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

High Voltage Sulphate Cathodes $Li_2M(SO_4)_2$ (M = Fe, Mn, Co): Atomic-Scale Studies of Lithium Diffusion, Surfaces and Voltage Trends

Supplementary Information

Table S1. Interatomic potentials and shell model parameters for $Li_2M(SO_4)_2$ (M = Fe, Mn, Co).

(a) Buckingham			
Interaction	A (eV)	ρ (Å)	C (eV·Å^6)
Li^+ - $O^{0.84-}$	4787.6	0.19998	0.0
Fe^{2+} - $O^{0.84-}$	7500.0	0.22	0.0
Mn^{2+} - $O^{0.84-}$	1210.85	0.2825	0.0
Co^{2+} - $O^{0.84-}$	1163.5	0.27	0.0
$O^{0.84-}$ - $O^{0.84-}$	103585.030	0.20	25.93
(b) Morse			
	D_e (eV)	a (Å^{-1})	r_0 (Å)
$O^{0.84-}$ - $S^{1.36+}$	5.0	1.20	1.505
(c) Three-body			
	K (eV·rad^{-2})	θ_0 (deg)	
$O^{0.84-}$ - $S^{1.36+}$ - $O^{0.84-}$	15.0	109.47	
(d) Shell model			
Species	Y (e)	k (eV·Å^{-2})	
Fe^{2+}	2.997	19.26	
Mn^{2+}	3.42	95.00	
Co^{2+}	3.503	110.50	

Table S2. Crystallographic data and atomic positions of $Li_2M(SO_4)_2$ (M = Co, Mn, Fe) and $LiFe(SO_4)_2$

$Li_2Co(SO_4)_2$[21]	$P\,2_1/c$	a = 4.9787(1) Å	b = 8.1113(1) Å	c = 8.7831(1) Å	β = 121.811(1)°	V = 301.416(1) Å^3
Atom	Wyckoff	Occupancy	x/a	y/b	z/c	B_{iso} (Å^2)
Co	2*a*	1.0	0	0	0	0.65(1)
Li	4*e*	1.0	0.002(1)	0.638(1)	0.103(1)	1.16(11)
S	4*e*	1.0	0.3361(2)	0.3046(1)	0.3024(1)	0.68(2)
O1	4*e*	1.0	0.1829(4)	0.4185(3)	0.1530(3)	0.70(4)
O2	4*e*	1.0	0.2048(5)	0.1365(2)	0.2466(3)	0.85(4)
O3	4*e*	1.0	0.2834(4)	0.3506(2)	0.4501(3)	0.73(4)
O4	4*e*	1.0	0.6794(4)	0.3022(2)	0.3748(3)	0.46(4)
$Li_2Mn(SO_4)_2$[22]	$P\,2_1/c$	a = 4.9920(1) Å	b = 8.3396(1) Å	c = 8.8614(1) Å	β = 121.230(5)°	V = 315.464(5) Å^3
Atom	Wyckoff	Occupancy	x/a	y/b	z/c	B_{iso} (Å^2)
Mn	2*a*	1.0	0	0	0	1.32(4)
Li	4*e*	1.0	0.021(3)	0.6326(14)	0.1010(16)	1.9(4)
S	4*e*	1.0	0.3284(5)	0.3030(3)	0.2970(3)	1.77(5)
O1	4*e*	1.0	0.1761(9)	0.4140(4)	0.1490(5)	0.84(10)
O2	4*e*	1.0	0.1954(9)	0.1405(5)	0.2460(5)	1.29(11)
O3	4*e*	1.0	0.2813(8)	0.3508(4)	0.4379(5)	1.80(12)
O4	4*e*	1.0	0.6619(8)	0.2974(5)	0.3607(5)	0.61(10)
$Li_2Fe(SO_4)_2$[21]	$P\,2_1/c$	a = 4.9886(1) Å	b = 8.2062(1) Å	c = 8.8293(1) Å	β = 121.7499(1)°	V = 307.359(1) Å^3
Atom	Wyckoff	Occupancy	x/a	y/b	z/c	B_{iso} (Å^2)
Fe	2*a*	1.0	0	0	0	0.49(1)
Li	4*e*	1.0	0.0176(12)	0.6307(7)	0.1060(7)	1.30(12)
S	4*e*	1.0	0.3340(2)	0.3040(1)	0.3015(1)	0.49(2)
O1	4*e*	1.0	0.1779(4)	0.4183(2)	0.1501(2)	0.48(4)
O2	4*e*	1.0	0.2007(4)	0.1376(2)	0.2482(2)	0.37(4)
O3	4*e*	1.0	0.2879(4)	0.3517(2)	0.4470(2)	0.63(5)
O4	4*e*	1.0	0.6762(4)	0.3003(2)	0.3703(2)	0.42(4)
$LiFe(SO_4)_2$[22]	$P\,2_1/c$	a = 4.7966(1) Å	b = 8.3638(1) Å	c = 7.9056(1) Å	β = 121.475(5)°	V = 270.465(3) Å^3
Atom	Wyckoff	Occupancy	x/a	y/b	z/c	B_{iso} (Å^2)
Fe	2*a*	1.0	0	0	0	0.49(2)
Li	4*e*	0.5	0.560(3)	0.0236(14)	0.5258(18)	1.1(3)
S	4*e*	1.0	0.3048(3)	0.1783(1)	0.7613(2)	0.27(2)
O1	4*e*	1.0	0.0455(4)	0.1275(2)	0.7997(3)	0.69(4)
O2	4*e*	1.0	0.2632(4)	0.1033(2)	0.5854(3)	0.66(4)
O3	4*e*	1.0	0.2824(4)	0.3572(2)	0.7377(3)	0.57(4)
O4	4*e*	1.0	0.3757(4)	0.6422(2)	0.5594(2)	0.55(4)

