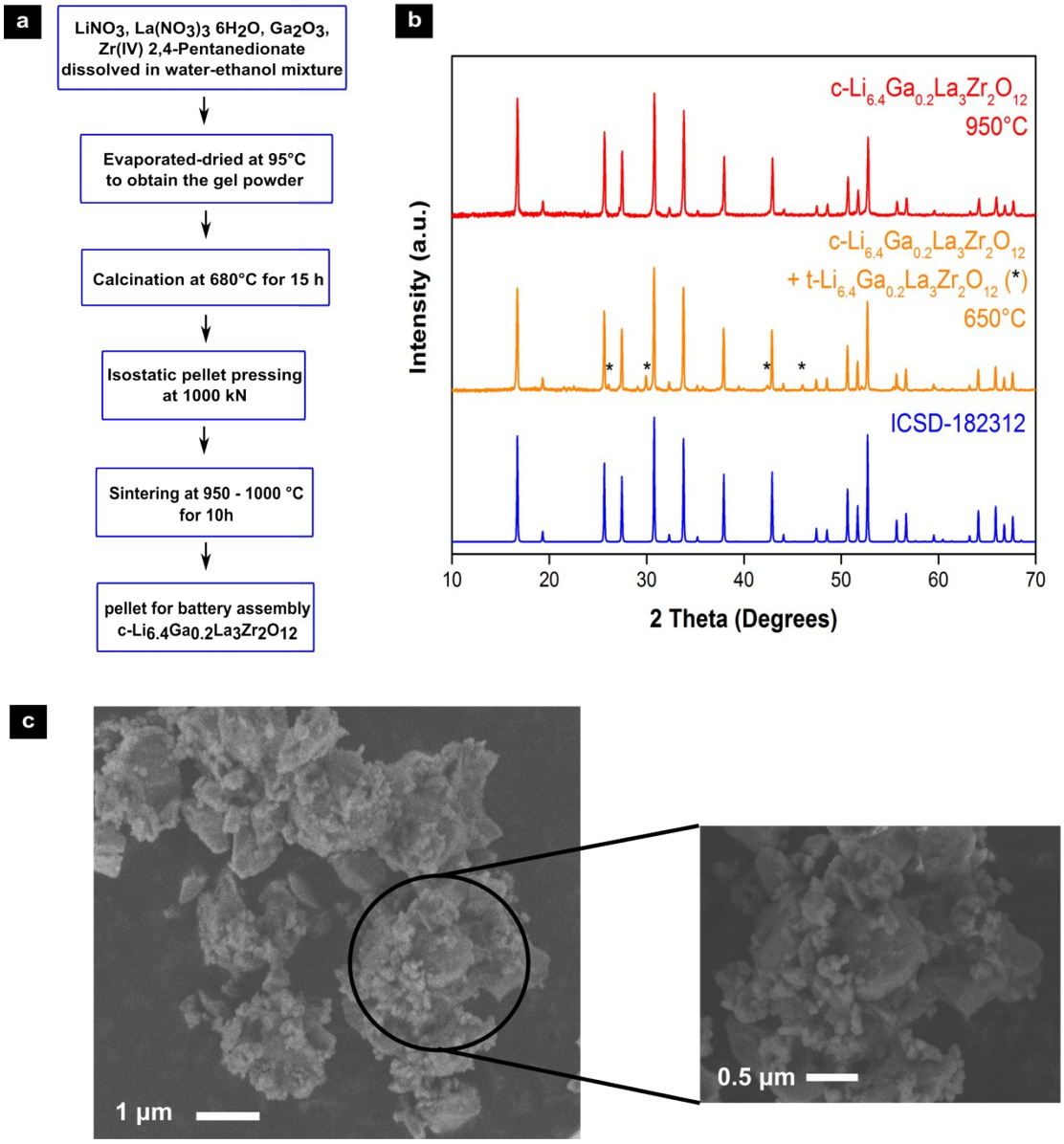
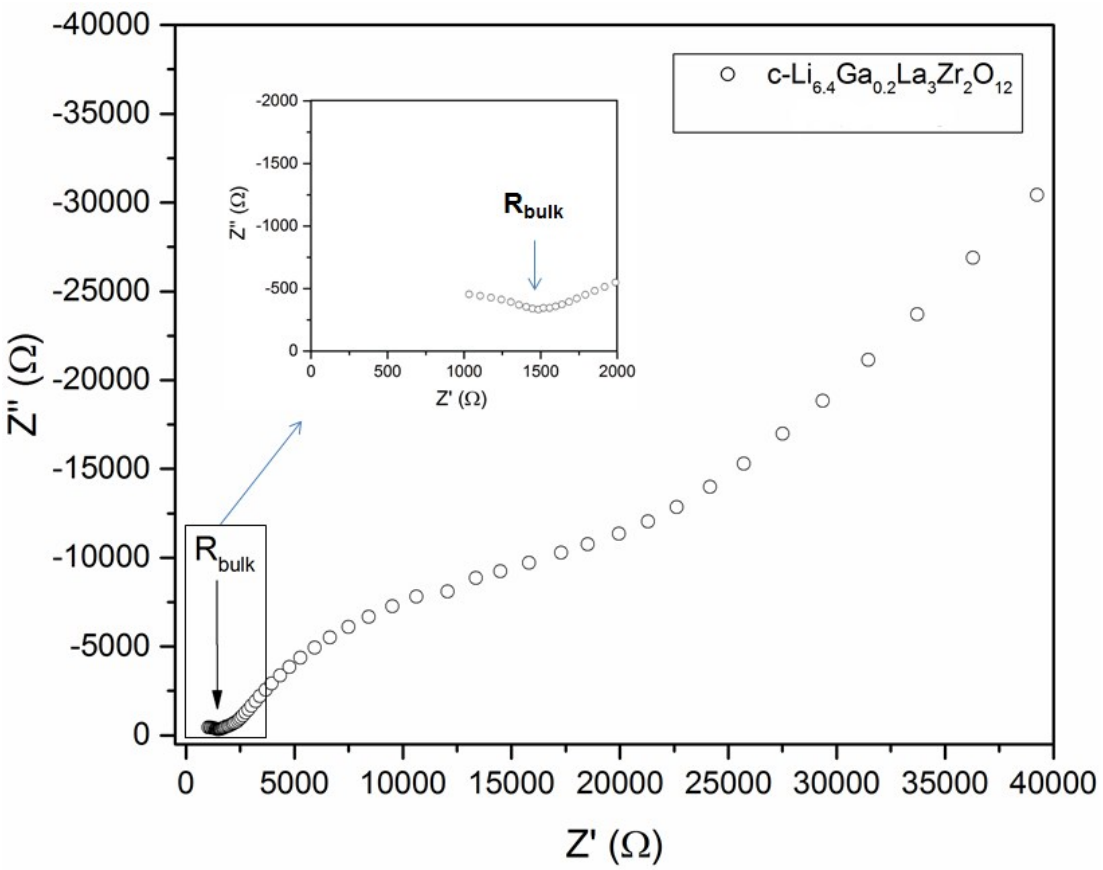
Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary information

