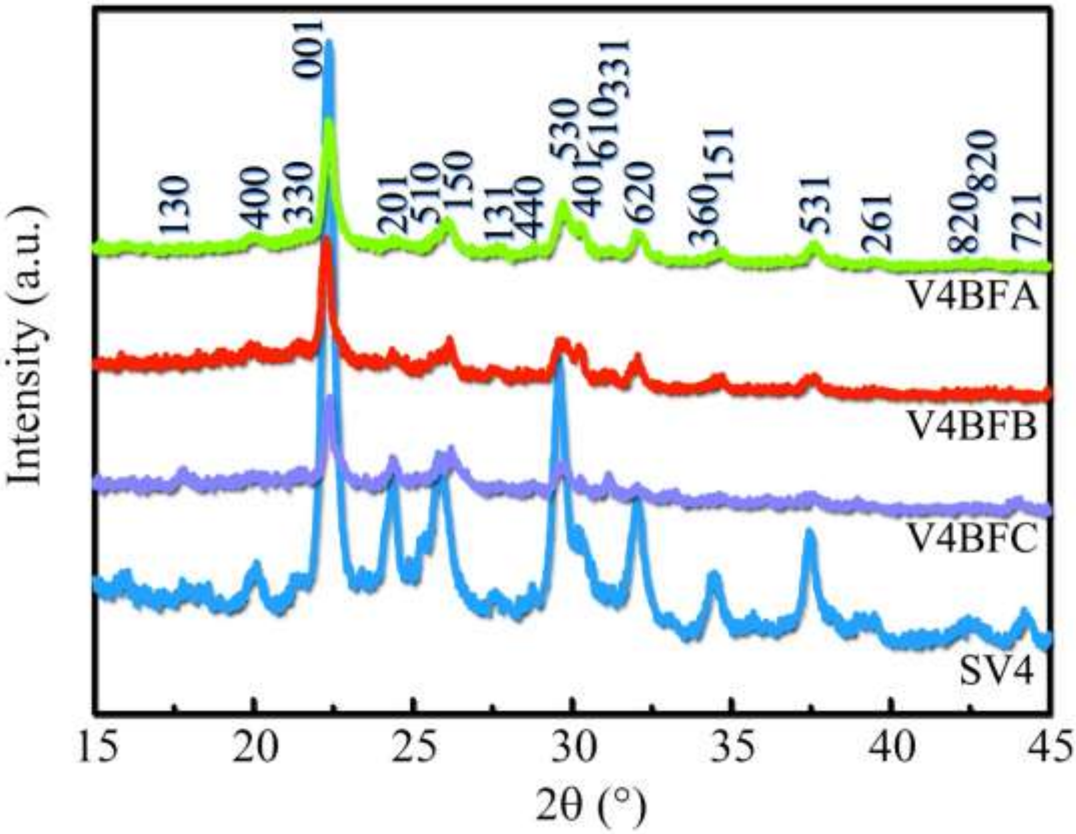

Figure S1. XRD patterns of V4BFA, V4BFB, V4BFC and SV4.

