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Hydroflux-Assisted Cold Sintering: Eutectic Mixtures for Boosting Ionic Conductivity in LATP Solid-State Electrolytes

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Supporting Information

Density measurement

The theoretical density of the hydroflux is calculated by the mixing rule, that is:

$$\rho_{Eutectic} = \frac{1}{\frac{\omega_{LiNO_3}}{\rho_{LiNO_3}} + \frac{\omega_{LiOH}}{\rho_{LiOH}}}$$

where ω_{LiNO_3} and ω_{LiOH} stand for the mass fractions of lithium nitrate and lithium hydroxide respectively. The ρ_{LiNO_3} and ρ_{LiOH} are the densities of lithium nitrate and lithium hydroxide, being 2.38 and 1.46 g/cm^3 respectively. To calculate the real density of the mixture LATP-Hydroflux the same procedure has been used but, in this case the theoretical density used for the LATP is 2.91 g/cm^3 measured by helium pycnometry.

$$\rho_{Theoretical} = \frac{1}{\frac{\omega_{Hydroflux}}{\rho_{Hydroflux}} + \frac{\omega_{LATP}}{\rho_{LATP}}}$$

To compare the different samples produced is a common methodology to use the relative density, ϕ, that is the quotient of the theoretical and the real density of the sample. As theoretical density of the sample authors used the previous equation. It must be considered that this density depends on the quantities used in the preparation.

$$\phi = \frac{\rho_{Sample}}{\rho_{Theoretical}}$$

The sample's real density is calculated by means of the Arquimedes' method with mercury immersion.

$$\rho_{Sample} = \left(\frac{m_{dry}}{m_{Hg}}\right) \cdot \rho_{Hg}$$

In this equation m_{dry} is the sample's mass after drying overnight, m_{Hg} the mass immersed in mercury and ρ_{Hg} the density of mercury (13.53 g/cm^3). When calculating the relative density, the obtention of porosity is a direct calculation because:

$$\phi + \varepsilon = 1$$

where ε is the sample's porosity. The previous equation considers that the sum of solid and pore volume equals one as expected. Results are shown in **Table S1**.

Table S1. Densities of the samples prepared.

Sample	**$\omega_{Hydroflux}$**	**$\rho_{LATP+Hydroflux}$ (g/cm^3)**	**ρ_{Sample} (g/cm^3)**	**ϕ (%)**
20@solids	0.20	2.71	2.18	80.5
20@no-H_2O	0.20	2.71	2.16	79.5
20@H_2O	0.20	2.71	2.29	84.3
15@H_2O	0.15	2.76	2.31	83.6

Table S2. Fitting results of the 20@solids sample.

T (ºC)	1000/T (K^{-1})	R_{tot} (Ω)	σ_{tot} (S cm^{-1})	ln (σ_{tot}·T)
87	2.78	390.4	$3.68\cdot10^{-4}$	-2.020
75	2.87	723.1	$1.99\cdot10^{-4}$	-2.670
66	2.95	1193.0	$1.21\cdot10^{-4}$	-3.197
58	3.02	1737.0	$8.28\cdot10^{-5}$	-3.597
51	3.08	2425.0	$5.93\cdot10^{-5}$	-3.952
47	3.12	3277.0	$4.39\cdot10^{-5}$	-4.265
44	3.15	4130.0	$3.48\cdot10^{-5}$	-4.506
41	3.18	4990.3	$2.88\cdot10^{-5}$	-4.705
39	3.20	5819.0	$2.47\cdot10^{-5}$	-4.865
37	3.22	6666.0	$2.16\cdot10^{-5}$	-5.007
36	3.23	7509.7	$1.91\cdot10^{-5}$	-5.130
34	3.26	8313.0	$1.73\cdot10^{-5}$	-5.238
33	3.27	9764.0	$1.47\cdot10^{-5}$	-5.402
32	3.28	10755.0	$1.34\cdot10^{-5}$	-5.502
31	3.29	11609.0	$1.24\cdot10^{-5}$	-5.582
30	3.30	12277.0	$1.17\cdot10^{-5}$	-5.641
30	*3.30*	*14885.0*	*$9.66\cdot10^{-6}$*	*-5.833*

Table S3. Fitting results of the 20@no-H_2O sample.

