Electronic Supplementary Material (ESI) for CrystEngComm.

The $Sc_2W_xMo_{3-x}O_{12}$ series as electrodes in alkali-ion batteries

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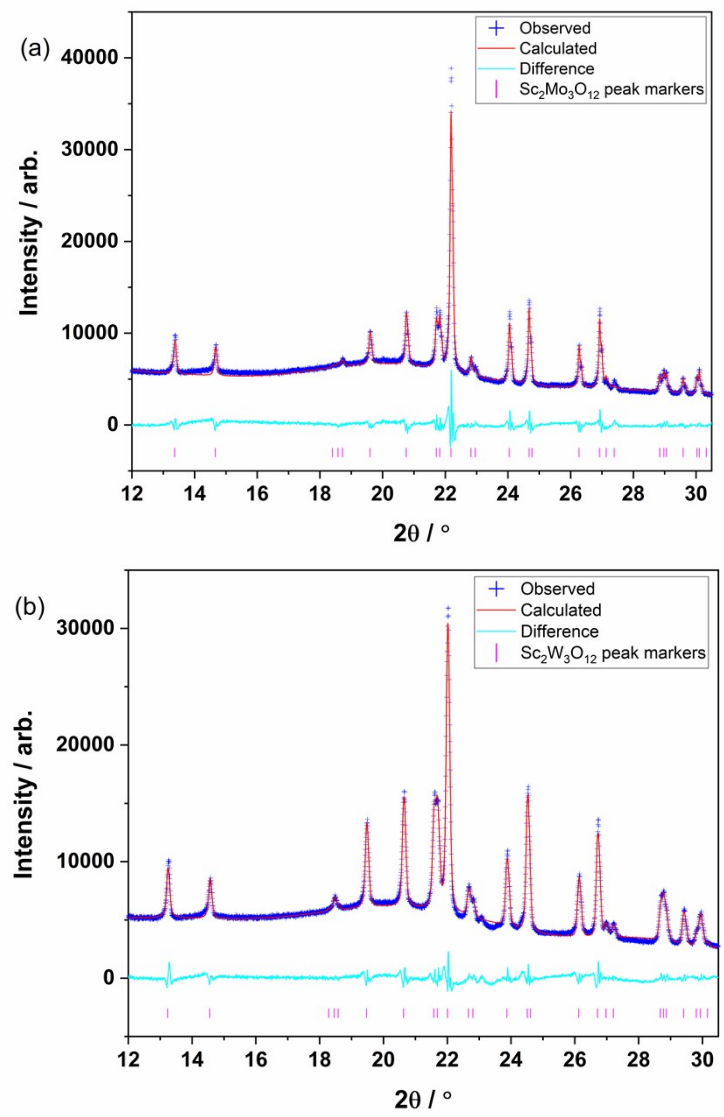

Figure s1 XRD data of (a) lithium discharged $Sc_2Mo_3O_{12}$ at 1.7 V (b) lithium discharged $Sc_2W_3O_{12}$ at 1.3 V.

Table s1 Structural table of lithium discharged $Sc_2Mo_3O_{12}$ at 1.7 V and lithium discharged $Sc_2W_3O_{12}$ at 1.3 V.

$Sc_2Mo_3O_{12}$					
Atom	**x**	**y**	**z**	**frac**	**Uiso**
Sc1	0.1124(16)	0.231(4)	0.456(5)	1	0.069(14)
Mo1	0.1455(6)	0.0787(17)	0.129(3)	1	0.058(12)
Mo2	0	0.5136(31)	0.25	1	0.074(22)
O1	0.1266(27)	0.245(11)	0.204(9)	1	0.10(4)
O2	0.1129(28)	-0.176(7)	0.162(9)	1	0.17(4)
O3	0.1460(29)	0.206(8)	-0.011(9)	1	0.13(5)
O4	0.1414(18)	0.033(6)	0.378(10)	1	0.01(3)
O5	0.114(5)	0.403(14)	0.393(7)	1	0.28(5)
O6	0.031(5)	0.622(15)	0.130(14)	1	0.24(6)

