Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

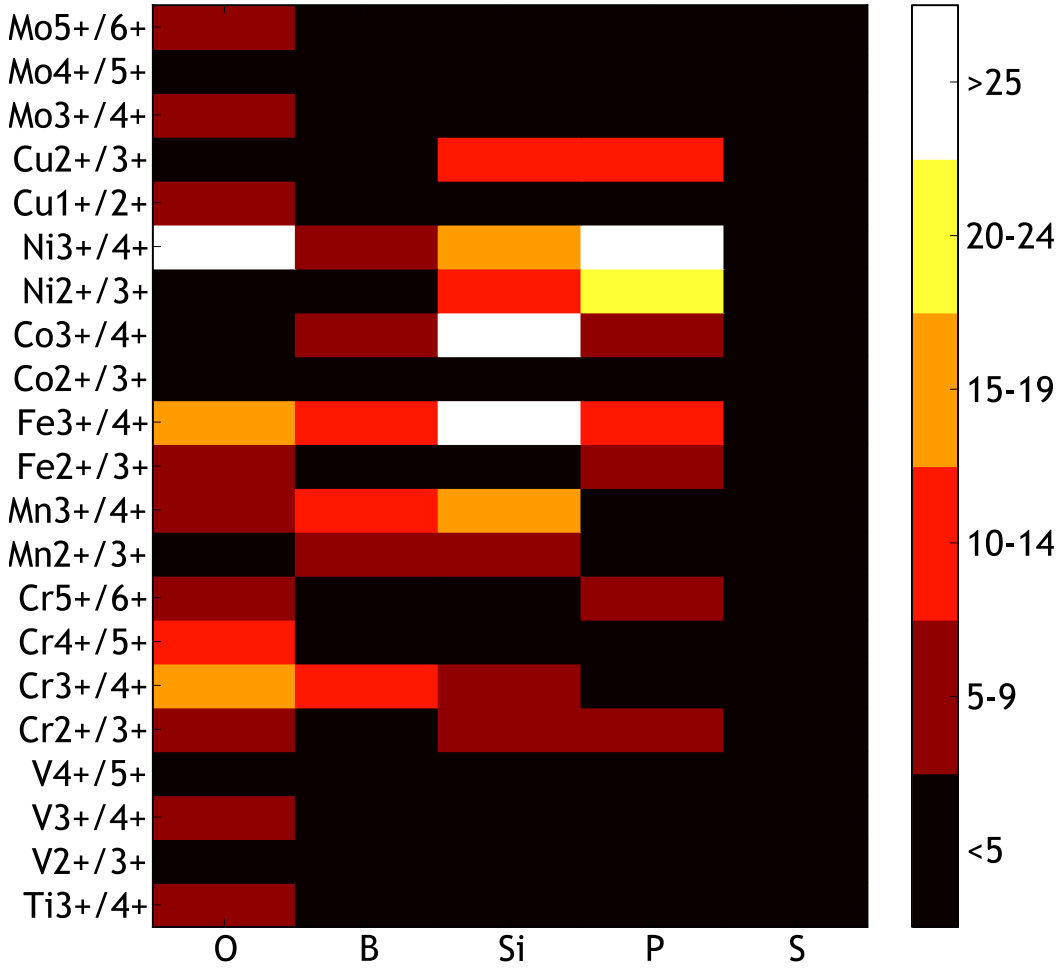

Figure S1 The number of compounds *excluded* by stability filtering, arranged by redox couple and anion. The 'O' anion group indicates oxides, whereas 'B', 'Si', 'P', and 'S' indicate borates, silicates, phosphates, and sulfates, respectively.