T (ºC)	1000/T (K^{-1})	R_{tot} (Ω)	σ_{tot} (S cm^{-1})	ln (σ_{tot}·T)
85	2.79	322.1	$4.95\cdot10^{-4}$	-1.730
64	2.97	586.1	$2.72\cdot10^{-4}$	-2.389
57	3.03	767.0	$2.08\cdot10^{-4}$	-2.679
51	3.08	939.4	$1.70\cdot10^{-4}$	-2.900
47	3.12	1121.2	$1.42\cdot10^{-4}$	-3.089
44	3.15	1263.4	$1.26\cdot10^{-4}$	-3.218
40	3.19	1413.0	$1.13\cdot10^{-4}$	-3.343
38	3.21	1546.5	$1.03\cdot10^{-4}$	-3.439
37	3.22	1664.9	$9.58\cdot10^{-5}$	-3.516
35	3.25	1769.0	$9.01\cdot10^{-5}$	-3.584
34	3.26	1853.5	$8.60\cdot10^{-5}$	-3.633
33	3.27	1935.5	$8.24\cdot10^{-5}$	-3.680
32	3.28	2020.3	$7.89\cdot10^{-5}$	-3.726
31	3.29	2093.8	$7.62\cdot10^{-5}$	-3.765
30	3.30	2214.5	$7.20\cdot10^{-5}$	-3.825
30	*3.30*	*2267.0*	*$7.03\cdot10^{-5}$*	*-3.848*

Table S4. Fitting results of the 20@H_2O sample.

T (ºC)	1000/T (K^{-1})	R_{tot} (Ω)	σ_{tot} (S cm^{-1})	ln (σ_{tot}·T)
80	2.83	129.4	$1.02 \cdot 10^{-3}$	-1.021
75	2.87	157.2	$8.40 \cdot 10^{-4}$	-1.230
70	2.91	185.8	$7.10 \cdot 10^{-4}$	-1.411
66	2.95	216.1	$6.11 \cdot 10^{-4}$	-1.574
62	2.98	250.0	$5.28 \cdot 10^{-4}$	-1.732
57	3.03	284.4	$4.64 \cdot 10^{-4}$	-1.876
54	3.06	320.4	$4.12 \cdot 10^{-4}$	-2.004
50	3.09	361.3	$3.65 \cdot 10^{-4}$	-2.136
46	3.13	399.3	$3.31 \cdot 10^{-4}$	-2.249
44	3.15	477.9	$2.76 \cdot 10^{-4}$	-2.435
38	3.21	590.6	$2.24 \cdot 10^{-4}$	-2.666
36	3.23	659.8	$2.00 \cdot 10^{-4}$	-2.783
32	3.28	746.0	$1.77 \cdot 10^{-4}$	-2.919
30	3.30	861.7	$1.53 \cdot 10^{-4}$	-3.070
30	*3.30*	*874.7*	*$1.51 \cdot 10^{-4}$*	*-3.085*

Table S5. Fitting results of the 15@H_2O sample.

T (ºC)	1000/T (K^{-1})	R_{tot} (Ω)	σ_{tot} (S cm^{-1})	ln (σ_{tot}·T)
68	2.93	812.2	$1.93 \cdot 10^{-4}$	-2.720
57	3.03	1185.0	$1.32 \cdot 10^{-4}$	-3.130
50	3.09	1647.4	$9.52 \cdot 10^{-5}$	-3.481
45	3.14	2122.0	$7.39 \cdot 10^{-5}$	-3.750
42	3.17	2474.4	$6.34 \cdot 10^{-5}$	-3.913
38	3.21	2908.3	$5.39 \cdot 10^{-5}$	-4.088
36	3.23	3319.1	$4.73 \cdot 10^{-5}$	-4.226
34	3.26	3702.7	$4.24 \cdot 10^{-5}$	-4.342
32	3.28	4019.3	$3.90 \cdot 10^{-5}$	-4.431
31	3.29	4328.0	$3.62 \cdot 10^{-5}$	-4.508
30	*3.30*	*4663.8*	*$3.36 \cdot 10^{-5}$*	*-4.586*

Table S6. Literature review of the LATP obtained via CSP.