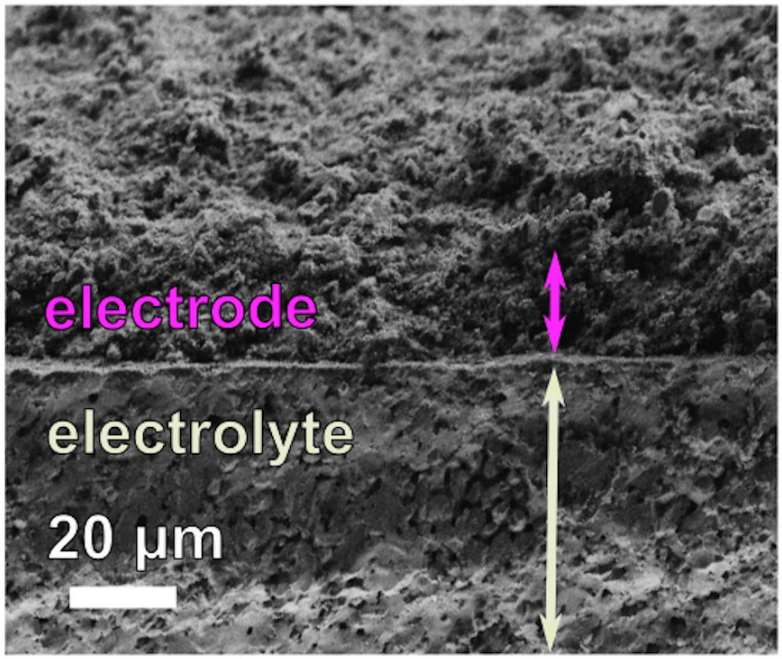


Supplementary Figure 1: (a) Scheme of the sol-gel combustion synthesis of the Ga^{3+} doped LLZO ($Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$). (b) Powder X-ray diffraction (XRD) pattern of $Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ reference (blue), powder after calcination 650°C (orange) and crushed pellet after sintering 950°C (red). (c) Scanning electron microscopy (SEM) images of sintered c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ powder.