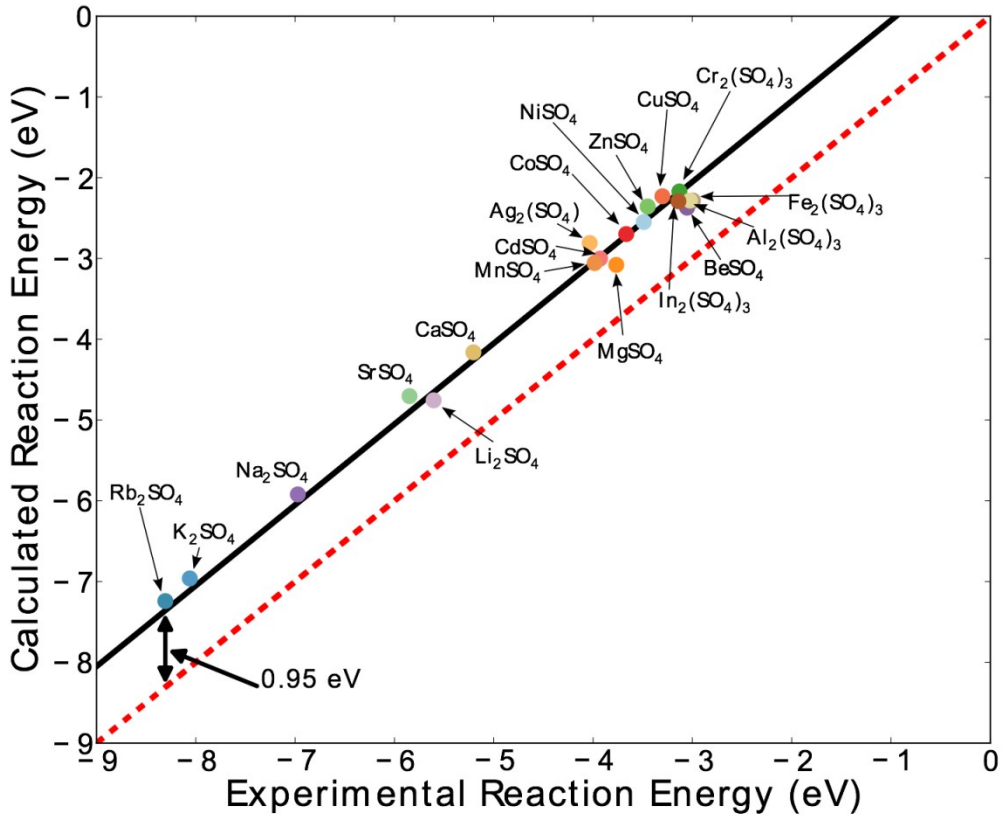

Figure S2 Computed versus experimental[45,46] reaction energies for sulfate compounds used to fit an enthalpy for SO_2 gas at ambient conditions. For alkali metals A, the reaction presented is $A_2O + SO_2 + 1/2O_2 \rightarrow A_2SO_4$, whereas for non-alkali metals the reaction presented is $BO + SO_2 + 1/2O_2 \rightarrow BSO_4$. In these reactions, SO_2 is the solid 0K ground state and the O_2 energy is taken from Wang et al.[40] The accuracy represented by the fitted value of the SO_2 gas energy (black line) is independent of the SO_2 reference chosen for these reactions but depends on the choice of O_2 reference. The RMS error after fitting is 156 meV/atom.

