Thermal plasma synthesis of Li_2S nanoparticles for application in lithium-sulfur batteries

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Supplementary Information

Molar compositions are provided as a function of temperature for the Li_2O-S-H_2, LiOH-S-H_2 and Li_2SO_4-C-H_2 systems, as calculated by Gibbs energy minimization in FactSage [1-3]. The mixture of reactants are provided by equations S1, S2 and S3.

$1/2\ Li_2O + 1/2\ S + 2\ H_2$ (eq. S1)

$2/3\ LiOH + 1/3\ S + 2\ H_2$ (eq. S2)

$0.22\ Li_2SO_4 + 0.78\ C + 9\ H_2$ (eq. S3)

The plasma state with dissociation and ionization was considered. As such, a total of 81 products are considered for these Li_2O-S-H_2 and LiOH-S-H_2 systems, as provided in Table S1. In comparison, 150 products are considered for the Li_2SO_4-C-H_2 systems, as provided in Table S2.

Table S1. Species considered for the molar compositions of the Li_2O-S-H_2 and LiOH-S-H_2 systems.

Gas phase		**Gas phase (cont.)**		**Liquid phase**		**Solid phase**	
1	H[-]	27	LiO	53	Li	70	Li
2	H	28	Li2O	54	LiH	71	LiH
3	H[+]	29	Li2O2	55	HOOH	72	H2O
4	H2[-]	30	LiOH	56	H2S2	73	SO3
5	H2	31	LiOH[+]	57	SO3	74	Li2O
6	H2[+]	32	(LiOH)2	58	H2SO4	75	Li2O2
7	Li[-]	33	S[-]	59	H2SO4(H2O)	76	LiOH
8	Li	34	S	60	H2SO4(H2O)2	77	S-alpha
9	Li[+]	35	S[+]	61	H2SO4(H2O)3	78	S-beta
10	Li2	36	S2	62	H2SO4(H2O)4	79	Li2S
11	LiH	37	S3	63	(H2SO4)2(H2O)13	80	Li2SO4-alpha
12	O[-]	38	S4	64	Li2O	81	Li2SO4-beta
13	O	39	S5	65	Li2O2		
14	O[+]	40	S6	66	LiOH		
15	O2[-]	41	S7	67	S		
16	O2	42	S8	68	Li2SO4		
17	O2[+]	43	HS	69	H2O		
18	O3	44	H2S				
19	OH[-]	45	H2S2				
20	OH	46	SO				
21	OH[+]	47	SO2				
22	H2O	48	SO3				
23	H3O[+]	49	SSO				
24	HOO	50	H2SO4				
25	HOOH	51	Li2SO4				
26	LiO[-]	52	----e[-]				

Table S2. Species considered for the molar composition of the Li_2SO_4-C-H_2 system.

Gas phase		Gas phase (cont.)		Gas phase (cont.)		Liquid phase		Solid phase	
1	H[-]	35	O2	69	HCOOH	102	Li	135	Li
2	H	36	O2[+]	70	CH3COOH	103	LiH	136	LiH
3	H[+]	37	O3	71	S[-]	104	HOOH	137	C-graphite
4	H2[-]	38	OH[-]	72	S	105	CH3OH	138	C-diamond
5	H2	39	OH	73	S[+]	106	C2H4O	139	H2O
6	H2[+]	40	OH[+]	74	S2	107	C2H4O	140	SO3
7	Li[-]	41	H2O	75	S3	108	CH3CH2OH	141	Li2C2
8	Li	42	H3O[+]	76	S4	109	HCOOH	142	Li2O
9	Li[+]	43	HOO	77	S5	110	CH3COOH	143	Li2O2
10	Li2	44	HOOH	78	S6	111	(CH2OH)2	144	LiOH
11	LiH	45	LiO[-]	79	S7	112	H2S2	145	Li2CO3
12	C[-]	46	LiO	80	S8	113	CS2	146	S-alpha
13	C	47	Li2O	81	HS	114	CH3SH	147	S-beta
14	C[+]	48	Li2O2	82	H2S	115	C2H4S	148	Li2S
15	C2[-]	49	LiOH	83	H2S2	116	(CH3)2S	149	Li2SO4-alpha
16	C2	50	LiOH[+]	84	CS	117	(CH3)2S	150	Li2SO4-beta
17	C3	51	(LiOH)2	85	CS2	118	CH3SSCH3		
18	C4	52	CO	86	CH3SH	119	H2CS3		
19	C5	53	C2O	87	C2H4S	120	SO3		
20	CH	54	CO2[-]	88	(CH3)2S	121	H2SO4		
21	CH[+]	55	CO2	89	(CH3)2S	122	H2SO4(H2O)		
22	CH2	56	C3O2	90	CH3SSCH3	123	H2SO4(H2O)2		
23	CH3	57	HCO	91	SO	124	H2SO4(H2O)3		
24	CH4	58	HCO[+]	92	SO2	125	H2SO4(H2O)4		
25	C2H	59	H2CO	93	SO3	126	(H2SO4)2(H2O)13		
26	C2H2	60	CH3O	94	SSO	127	(CH3)2SO		
27	C2H3	61	CH3O	95	H2SO4	128	Li2O		
28	C2H4	62	CH3OH	96	Li2SO4	129	Li2O2		
29	C2H5	63	CH2CO	97	COS	130	LiOH		
30	C2H6	64	C2H4O	98	C2H4OS	131	Li2CO3		
31	O[-]	65	C2H4O	99	(CH3)2SO	132	S		
32	O	66	CH3CH2OH	100	(CH3)2SO2	133	Li2SO4		
33	O[+]	67	CH3CH2OH	101	----e[-]	134	H2O		
34	O2[-]	68	COOH						