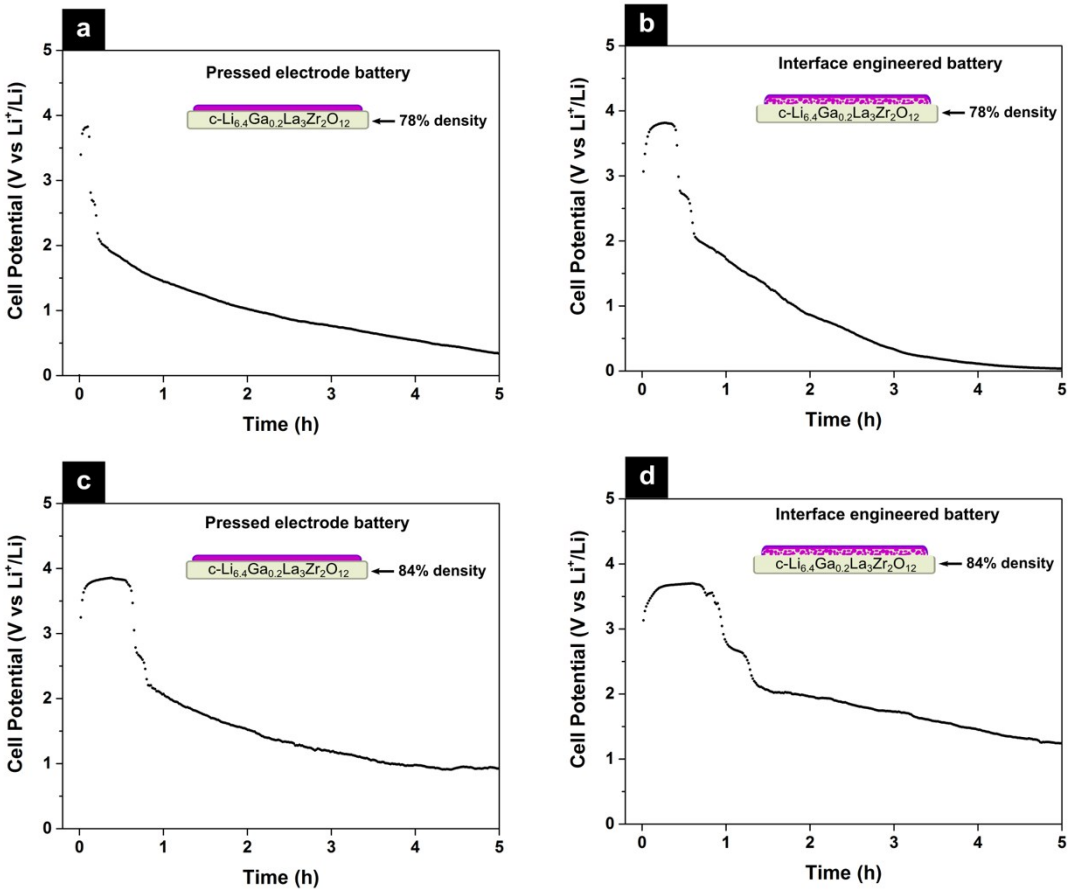


Supplementary Figure 2: Nyquist plot of a c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ pellet with Pt electrodes measured at room temperature.

The ionic conductivity of a sintered c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ pellet was determined by AC impedance spectroscopy in air. A typical Nyquist plot is shown in Supplementary Figure 2. The impedance data were fitted with an equivalent circuit of $(R_{bulk})(R_{gb}C_{gb})(C_{electrode})$, denoting bulk resistance, grain boundary resistance and capacitance and double layer capacitance. Ionic conductivities in the range of ~ 10^{-3} S/cm (R_{bulk}) and 10^{-5} S/cm (R_{total}) are determined for the c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ pellet at ambient conditions. These results are comparable to earlier reports.[23]



Supplementary Figure 3: Scanning electron microscopy (SEM) image of the cross section of a non pressed pellet with composite electrode.