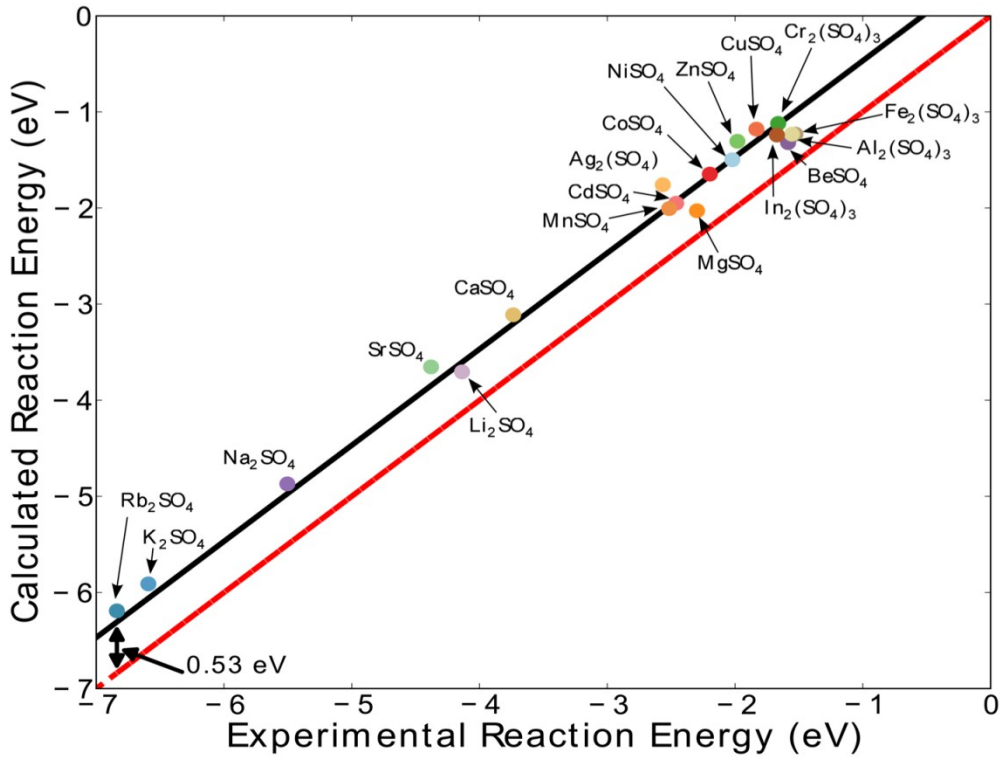

Figure S3 Computed versus experimental[45,46] reaction energies for sulfate compounds used to fit an enthalpy for SO_3 gas at ambient conditions. For alkali metals A, the reaction presented is $A_2O + SO_3 \rightarrow A_2SO_4$, whereas for non-alkali metals the reaction presented is $BO + SO_3 \rightarrow BSO_4$. In these reactions, SO_3 is the solid 0K ground state. The accuracy represented by the final fitted value of the SO_3 gas energy (black line) is independent of the SO_3 reference chosen for these reactions. The RMS error after fitting is 156 meV/atom. Note that this error is the same as the SO_2 fit because the same data set is used for the fitting.

Element	VASP title	number of electrons	*+(U-J)* correction
B	PAW_PBE B 06Sep2000	3	N/A
Li	PAW_PBE Li 17Jan2003	1	N/A
O	PAW_PBE O 08Apr2002	6	N/A
P	PAW_PBE P 17Jan2003	5	N/A
S	PAW_PBE S 17Jan2003	6	N/A
Si	PAW_PBE Si 05Jan2001	4	N/A
Co	PAW_PBE Co 06Sep2000	9	5.7
Cr	PAW_PBE Cr 06Sep2000	6	3.5
Cu	PAW_PBE Cu 05Jan2001	11	4
Fe	PAW_PBE Fe 06Sep2000	8	4
Mn	PAW_PBE Mn 06Sep2000	7	3.9
Mo	PAW_PBE Mo_pv 08Apr2002	12	4.38
Ni	PAW_PBE Ni 06Sep2000	10	6
Ti	PAW_PBE Ti 08Apr2002	4	0
V	PAW_PBE V_pv 07Sep2000	11	3.1

Table S1 Pseudopotentials and DFT+U parameters used in this work.