Experimental

$Li_2M(SO_4)_2$ (M = Co, Mn, Fe) samples were prepared using the procedure described in previous reports[21,22], which consists of the following steps: (i) ball-milling of the precursors MSO_4 and Li_2SO_4 taken in a stoichiometric ratio, (ii) pressing the resulting mixture into a pellet, (iii) annealing of the pellet at 310°C for 12 to 48 hours working either under air (M = Co, Mn) or in a quartz tube sealed under vacuum (M = Fe). The delithiated samples $LiFe(SO_4)_2$ were obtained

from chemical oxidation of the $Li_2Fe(SO_4)_2$ phase using NO_2BF_4 in acetonitrile as an oxidizing agent.

The $Li_2M(SO_4)_2$ structure was precisely determined from Synchrotron X-ray diffraction patterns of $Li_2Co(SO_4)_2$ and $Li_2Fe(SO_4)_2$ (11-BM beamline, APS-ANL, Argonne USA).[21] This model was later used to refine the laboratory XRD pattern of $Li_2Mn(SO_4)_2$ (Bruker D8 diffractometer, using a Cu radiation source: $\lambda_{K\alpha1}$ = 1.54056 Å, $\lambda_{K\alpha2}$ = 1.54439 Å).[22] Neutron powder diffraction was used to determine the structure of $LiFe(SO_4)_2$, in particular to accurately localize the light Li atoms; a joint refinement was finally performed against both Synchrotron XRD and neutron diffraction data.[22]

Table S3. Li-Li separations for Li Migration Paths (illustrated in Fig. 3) in $Li_2M(SO_4)_2$ (M = Fe, Mn, Co).

	Li-Li Separation (Å)		
Path	$Li_2Fe(SO_4)_2$	$Li_2Mn(SO_4)_2$	$Li_2Co(SO_4)_2$
L1	2.79	2.89	2.87
L2	4.82	4.82	4.75
L3	4.88	4.95	4.81
L4	4.96	5.10	4.87
L5	4.99	4.99	4.96

Table S4. Calculated (DFT) and Experimental Structural Parameters of $Li_2M(SO_4)_2$ (M = Fe, Mn, Co).