Supplementary Figure 4: Cell potential versus time for first charging process (2A/kg) of an all-solid-state battery based on c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ with $LiMn_{1.5}Ni_{0.5}O_4$ and Li-metal electrodes measured at 95°C. (a, c) Batteries with non-modified electrolyte-cathode interface and pellet densities of (a) 78% and (c) 84%. (b, d) Batteries with modified electrolyte-cathode interface and pellet densities of (b) 78% and (d) 84%.

Supplementary Table 1. Indexed Powder XRD of c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ in electrode composite before battery operation using Werner's algorithm (TREOR).

Wavelength : 1.540598

Number of accepted peaks : 20

Crystal system : Cubic or lower
Maximum cell edge : 15.0
Maximum cell volume : 3000.0
2Theta window : 0.050

Maximum unindexed lines for refinement : 1
Required Figure of Merit : 5.0

Selected solution

Symmetry	a	b	c	Volume	FOM	unindexed
Cubic	12.9907	12.9907	12.9907	2192.3	57.9	0

Peak list

N	2Th(obs)	H	K	L	2Th(calc)	obs-calc	Int	d(obs)	d(calc)
1	16.6963	2	1	1	16.7030	-0.00671	100.0	5.30555	5.30342
2	19.3094	2	2	0	19.3100	-0.00061	39.1	4.59305	4.59290
3	25.6375	3	2	1	25.6374	0.00014	73.4	3.47188	3.47190
4	27.4243	4	0	0	27.4409	-0.01663	59.3	3.24960	3.24767
5	30.7409	4	2	0	30.7554	-0.01452	96.8	2.90614	2.90480
6	32.2994	3	3	2	32.2966	0.00283	25.0	2.76939	2.76962
7	33.7651	4	2	2	33.7747	-0.00964	83.0	2.65245	2.65171
8	37.9036	5	2	1	37.9044	-0.00079	55.0	2.37181	2.37176
9	42.8771	6	1	1	42.8800	-0.00292	51.2	2.10751	2.10737
10	47.4300	6	3	1	47.4274	0.00257	23.0	1.91527	1.91537
11	48.4788	4	4	4	48.5123	-0.03350	41.3	1.87626	1.87504
12	50.6307	6	4	0	50.6296	0.00107	41.0	1.80145	1.80148
13	51.6649	5	5	2	51.6644	0.00051	32.0	1.76779	1.76781
14	52.6809	6	4	2	52.6846	-0.00368	63.8	1.73607	1.73595
15	55.6626	7	3	2	55.6664	-0.00384	25.9	1.64992	1.64982
16	56.6354	8	0	0	56.6367	-0.00132	27.1	1.62387	1.62383
17	65.8393	8	4	2	65.8389	0.00040	26.6	1.41739	1.41740
18	66.7287	7	6	1	66.7191	0.00961	20.2	1.40064	1.40082
19	70.1860	7	6	3	70.1851	0.00090	19.1	1.33987	1.33989
20	79.3905	10	4	0	79.3810	0.00946	23.2	1.20603	1.20615

Supplementary Table 2. Indexed Powder XRD of c-$Li_{6.4}Ga_{0.2}La_3Zr_2O_{12}$ in electrode composite after battery operation using Werner's algorithm (TREOR).

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Wavelength : 1.540598

Number of accepted peaks : 20

Crystal system      : Cubic or lower
Maximum cell edge   : 15.0
Maximum cell volume : 3000.0
2Theta window       : 0.050

Maximum unindexed lines for refinement : 1
Required Figure of Merit : 5.0

Selected solution

Symmetry          a        b        c      Volume     FOM    unindexed
Cubic         12.9825  12.9825  12.9825   2188.1     50.8       0