Composition	P (MPa)	T (ºC)	t	d_{50} (µm)	TLP	Post-annealing	ϕ (%)	σ (S cm^{-1})	E_a (eV)	Ref.
					NMP (30 vol.%)		74±2	$2.07\cdot10^{-5}$	0.41±0.02	
					H_2O + NMP (30 vol.%)		79±2	$2.79\cdot10^{-5}$	0.40±0.02	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	420	120	1h	0.3-0.4	Hac - 1M + NMP (30 vol.%)	650 ºC - 2h	93±2	$8.04\cdot10^{-5}$	0.37±0.02	1
					Hac - 1M + DMSO (30 vol.%)		84±2	$3.03\cdot10^{-5}$	0.39±0.02	
					H_2O (20 wt.%) + LiTFSi (0 wt.%)		90.6±0.7	$(2.7\pm0.89)\cdot10^{-5}$	0.26	
					H_2O (20 wt.%) + LiTFSi (4 wt.%)		90.7±2.3	$(5.9\pm2.1)\cdot10^{-5}$	-	
$Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$	620	130	2h	1.15	H_2O (20 wt.%) + LiTFSi (11 wt.%)	No	91.1±0.8	$(7.8\pm1.0)\cdot10^{-5}$	-	2
					H_2O (20 wt.%) + LiTFSi (17 wt.%)		91.1±2.7	$(18\pm4.7)\cdot10^{-5}$	0.26	
					H_2O (20 wt.%) + LiTFSi (22 wt.%)		93.4±0.2	$(14\pm1.9)\cdot10^{-5}$	-	
			5 min		H_2O (30 wt.%)	Green samples are heated up to 650 ºC for 2 h and after the CSP was launched	-	$14\cdot10^{-5}$	-	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	25	200	10 min	1-5	H_2O (30 wt.%)		-	$18\cdot10^{-5}$	-	3
			30 min		H_2O (30 wt.%)		-	$30\cdot10^{-5}$	-	
	600	140	1h		LiAc·$2H_2O$ (3.2 wt.% dry)		75±1.5	$0.02\cdot10^{-5}$	-	
	600 → 510	140 → 200	30 min → 1h		LiAc·$2H_2O$ (3.2 wt.% dry)		87±1.5	$0.10\cdot10^{-5}$	-	
	600	140	1h		HAc - 1.66M (20 wt.%)		88±1.5	$0.25\cdot10^{-5}$	-	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	600 → 510	140 → 200	30 min → 1h	0.8	HAc - 1.66M (20 wt.%)	No	94±1.5	$0.82\cdot10^{-5}$	-	4
	600 → 510	140 → 200	30 min → 1h		H_2O (20 wt.%)		94±1.5	$1.26\cdot10^{-5}$	-	
	600 → 510	140 → 200	30 min → 1h		LiOH·H_2O - 0.1M (20 wt.%)		90±1.5	-	-	
		150					75.2	-	-	
		200				No	-	-	-	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	250	250	1h	0.03-0.18	H_2O (30 wt.%)		83.0	$0.20\cdot10^{-5}$	-	5
						700 ºC - 1h	79.3	$0.39\cdot10^{-5}$	-	
		250		0.04-0.20		800 ºC - 1h	87.7	$2.86\cdot10^{-5}$	-	