$Sc_2W_3O_{12}$					
label	**x**	**y**	**z**	**frac**	**Uiso**
Sc1	0.493(20)	0.40(4)	0.27(7)	1	0.10(16)
W1	0.25	0	0.478(28)	1	0.25(14)
W2	0.111(10)	0.362(12)	0.398(8)	1	0.19(6)
O1	0.271(22)	0.10(3)	0.199(8)	1	0.14(11)
O2	0.006(12)	0.121(5)	0.331(13)	1	0.0(13)
O3	-0.07(19)	0.365(14)	0.12(6)	1	0.22(5)
O4	0.23(13)	0.36(5)	0.161(8)	1	0.20(25)
O5	-0.21(7)	0.35(7)	0.47(3)	1	0.1(4)
O6	0.377(15)	0.35(14)	0.32(5)	1	0.03(23)

Table s2 Comparison of the discharge capacities of lithium discharged $Sc_2Mo_3O_{12}$ and $Sc_2W_3O_{12}$ with low cut-off potential 0.1V and high cut-off potential 0.5V.

Sample	Cut-off potential	Discharge capacity / mAh g^{-1}		
		1st	3rd	5th
Li discharged $Sc_2Mo_3O_{12}$	0.1	1199.8	445.6	348.9
Li discharged $Sc_2Mo_3O_{12}$	0.5	486.3	178.7	159.4
Li discharged $Sc_2W_3O_{12}$	0.1	710.5	260.3	209.2
Li discharged $Sc_2W_3O_{12}$	0.5	282.65	41.8	43.8

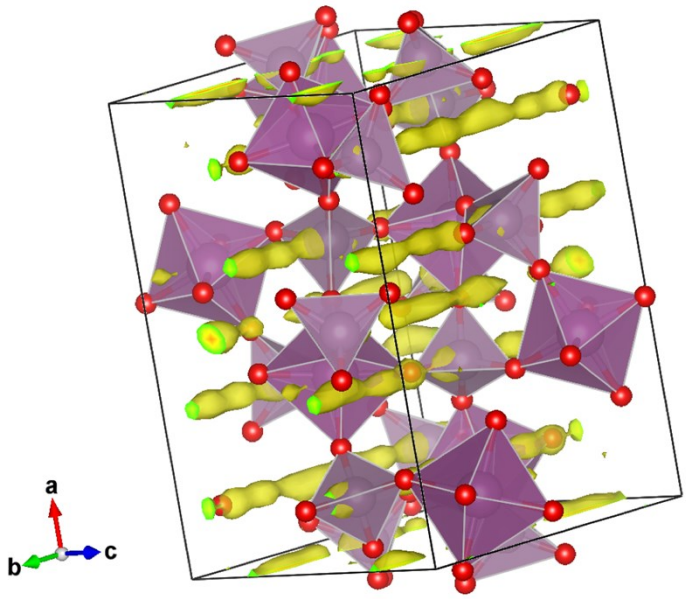

Figure s2 Fourier difference map of potassium discharged $Sc_2Mo_3O_{12}$ where the yellow regions are the electron density.