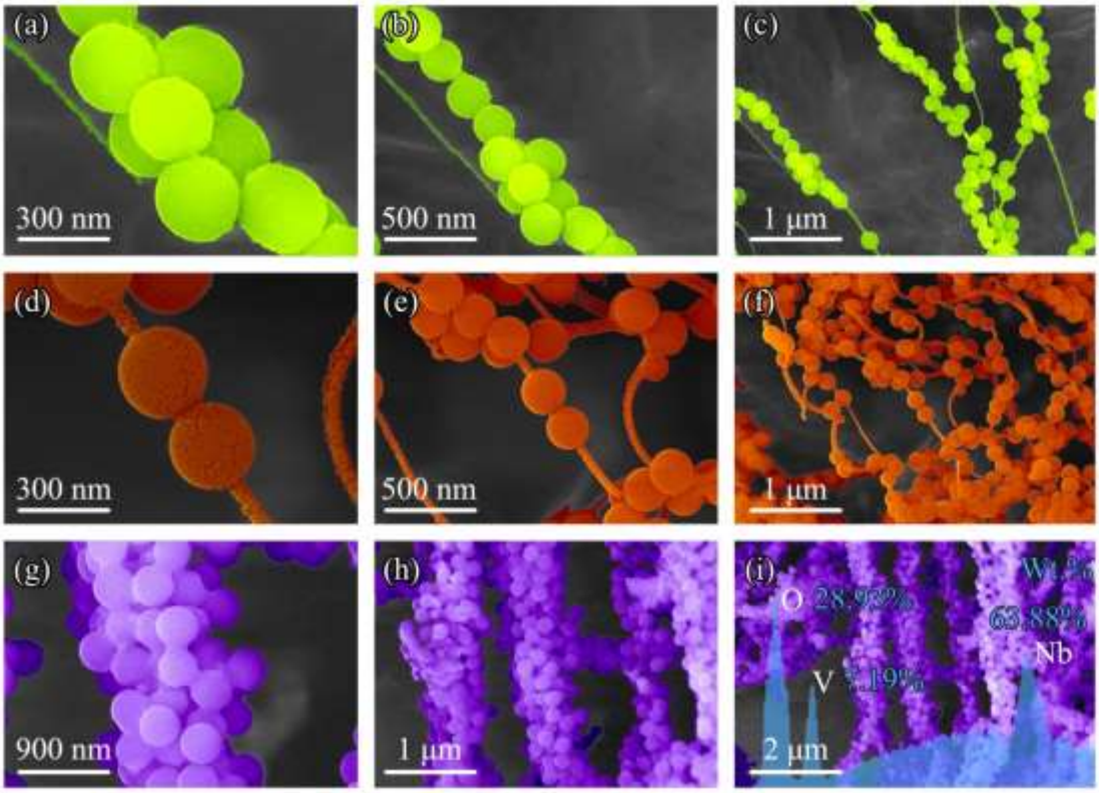

Figure S2. SEM images of (a-c) V4BFA; (d-f) V4BFB; (g-i) V4BFC and (i) EDS images of $V_4Nb_{18}O_{55}$.

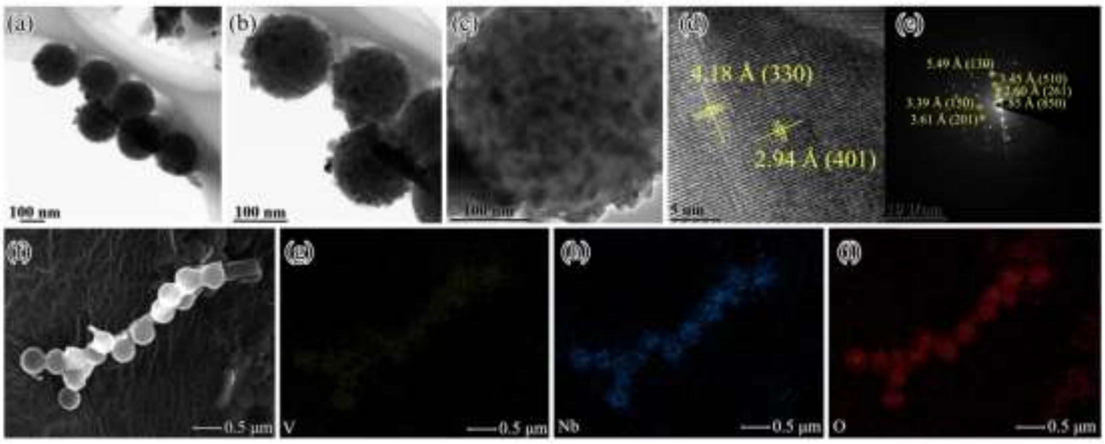

Figure S3. (a-c) TEM images, (d) HRTEM images, (e) SAED images and (f-i) elemental mapping images of V4BFB.

