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Lithiation of $V_2O_3(SO_4)_2$ – a Flexible Insertion Host

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SUPPORTING INFORMATION

Table S1. *Atomic coordinates and isotropic thermal parameters (Uiso×100, Å²) of $V_2O_3(SO_4)_2$ obtained from the combined Rietveld refinement shown in Figure 2 (b) and (c).*

$V_2O_3(SO_4)_2$ Space group $P2_1/a$

a = 9.4731(8) Å, b = 8.9256(8) Å, c = 9.9165(9) Å, β = 104.702(7) °, V = 811.0(1) Å^3

Z = 4, density = 2.802 g cm^{-3}

Atom	Wyckoff site	x	y	z	Occupancy	U_{iso}×100 (Å²)
V1	4*e*	0.8809(8)	0.6207(9)	0.17258(7)	1	1.2(2)
V2	4*e*	0.1431(8)	0.3759(8)	0.3339(7)	1	1.3(3)
S1	4*e*	0.0734(12)	0.0734(11)	0.4736(1)	1	0.9(2)
S2	4*e*	0.2121(12)	0.2121(10)	0.1065(10)	1	0.7(2)
O1	4*e*	0.7470(2)	0.7470(2)	0.2443(3)	1	1.3(3)
O2	4*e*	0.1459(2)	0.1459(3)	0.2459(3)	1	1.5(4)
O3	4*e*	0.9829(3)	0.9829 (3)	0.2368(3)	1	0.5(1)
O4	4*e*	0.3299(2)	0.3299(2)	0.0904(2)	1	0.3(2)
O5	4*e*	0.2138(2)	0.2138(2)	0.0157(2)	1	0.3(2)
O6	4*e*	0.2565(2)	0.2565(2)	0.2535(3)	1	0.3(2)
O7	4*e*	0.0709(2)	0.0709(3)	0.0716(2)	1	0.3(2)
O8	4*e*	0.1684(2)	0.1684(2)	0.5239(2)	1	0.6(3)
O9	4*e*	0.9470(3)	0.9470(3)	0.5351(2)	1	0.6(3)
O10	4*e*	0.0108(3)	0.0108(3)	0.3195(3)	1	0.6(3)
O11	4*e*	0.1448(3)	0.1448(2)	0.4917(3)	1	0.6(3)

χ^2 = 10.06, $R_{wp,\ PXRD}$ = 6.23%, $R_{wp,\ NPD}$ = 6.11%

Table S2. *V-O bond lengths in $V_2O_3(SO_4)_2$ obtained from the Rietveld refinement shown in Figure 2 (b) and (c).*

V(1)-O	Bond length/ Å	V(2)-O	Bond length/ Å
V(1)-O(1)	1.598(8)	V(2)-O(2)	1.590(3)
V(1)-O(3)	1.686(7)	V(2)-O(3)	1.781(4)
V(1)-O(4)	2.012(5)	V(2)-O(6)	1.924(9)
V(1)-O(5)	1.972(4)	V(2)-O(8)	1.991(7)
V(1)-O(7)	2.314(7)	V(2)-O(9)	1.972(5)
O(1)-O(10)	1.957(6)	V(2)-O(11)	2.340(8)

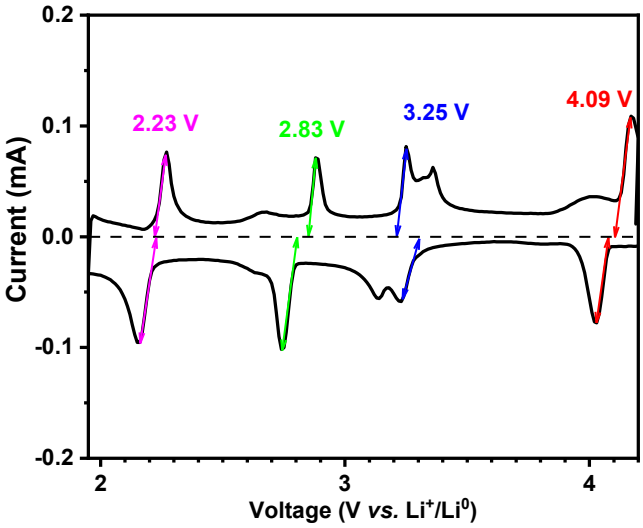

Figure S1. *Voltammogram of the first cycle obtained from potentiostatic cycling of $V_2O_3(SO_4)_2$ versus Li^+/Li^0, collected at a slow scan rate of 5.6 μV s^{-1} between 4.20 and 1.95 V.*