Peak list

  N   2Th(obs)     H   K   L   2Th(calc)   obs-calc      Int      d(obs)  d(calc)
  1   16.7231      2   1   1    16.7137     0.00943    100.0     5.29709  5.30006
  2   19.3445      2   2   0    19.3224     0.02213     54.2     4.58479  4.58999
  3   25.6638      3   2   1    25.6539     0.00992     70.4     3.46839  3.46971
  4   27.4774      4   0   0    27.4587     0.01874     57.3     3.24344  3.24561
  5   30.7784      4   2   0    30.7754     0.00300     82.6     2.90268  2.90296
  6   32.3296      3   3   2    32.3176     0.01200     26.5     2.76687  2.76787
  7   33.8045      4   2   2    33.7968     0.00771     69.2     2.64945  2.65003
  8   37.9384      5   2   1    37.9293     0.00907     47.3     2.36971  2.37026
  9   42.9160      6   1   1    42.9085     0.00746     45.0     2.10568  2.10603
 10   47.4644      6   3   1    47.4593     0.00506     22.8     1.91396  1.91416
 11   48.5354      4   4   4    48.5450    -0.00963     33.2     1.87420  1.87386
 12   50.6713      6   4   0    50.6640     0.00731     36.8     1.80010  1.80034
 13   51.7057      5   5   2    51.6996     0.00615     29.3     1.76649  1.76669
 14   52.7198      6   4   2    52.7205    -0.00075     52.5     1.73488  1.73485
 15   55.7057      7   3   2    55.7048     0.00091     22.5     1.64875  1.64877
 16   56.6774      8   0   0    56.6759     0.00154     25.0     1.62276  1.62281
 17   65.8786      8   4   2    65.8859    -0.00732     23.8     1.41664  1.41650
 18   66.7717      7   6   1    66.7669     0.00478     18.1     1.39985  1.39993
 19   70.2266      7   6   3    70.2361    -0.00954     18.4     1.33920  1.33904
 20   79.4382     10   4   0    79.4413    -0.00314     21.7     1.20543  1.20539
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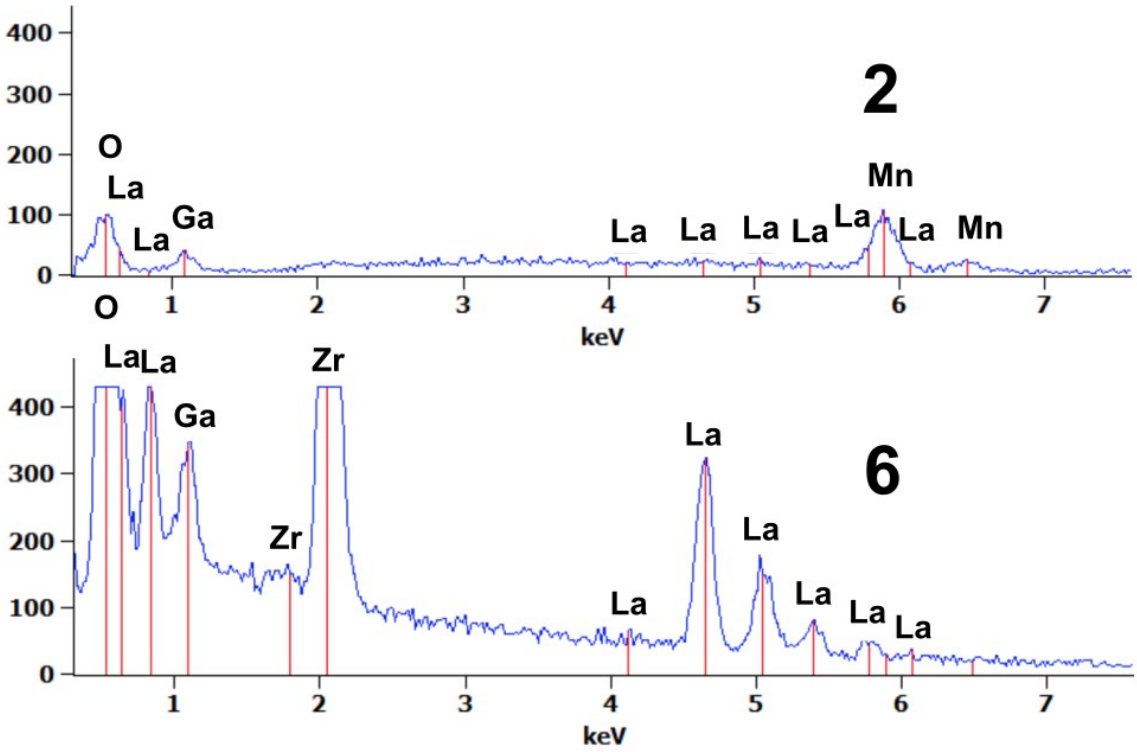

Supplementary Figure 5: Energy-dispersive X-ray spectroscopy (EDS) data from the marked regions 2 and 6 in Figure 4 (a).