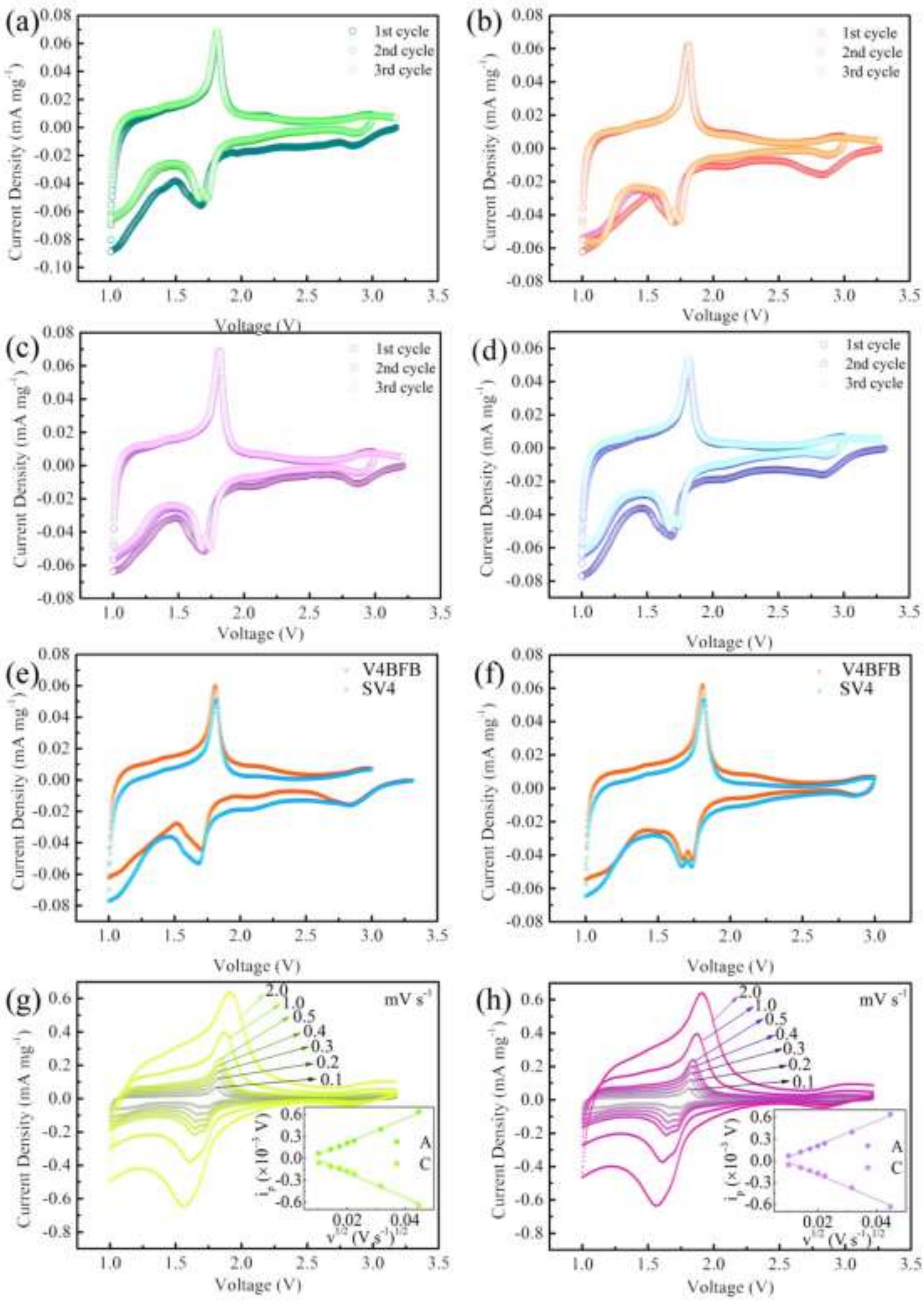

Figure S4. (a-d) CV curves of V4BFA, V4BFB, V4BFC and SV4 at rate of 0.1 mV s^{-1}; (e) the first cycle and (f) the second cycle of CV curves of V4BFB and SV4 at rate of 0.1 mV s^{-1}; CV curves at different scan rates of (g) V4BFA and (h) V4BFC.