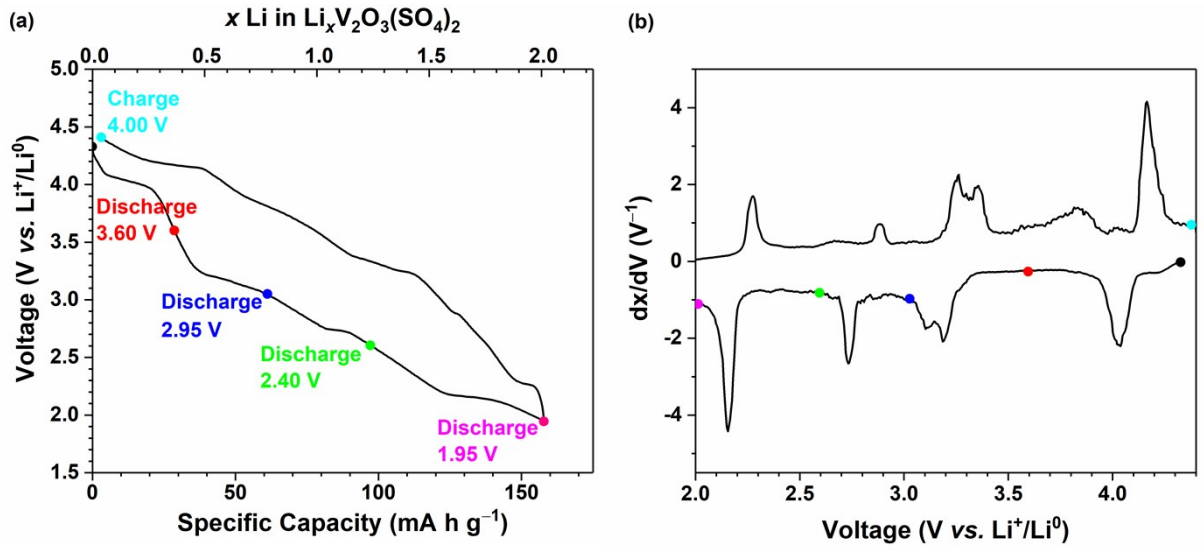

Figure S2. *First cycle of a $V_2O_3(SO_4)_2$||Li cell cycled between 4.20 V and 1.95 V, illustrating the voltages chosen to characterise the Li^+ insertion/extraction showing the (a) voltage-capacity curve and (b) the corresponding derivative dx/dV curve.*