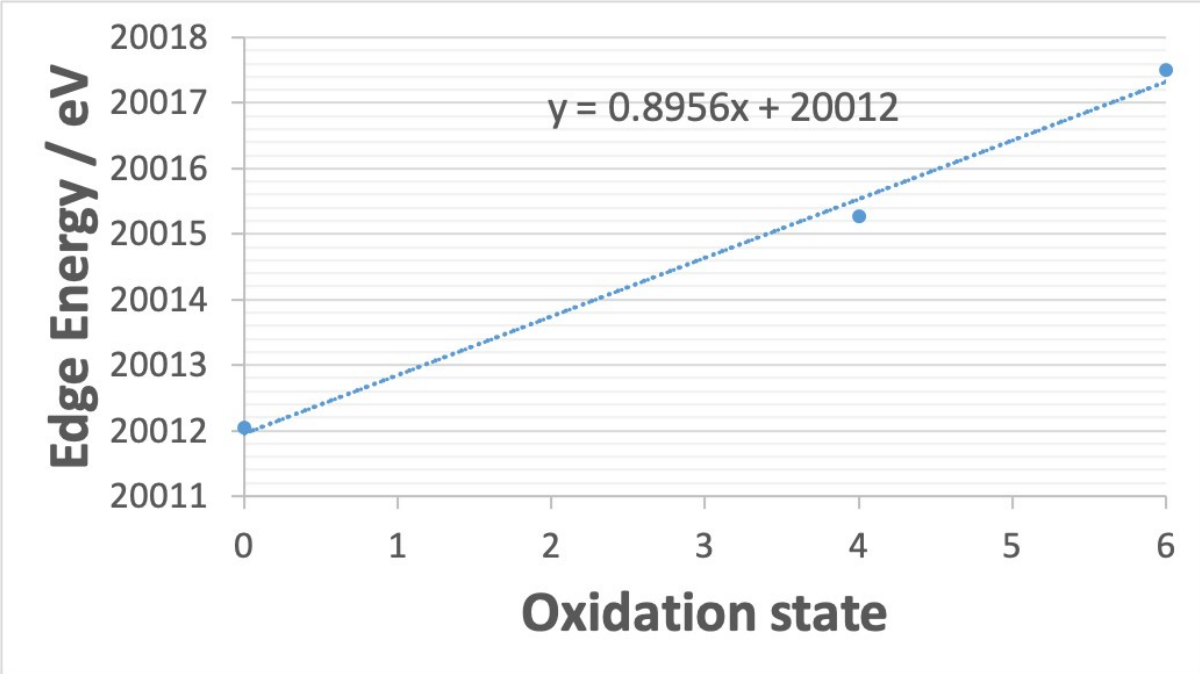

Figure s3 Linear interpolation between the edge energies of Mo metal, MoO_2 as Mo(IV) and MoO_3 as Mo(VI) reference

Table s3 Comparison between the number of inserted ions per formula unit inferred from the change in Mo oxidation state (see Figure 7a) and the inserted ions calculated from Faraday's law of electrolysis.

Sample (with 100% discharge)		Avg. Mo oxidation state number	Inserted alkali ions per formula unit from Mo-edge XANES	Inserted alkali ions per formula unit from electrochemistry	Difference
$Sc_2Mo_3O_{12}$	**Li**	4.12	5.63	25.5	19.87
	Na	5.97	0.08	9.9	9.82
	K	5.91	0.27	5.8	5.53
$Sc_2W_{0.5}Mo_{2.5}O_{12}$	**Li**	3.01	8.97	18.7	9.73
	Na	5.78	0.65	7.5	6.85
	K	5.63	1.10	5.2	4.10
$Sc_2W_{1.5}Mo_{1.5}O_{12}$	**Li**	2.87	9.39	19.5	10.11
	Na	4.32	5.05	7.3	2.25
	K	5.84	0.48	4.5	4.02
$Sc_2W_{2.5}Mo_{0.5}O_{12}$	**Li**	3.85	6.46	20.6	14.14
	Na	5.45	1.64	7	5.36
	K	5.85	0.44	4.8	4.36

Table s4 Estimated fractions of Mo in various oxidation state in the discharged samples (assuming stepwise reduction from 6+ to 4+ to 0).

Sample (with 100% discharge)		Mo oxidation state number	Mo/Mo^{4+}/Mo^{6+} fraction (%)		
			Mo	Mo^{4+}	Mo^{6+}
$Sc_2Mo_3O_{12}$	Li	4.12	/	93.91	6.09
	Na	5.97	/	1.27	98.73
	K	5.91	/	4.55	95.45
$Sc_2W_{0.5}Mo_{2.5}O_{12}$	Li	3.01	24.78	75.22	/
	Na	5.78	/	10.92	89.08
	K	5.63	/	18.26	81.74
$Sc_2W_1Mo_2O_{12}$	Li	3.64	8.90	91.10	/
	Na	5.99	/	0.32	99.68
	K	5.85	/	7.27	92.73
$Sc_2W_{1.5}Mo_{1.5}O_{12}$	Li	2.87	28.23	71.77	/
	Na	4.32	/	84.09	15.91
	K	5.84	/	8.04	91.96
$Sc_2W_2Mo_1O_{12}$	Li	3.11	22.31	77.69	/
	Na	4.17	/	91.75	8.25
	K	5.82	/	8.79	91.21
$Sc_2W_{2.5}Mo_{0.5}O_{12}$	Li	3.85	3.85	96.15	/
	Na	5.45	/	27.37	72.63
	K	5.85	/	7.26	92.74