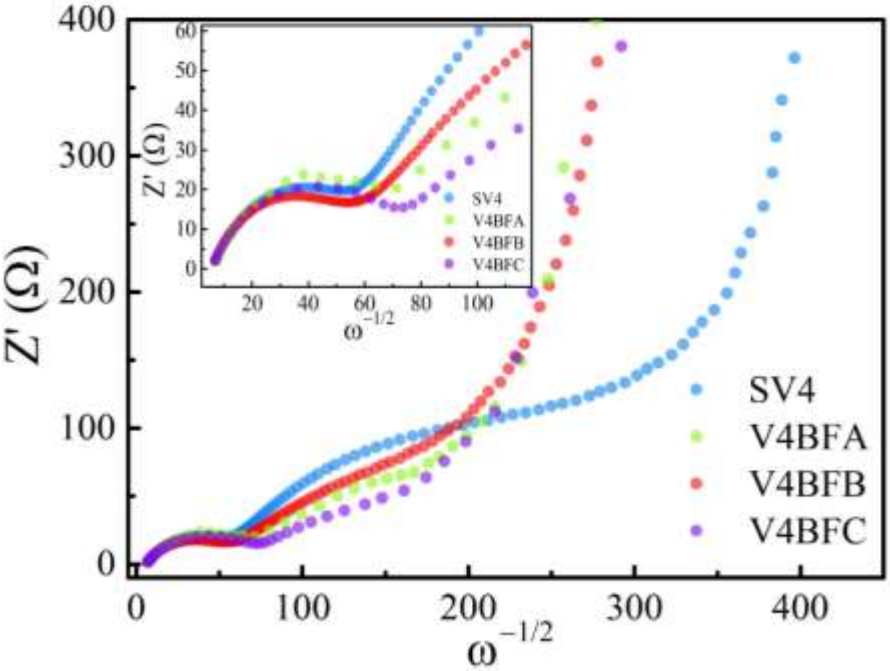

Figure S5. The EIS results of V4BFA, V4BFB, V4BFC and SV4.

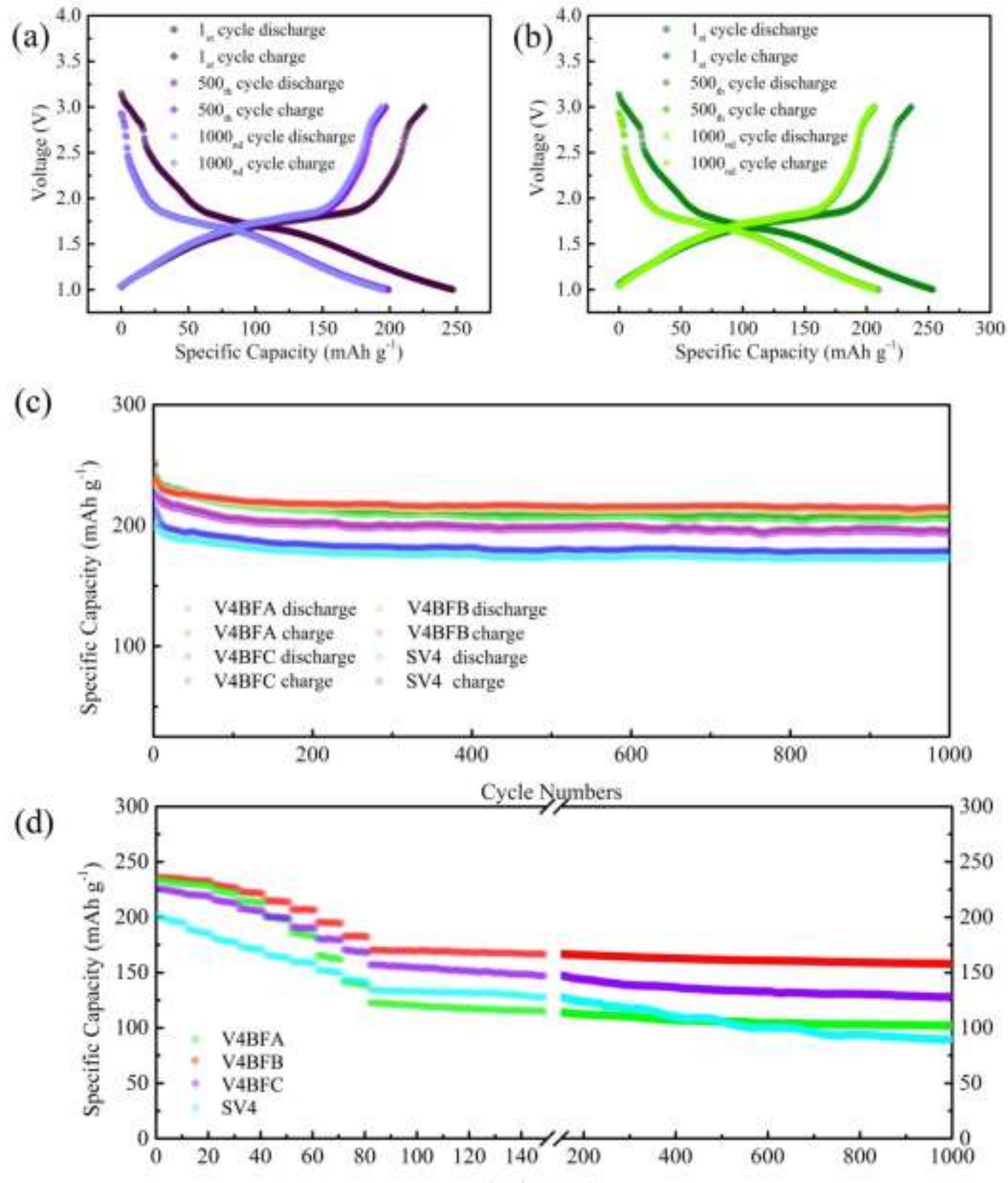

Figure S6. (a-b) Discharge and charge curves of V4BFA and V4BFC. (c) Cyclability and (d) rate performance of V4BFA, V4BFB, V4BFC and SV4.