compound	technique / environment	decomp. temp (Celsius)	voltage at state-of-charge (V)	reference / notes
CoPO4	XRD / argon	<200		ref[17] (O2 release hypothesized)
Fe2(SO4)3	argon	600	3.9	ref[78]
FePO4	DSC sealed tubes	221	3.8	ref[51]
FePO4	DSC electrolyte	340		ref[16]
FePO4	DSC electrolyte	250		ref[52]
FePO4	DSC sealed tubes	>400		ref[15]
FePO4	DSC / electrolyte	250		ref[15]
FePO4	L80 calorimetry / electrolyte	218	4.2	ref[53]
Li0.5CoO2	DSC sealed tubes	180	4.2	ref[51]
Li0.5CoO2	dsc argon sealed	170	4.2	ref[54]
Li0.5CoO2	dsc argon sealed	200		ref[55]
Li0.5CoO2	dTG air	230		ref[55]
Li0.5CoO2	DSC electrolyte	200		ref[55]
Li0.5CoO2	DSC electrolyte	170	4.2	ref[58] (x~0.5 hypothesized)
Li0.5NiO2	DSC sealed tubes	187	4.0	ref[51]
LiFeP2O7	DSC+TG / Ar	>600		ref[66]
LiFePO4	DSC electrolyte	275		ref[15]
LiFePO4	DSC electrolyte	>400C		ref[16]
LiFePO4	TGA / argon	>400		ref[15]
LiMnPO4	air/ambient vacuum XRD	>410		ref[56]
LiMnPO4	DSC / electrolyte	275		ref[15]
LiMnPO4	TGA / argon	>400		ref[15]
LiMnPO4	DSC electrolyte	232		ref[57]
LixMn2O4	L80 calorimetry / electrolyte	152	4.3	ref[53]
LixMn2O4	C80 calorimetry /argon	151	4.3	ref[62]
Mn2O4	DSC sealed tubes	207	4.2	ref[51]
MnPO4	air/ambient vacuum XRD	210		ref[56]
MnPO4	DSC electrolyte	194		ref[57]
MnPO4	sealed tubes	>300		ref[57]
MnPO4	Argon	490		ref[59] (peaks exist starting at 180C hypothesize they are not O2 release)
MnPO4	DSC+TGA/sealed tubes	120		ref[15]

MnPO4	DSC / electrolyte	150		ref[15] (li content < 0.17)
MnSiO4	nitrogen	200	4.7	ref[61]
NiPO4	unknown	room temp		ref[64]
V2(PO4)3	dsc in presence of electrolyte	210	4.8	ref[60]

Table S2 Experimental O_2 release data from the literature. Note that we have focused only on reports of bulk materials, and do not include studies of mixed metal compounds (which are not computed in this work). When possible, we attempted to use temperature values reported within the text of the reports, otherwise the value represents a best guess as to onset temperature from reading the experimental data. In addition, where the experiments report a voltage at the state of charge of the O_2 release measurement, we have also listed this voltage.

	p/p_0	1E-01	1E-02	1E-03	1E-04	1E-05	1E-06
T at p_0 (°C)							
0		-21	-39	-55	-69	-81	-92
100		72	49	28	9	-7	-22
200		166	137	111	87	67	48
300		260	225	194	167	142	120
400		354	314	278	246	217	192
500		448	403	362	326	294	264
600		543	492	447	406	370	337
700		637	581	531	487	447	410
800		731	670	616	567	523	484
900		826	760	701	648	601	557
1000		920	849	786	729	678	631
1100		1015	939	871	810	755	705
1200		1110	1029	957	892	833	780
1300		1204	1119	1042	973	911	854
1400		1299	1209	1128	1055	989	929
1500		1394	1299	1213	1136	1067	1003
1600		1489	1389	1299	1218	1145	1078
1700		1583	1479	1385	1300	1223	1153
1800		1678	1569	1471	1382	1302	1228
1900		1773	1659	1557	1464	1380	1304
2000		1868	1750	1643	1547	1459	1379
2100		1963	1840	1729	1629	1538	1454
2200		2058	1931	1816	1711	1617	1530
2300		2153	2021	1902	1794	1696	1606
2400		2248	2112	1988	1877	1775	1682
2500		2343	2202	2075	1959	1854	1758

Table S3 Variation of O_2 release temperature with ambient pressure according to Eq. 1. Lower partial pressures of O_2 (more reducing environments) result in lower predicted O_2 release temperatures.

compound	Voltage (V)	O2 release T (°C)
CoO_2	3.93	-273
$Li_{0.5}CoO_2$	3.96	117
MnO_2	3.32	269
$FePO_4$	3.50	1205

Table S4 Computed voltages and oxygen release pressures for common cathode materials