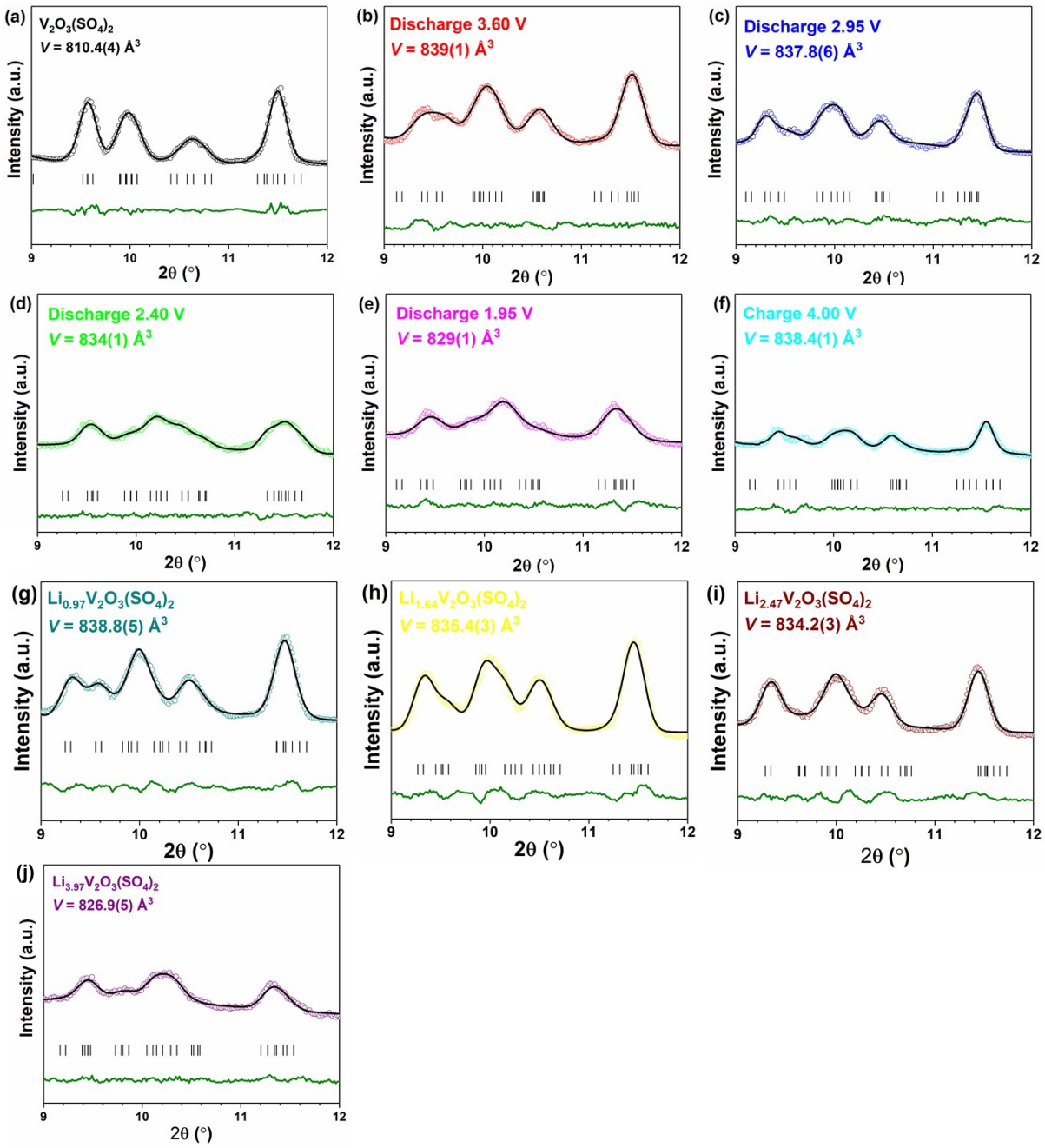

Figure S3. *Portions of the Rietveld fits of the PXRD patterns for (a) $V_2O_3(SO_4)_2$, (b) the electrode discharged to 3.60 V, (c) discharged to 2.95 V, (d) discharged to 2.40 V, (e) discharged to 1.95 V, (f) charged to 4.00 V, (g) chemically lithiated phased $Li_{0.97}V_2O_3(SO_4)_2$, (h) $Li_{1.64}V_2O_3(SO_4)_2$, (i) $Li_{2.47}V_2O_3(SO_4)_2$, (j) $Li_{3.97}V_2O_3(SO_4)_2$.*

Table S3. *Unit cell parameters of $V_2O_3(SO_4)_2$, and the lithiated samples obtained from Rietveld fits shown in Figure S3.*

Sample	Unit cell parameters					R_{wp}/ %
	a/ Å	*b*/ Å	*c*/ Å	β/ °	*V*/ Å^3	
$V_2O_3(SO_4)_2$	9.469(2)	8.921(2)	9.919(2)	104.713(8)	810.4(4)	5.22
Discharge 3.60 V	9.543(6)	8.857(5)	10.216(7)	103.48(3)	839(1)	5.22
Discharge 2.95 V	9.507(4)	8.810(3)	10.273(4)	103.18(3)	837.8(6)	4.40
Discharge 2.40 V	9.608(9)	8.798(7)	10.194(8)	104.56(4)	834(1)	4.43
Discharge 1.95 V	9.613(5)	8.765(5)	10.202(5)	105.24(3)	829(1)	4.50
Charge 4.00 V	9.6063(7)	8.8732(7)	10.1498(8)	104.286(7)	838.4(1)	4.71
$Li_{0.97}V_2O_3(SO_4)_2$	9.527(3)	8.845(2)	10.231(3)	103.34(2)	8.38.8(5)	5.10
$Li_{1.64}V_2O_3(SO_4)_2$	9.527(2)	8.814(2)	10.229(2)	103.46(1)	835.4(3)	4.29
$Li_{2.47}V_2O_3(SO_4)_2$	9.522(2)	8.819(2)	10.212(2)	103.43(1)	834.2(3)	3.24
$Li_{3.97}V_2O_3(SO_4)_2$	9.608(3)	8.752(3)	10.188(3)	105.18(2)	826.9(5)	2.18