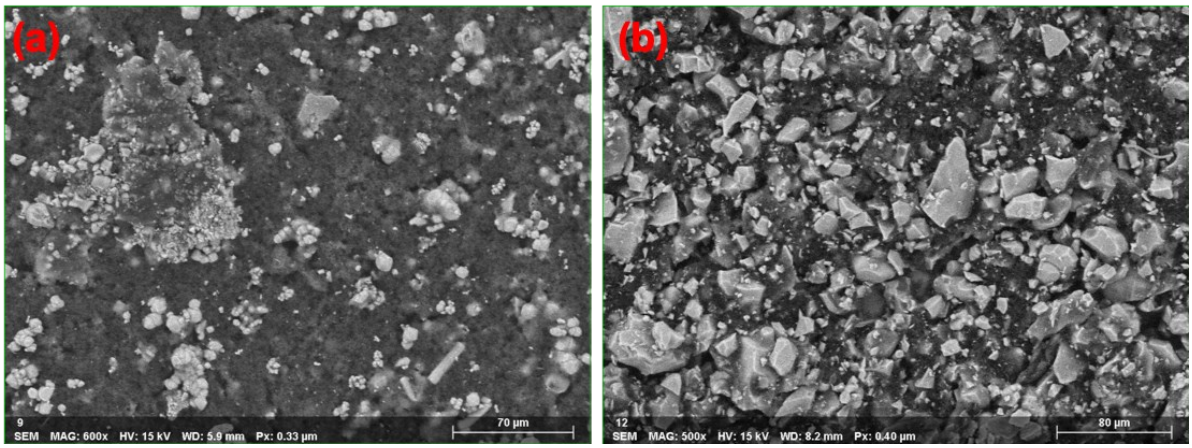

Figure s4 SEM images of (a) $Sc_2Mo_3O_{12}$ electrode and (b) lithium discharged $Sc_2Mo_3O_{12}$.

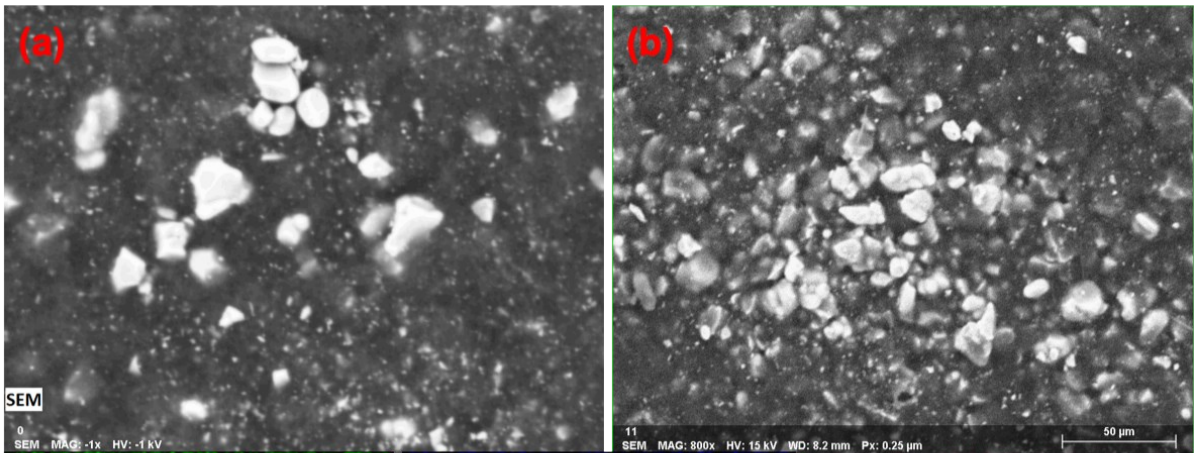

Figure s5 SEM images of (a) $Sc_2W_3O_{12}$ electrode and (b) lithium discharged $Sc_2W_3O_{12}$.