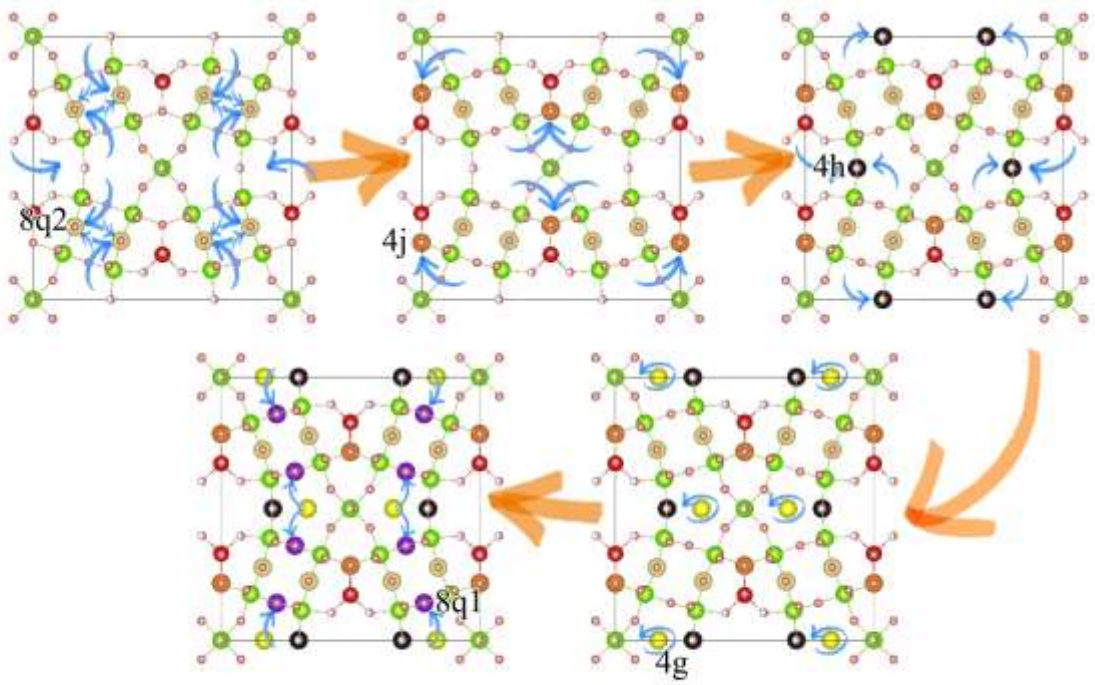

Figure S7. Lithium ions storage mechanism in $V_4Nb_{18}O_{55}$ during the discharge process.

Table S1. Diffusion coefficient calculated by CV test and EIS test.

	D_{Li}^{+} ($cm^2\ s^{-1}$)			
	V4BFA	V4BFB	V4BFC	SV4
CV	2.2327×10^{-11}	2.3337×10^{-11}	2.2537×10^{-11}	1.5203×10^{-11}
EIS		2.3881×10^{-14}		1.3894×10^{-14}

Table S2. The value of electrochemical parameters calculated from EIS test.

	R_s (Ω)	CPE_f (μF)	R_f (Ω)	CPE_{ct} (μF)	R_{ct} (Ω)	W (Ω)
SV4	8.043	1.046	38.84	98.76	92.18	1.675
V4BFA	7.094	0.9912	22.7	4.038	84.18	1.517
V4BFB	7.236	0.9717	17.77	2.893	30.59	1.46
V4BFC	7.87	1.021	43.16	3.748	92.11	1.564

Table S3. The comparative values of various parameters between previously reported electrode materials and $V_4Nb_{18}O_{55}$.