Although the temperature reached within the core of the plasma jet is higher than 2000 K, we limit the plots to the 300-2000 K range where the nucleation, growth and quench of the Li_2S particles will occur. The 16 species that reached molar fractions above 10^{-4} are shown in Figure S1 for the Li_2O-S-H_2 and LiOH-S-H_2 systems, while 23 species reached that threshold value for the Li_2SO_4-C-H_2 system.

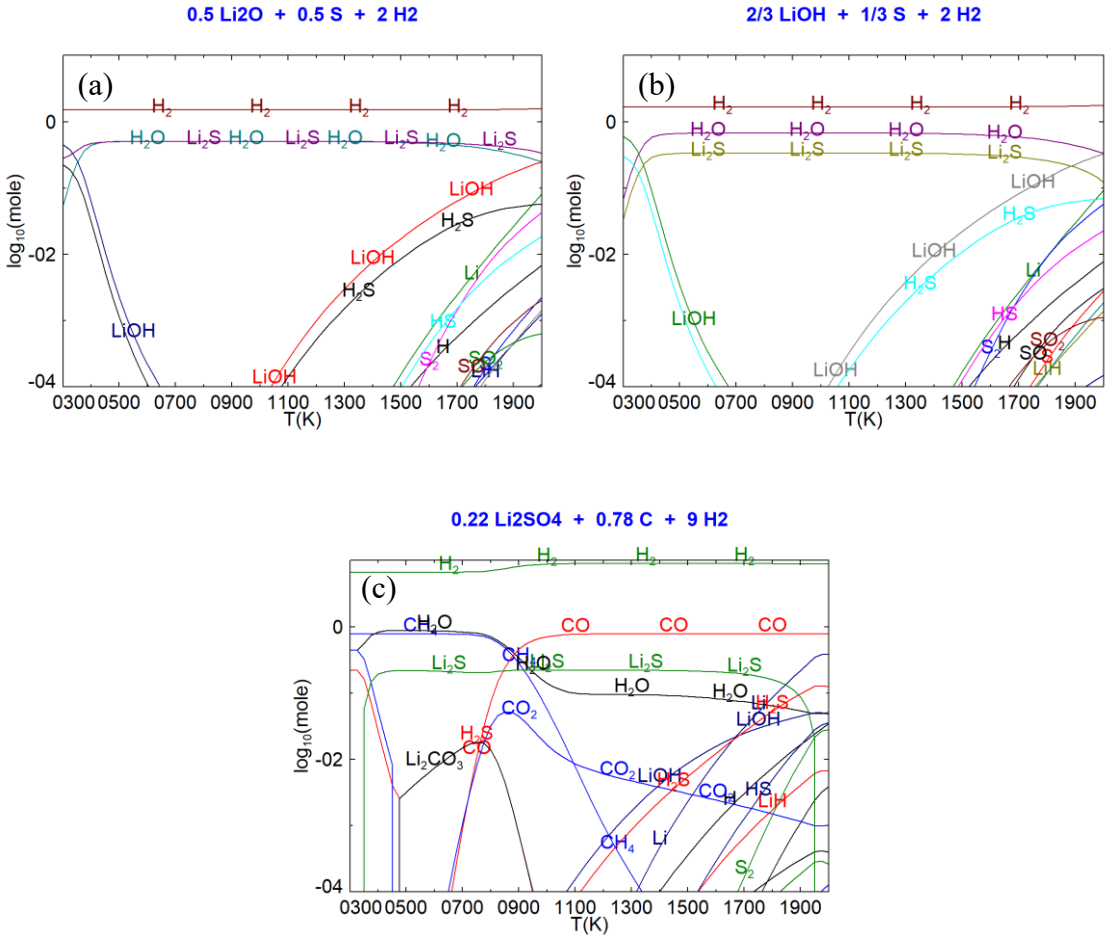

Figure S1: Molar compositions at equilibrium for the (a) Li_2O-S-H_2, (b) LiOH-S-H_2 and (c) Li_2SO_4-C-H_2 systems.