				0.05-0.38		900 ºC - 1h	87.4	$42.9\cdot10^{-5}$	-	
				0.4-1.7		1000 ºC - 1h	96.0	$14.6\cdot10^{-5}$	-	
				0.8-2		1100 ºC - 1h	96.3	$2.23\cdot10^{-5}$	-	
					HAc - 3M + 2 wt.% Bi_2O_3 (5 wt.%)			$0.03\cdot10^{-5}$	0.565	
					HAc - 3M + 2 wt.% Bi_2O_3 (10 wt.%)			$0.92\cdot10^{-5}$	0.368	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	700	150	1.5h	0.190	HAc - 3M + 2 wt.% Bi_2O_3 (15 wt.%)	No	95	$3.02\cdot10^{-5}$	0.367	6
					HAc - 3M + 2 wt.% Bi_2O_3 (20 wt.%)			$3.49\cdot10^{-5}$	0.365	
					HAc - 3M + 2 wt.% Bi_2O_3 (25 wt.%)			$4.00\cdot10^{-5}$	0.355	
					HAc - 3M (5 wt.%)			$5.77\cdot10^{-5}$	0.307	
$0.9(Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3)$ + 0.1(2PEO:LiTFSi)	700	150	1.5h	0.190	HAc - 3M (10 wt.%)	No	>98	$6.94\cdot10^{-5}$	0.308	7
					HAc - 3M (12.5 wt.%)			$9.50\cdot10^{-5}$	0.306	
					HAc - 3M (15 wt.%)			$13.2\cdot10^{-5}$	0.298	
					HAc - 3M (25 wt.%)			$3.70\cdot10^{-5}$	0.36	
					HAc - 3M + 1 wt.% Bi_2O_3 (25 wt.%)			$4.47\cdot10^{-5}$	0.37	
					HAc - 3M + 2 wt.% Bi_2O_3 (25 wt.%)			$4.48\cdot10^{-5}$	0.35	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	700	150	1.5h	0.190	HAc - 3M + 3 wt.% Bi_2O_3 (25 wt.%)	No	82*	$4.45\cdot10^{-5}$	0.35	8
					HAc - 3M + 4 wt.% Bi_2O_3 (25 wt.%)			$3.97\cdot10^{-5}$	0.35	
					HAc - 3M + 5 wt.% Bi_2O_3 (25 wt.%)			$3.73\cdot10^{-5}$	0.35	
				1.208	HAc - 3M (15 wt.%)		78.7*	$0.37\cdot10^{-5}$	0.560	
				0.875	HAc - 3M (15 wt.%)		80.2*	$11.7\cdot10^{-5}$	0.343	
				0.645	HAc - 3M (15 wt.%)		81.1*	$8.41\cdot10^{-5}$	0.372	
				0.415	HAc - 3M (15 wt.%)		81.8*	$5.55\cdot10^{-5}$	0.384	
$Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$	700	150	1.5h	0.190	HAc - 3M (15 wt.%)	No	81.9*	$3.09\cdot10^{-5}$	0.389	9
				1.208	HAc - 3M (17.5 wt.%)		78.7*	$3.86\cdot10^{-5}$	0.383	
				1.208	HAc - 3M (20 wt.%)		78.5*	$16.9\cdot10^{-5}$	0.317	
				0.875	HAc - 3M (20 wt.%)		79.8*	$12.5\cdot10^{-5}$	0.356	

	0.645	HAc - 3M (20 wt.%)		80.8*	$8.21 \cdot 10^{-5}$	0.384
	0.415	HAc - 3M (20 wt.%)		81.2*	$6.90 \cdot 10^{-5}$	0.363
	0.376	HAc - 3M (20 wt.%)		81.2*	$6.40 \cdot 10^{-5}$	0.368
	0.268	HAc - 3M (20 wt.%)		81.4*	$5.17 \cdot 10^{-5}$	0.380
	0.190	HAc - 3M (20 wt.%)		81.5*	$3.15 \cdot 10^{-5}$	0.386

*Measured by mercury inmersion, considering open and closed porosity

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