	SCL. (mAh g^{-1})	SCH. (mAh g^{-1})	Cyc.	IE.	DC. (cm^2 s^{-1})	Pla. (V)
M-Nb_2O_5	170	144	88%	96%	1.1×10^{-12}	1.37
H-Nb_2O_5	164	128	85%	96%	1.6×10^{-12}	1.37
T-Nb_2O_5	156	86	83%	96%	1.0×10^{-13}	1.37
TT-Nb_2O_5	139	56	80%	96%	4.7×10^{-14}	1.37
V_2O_5	440	137	55%	99%	1.1×10^{-8}	3.30
$Li_4Ti_5O_{12}$	170	62	86%	80%	5.1×10^{-12}	1.55
$Na_2Li_2Ti_6O_{14}$	185	67	90%	49%	5.3×10^{-16}	1.55
$PbLi_2Ti_6O_{14}$	126	86	49%	98%	1.7×10^{-15}	1.25
$BaLi_2Ti_6O_{14}$	163	142	86%	92%	6.0×10^{-17}	1.49
$SrLi_2Ti_6O_{14}$	145	92	86%	90%	1.2×10^{-14}	1.44
$Ti_2Nb_{10}O_{29}$	300	235	90%	94%	8.9×10^{-18}	1.68
$TiNb_2O_7$	281	128	84%	97%	1.0×10^{-12}	1.75
$TiNb_{24}O_{62}$	240	103	68%	89%	2.0×10^{-9}	1.68
$WNb_{12}O_{33}$	226	142	86%	83%	7.7×10^{-12}	1.75
$V_4Nb_{18}O_{55}$	236	157	89%	94%	2.2×10^{-11}	1.75
	SCL. (mAh g^{-1})	TC. (mAh g^{-1})	Cyc.	IE.	ED. (Wh kg^{-1})	Pla. (V)
$GeNb_{18}O_{47}$	195	386	82%	96%	322	1.65

VNb_9O_{25}	200	416	76%	81%	340	1.70
PNb_9O_{25}	200	219	95%	96%	340	1.70

Table S4. Atomic coordinates and occupancy of $V_4Nb_{18}O_{55}$.

Atom	x	y	Z	Occupancy
O	0.17945	0.39002	0.50000	1.000
O	0.10652	0.18537	0.50000	1.000
Nb	0.12295	0.17639	0.00000	1.000
Nb	0.18724	0.38910	0.00000	1.000
O	0.07110	0.08263	0.00000	1.000
O	0.21276	0.13283	-0.00000	1.000
O	0.15830	0.28089	0.00000	1.000
O	-0.07638	0.59968	0.00000	0.500
V	0.00000	0.34680	0.00000	1.000
O	0.00000	0.24718	-0.00000	1.000
Nb	0.00000	0.00000	0.00000	1.000
O	0.19272	0.50000	0.00000	0.500
O	0.00000	0.34535	0.50000	1.000
O	0.00000	0.00000	0.50000	0.500

Table S5. Atomic coordinates and occupancy of $Li_{28}V_4Nb_{18}O_{55}$.

Atom	x	y	Z	Occupancy
O	0.18043	0.39031	0.50000	1.000
O	0.11407	0.18443	0.50000	1.000
Li	0.09414	0.70555	0.50000	1.000
Nb	0.13191	0.17130	0.00000	1.000
Nb	0.17741	0.38601	0.00000	1.000
O	0.07519	0.07977	0.00000	1.000
O	0.21894	0.13508	-0.00000	1.000
O	0.16018	0.27750	0.00000	1.000
O	-0.07835	0.60325	-0.00000	0.500
V	0.00000	0.34194	0.00000	1.000
O	0.00000	0.24462	0.00000	1.000
Nb	0.00000	0.00000	0.00000	1.000
O	0.18533	0.50000	0.00000	0.500
O	0.00000	0.34220	0.50000	1.000
O	0.00000	0.00000	0.50000	0.500
Li	-0.19783	0.50000	0.50000	1.000
Li	-0.08181	0.50000	1.00000	1.000
Li	0.00000	0.14470	1.00000	1.000
Li	0.25000	0.75000	1.00000	1.000
Li	0.13554	1.00000	1.00000	1.000

Table S6. Diffusion barriers and coefficient (eV) for lithium moving along different paths in $V_4Nb_{18}O_{55}$.

	Path 1	Path 2	Path 3	Path 4	Path 5	Path 6	Path 7
Barrier	0.209	0.502	0.315	0.226	0.259	0.286	0.805
D_{Li} [a]	3.99×10^{-6}	1.51×10^{-10}	3.77×10^{-7}	1.11×10^{-6}	6.32×10^{-7}	2.21×10^{-7}	3.8×10^{-16}

[a] Theoretical diffusion coefficient (in $cm^2 \cdot s^{-1}$) .