Molar composition calculations at equilibrium can also be useful to understand which solid phases should condense as the temperature drops along the plasma jet, following the initial vaporization of the precursors. It is hypothesized that gas phase reaction occurs, nanoparticles nucleate from the vapor phase, grow by condensation and aggregate. Under equilibrium and as temperature drop in the LiOH-S-H_2 system, the first solid to form is Li_2S. With the Li_2SO_4-C-H_2 system, Li_2S is the first solid to form from the vapor phase for Li_2SO_4/(Li_2SO_4+C) molar ratios greater than 0.2. Below that value, C is the first solid to form. To illustrate these statements, Figure S2 shows the molar composition of the solid phase only.

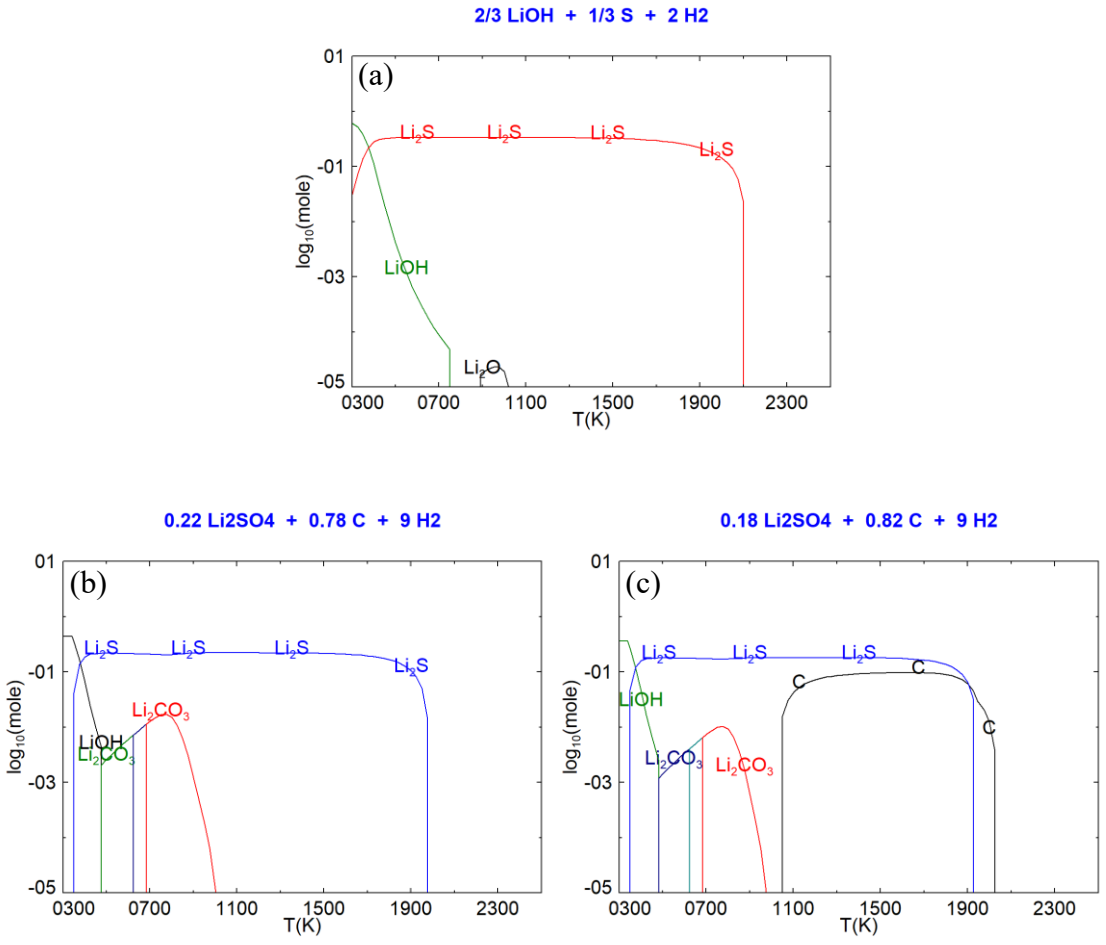

Figure S2: Solid phase molar compositions at equilibrium for the (a) LiOH-S-H_2, (b) Li_2SO_4-C-H_2 (ratio of 0.22) and (c) Li_2SO_4-C-H_2 (ratio of 0.18) systems.

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