Parameter	a (Å)	b (Å)	c (Å)	β (°)
		$Li_2Fe(SO_4)_2$		
calc. (GGA+U)	5.0453	8.2894	8.9848	121.80
expt.[21]	4.9886	8.2062	8.8293	121.75
Δ	0.0567	0.0832	0.1555	0.05
		$Li_2Mn(SO_4)_2$		
calc. (GGA+U)	5.0537	8.4295	9.0098	120.95
expt.[22]	4.9920	8.3396	8.8614	121.23
Δ	0.0617	0.0899	0.1484	-0.28
		$Li_2Co(SO_4)_2$		
calc. (GGA+U)	5.0248	8.1970	8.9149	121.30
expt.[21]	4.9787	8.1113	8.7831	121.81
Δ	0.0461	0.0857	0.1318	-0.51
		$LiFe(SO_4)_2$		
calc. (GGA+U)	4.8913	8.4477	8.0559	121.30
expt.[22]	4.7966	8.3638	7.9056	121.48
Δ	0.0947	0.0839	0.1503	-0.18

Table S5. Calculated (DFT) Crystallographic data and atomic positions of $Li_2Fe(SO_4)_2$ and $LiFe(SO_4)_2$.

$Li_2Fe(SO_4)_2$	*P* 1	*a* = 5.0453 Å	*b* = 8.2894 Å	*c* = 8.9848 Å	*β* = 121.80°
Atom		*x*/*a*	*y*/*b*	*z*/*c*	
Li1		0.0110	0.6347	0.1009	
Li2		0.9890	0.3653	0.8991	
Li3		0.9890	0.1347	0.3991	
Li4		0.0110	0.8653	0.6009	
Fe1		0.0000	0.0000	0.0000	
Fe2		0.0000	0.5000	0.5000	
S1		0.3322	0.3058	0.3013	
S2		0.6678	0.6942	0.6987	
S3		0.6678	0.8058	0.1987	
S4		0.3322	0.1942	0.8013	
O1		0.1771	0.4182	0.1519	
O2		0.8229	0.5818	0.8481	
O3		0.8229	0.9182	0.3481	
O4		0.1771	0.0818	0.6519	
O5		0.2040	0.1391	0.2476	
O6		0.7960	0.8609	0.7524	
O7		0.7960	0.6391	0.2524	
O8		0.2040	0.3609	0.7476	
O9		0.2810	0.3526	0.4444	
O10		0.7190	0.6474	0.5556	
O11		0.7190	0.8526	0.0556	
O12		0.2810	0.1474	0.9444	
O13		0.6765	0.3057	0.3727	
O14		0.3235	0.6943	0.6273	
O15		0.3235	0.8057	0.1273	
O16		0.6765	0.1943	0.8727	

$LiFe(SO_4)_2$	*P* 1	*a* = 4.8913 Å	*b* = 8.4477 Å	*c* = 8.0559 Å	*β* = 121.30°
Atom		*x*/*a*	*y*/*b*	*z*/*c*	
Li1		0.5000	0.0000	0.0000	
Li2		0.5000	0.5000	0.5000	
Fe1		0.0000	0.0000	0.5000	
Fe2		0.0000	0.5000	0.0000	
S1		0.3066	0.1783	0.2637	
S2		0.6934	0.8217	0.7363	
S3		0.6934	0.6783	0.2363	
S4		0.3066	0.3217	0.7637	
O1		0.0560	0.1264	0.3062	
O2		0.9440	0.8736	0.6938	
O3		0.9440	0.6264	0.1938	
O4		0.0560	0.3736	0.8062	
O5		0.2604	0.1043	0.0894	
O6		0.7396	0.8957	0.9106	
O7		0.7396	0.6043	0.4106	
O8		0.2604	0.3957	0.5894	
O9		0.2841	0.3560	0.2396	
O10		0.7160	0.6440	0.7604	
O11		0.7160	0.8560	0.2604	
O12		0.2840	0.1440	0.7400	
O13		0.3716	0.6430	0.0606	
O14		0.6284	0.3570	0.9394	
O15		0.6284	0.1430	0.4394	
O16		0.3716	0.8570	0.5606	