Table S4. *Structural parameters obtained from fits of the vanadium K-edge EXAFS spectra Fourier transform of the electrochemically lithiated samples of $V_2O_3(SO_4)_2$ at various states of discharge shown in Figure 8 (b).*

Sample	V-X	Coordination number, N	R/ Å	σ^2/ 10^{-3} Å^2	R-factor/ %
$V_2O_3(SO_4)_2$	V=O	1	1.60(4)	0.002(1)	1.7
	V-O	1	1.80(2)	0.002(2)	
	V-O_{eq}	3	1.97(12)	0.004(1)	
	V···O	1	2.46(3)	0.015(9)	
	V-O-S	2	3.18(8)	0.010(2)	
Discharge 3.6 V	V=O	1	1.57(1)	0.003(1)	1.2
	V-O	1	1.76(2)	0.009(7)	
	V-O_{eq}	3	1.97(1)	0.004(1)	
	V···O	1	2.42(4)	0.009(5)	
	V-O-S	2	3.16(6)	0.013(3)	
Discharge 2.95 V	V=O	1	1.56(6)	0.003(2)	1.4
	V-O	1	1.77(1)	0.003(1)	
	V-O_{eq}	3	1.95(1)	0.002(1)	
	V···O	1	2.36(2)	0.007(4)	
	V-O-S	2	3.11(11)	0.012(2)	
Discharge 2.40 V	V=O	1	1.56(1)	0.002(2)	1.7
	V-O	1	1.78(1)	0.004(4)	
	V-O_{eq}	3	1.96(1)	0.003(1)	
	V···O	1	2.38(6)	0.009(7)	
	V-O-S	2	3.22(7)	0.013(4)	
Discharge 1.95 V	V=O	1	1.60(4)	0.004(2)	1.9
	V-O	1	1.83(5)	0.006(15)	
	V-O_{eq}	3	1.98(3)	0.005(4)	
	V···O	1	2.46(9)	0.008(6)	
	V-O-S	2	3.16(7)	0.017(5)	
Charge 4.00 V	V=O	1	1.57(1)	0.004(2)	2.0
	V-O	1	1.78(1)	0.008(7)	
	V-O_{eq}	3	1.97(2)	0.003(1)	
	V···O	1	2.44(15)	0.009(6)	
	V-O-S	2	3.17(5)	0.014(4)	

Table S5. *Structural parameters obtained from fits of the vanadium K-edge EXAFS spectra Fourier transform of the chemically lithiated samples of $V_2O_3(SO_4)_2$ shown in Figure 8 (d).*

Sample	V-X	N	R/ Å	σ^2/ 10^{-3} Å^2	R-factor/ %
$V_2O_3(SO_4)_2$	V=O	1	1.60(4)	0.002(1)	1.7
	V-O	1	1.80(2)	0.002(2)	
	V-O_{eq}	3	1.97(12)	0.004(1)	
	V···O	1	2.46(3)	0.015(9)	
	V-O-S	2	3.18(8)	0.010(2)	
$Li_{0.97}V_2O_3(SO_4)_2$	V=O	1	1.58(2)	0.001(2)	1.8
	V-O	1	1.76(2)	0.003(6)	
	V-O_{eq}	3	1.98(2)	0.003(2)	
	V···O	1	2.47(9)	0.014(14)	
	V-O-S	2	3.22(5)	0.017(6)	
$Li_{1.64}V_2O_3(SO_4)_2$	V=O	1	1.58(2)	0.002(1)	1.8
	V-O	1	1.82(4)	0.007(12)	
	V-O_{eq}	3	1.96(6)	0.004(3)	
	V···O	1	2.39(1)	0.004(4)	
	V-O-S	2	3.14(8)	0.015(4)	
$Li_{2.47}V_2O_3(SO_4)_2$	V=O	1	1.61(4)	0.003(1)	1.8
	V-O	1	1.94(16)	0.017(23)	
	V-O_{eq}	3	1.99(3)	0.006(2)	
	V···O	1	2.40(3)	0.009(6)	
	V-O-S	2	3.22(1)	0.019(5)	
$Li_{3.97}V_2O_3(SO_4)_2$	V=O	2	1.67(20)	0.017(1)	1.0
	V-O_{eq}	3	2.04(4)	0.012(1)	
	V···O	1	2.56(26)	0.012(1)	
	V-O-S	2	3.22(1)	0.022(3)	