

Supplementary information

Polycationic doping of the LATP ceramic electrolyte for lithium-ion batteries

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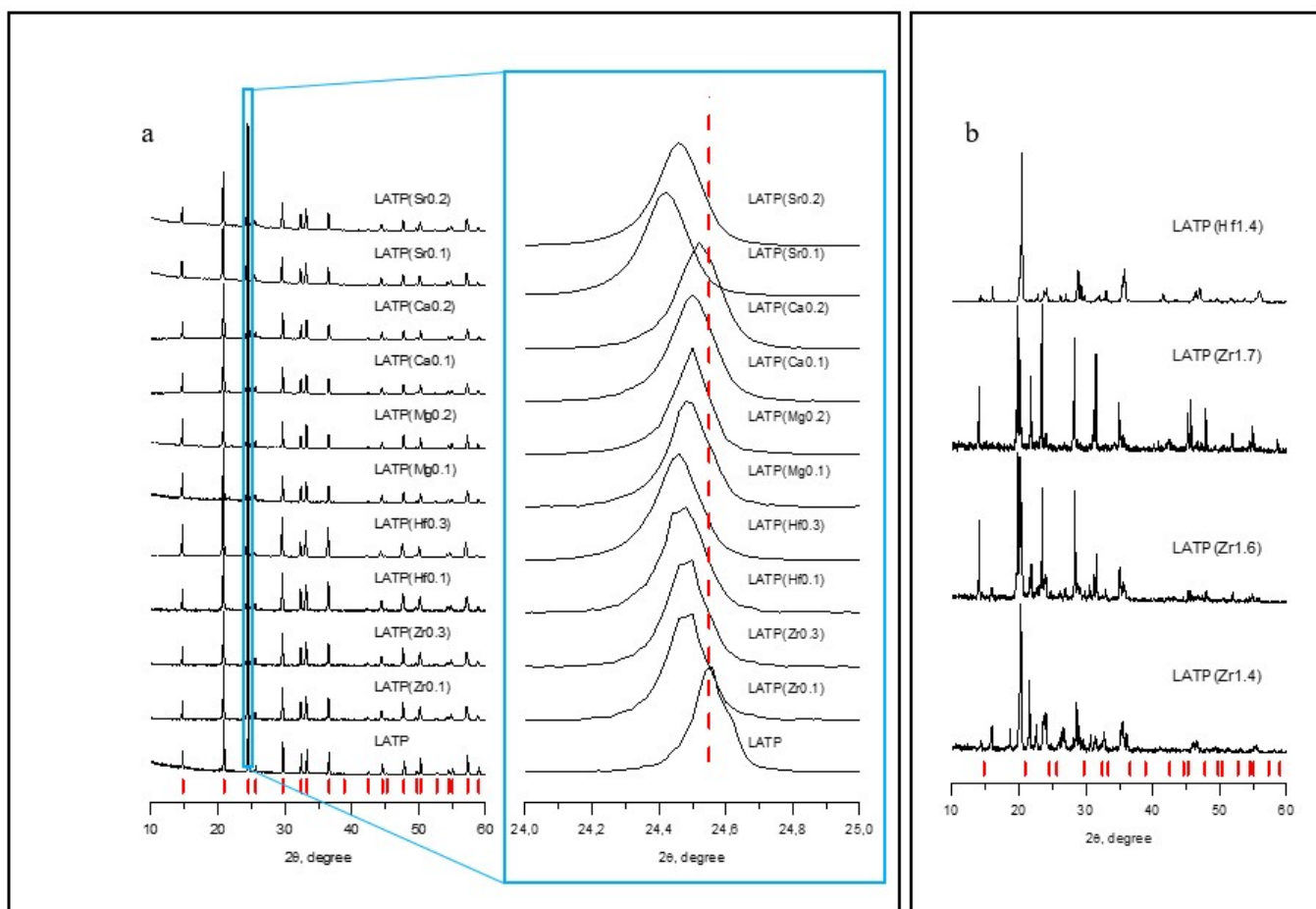


Figure S1. Diffraction patterns of doped LATP samples with various levels of cation substitutions: (a) XRD patterns with enlarged peaks around $2\theta \approx 24.5^\circ$, (b) XRD patterns with higher tetravalent cation substitution. Red tick marks represent NASICON phase with space group R-3c.

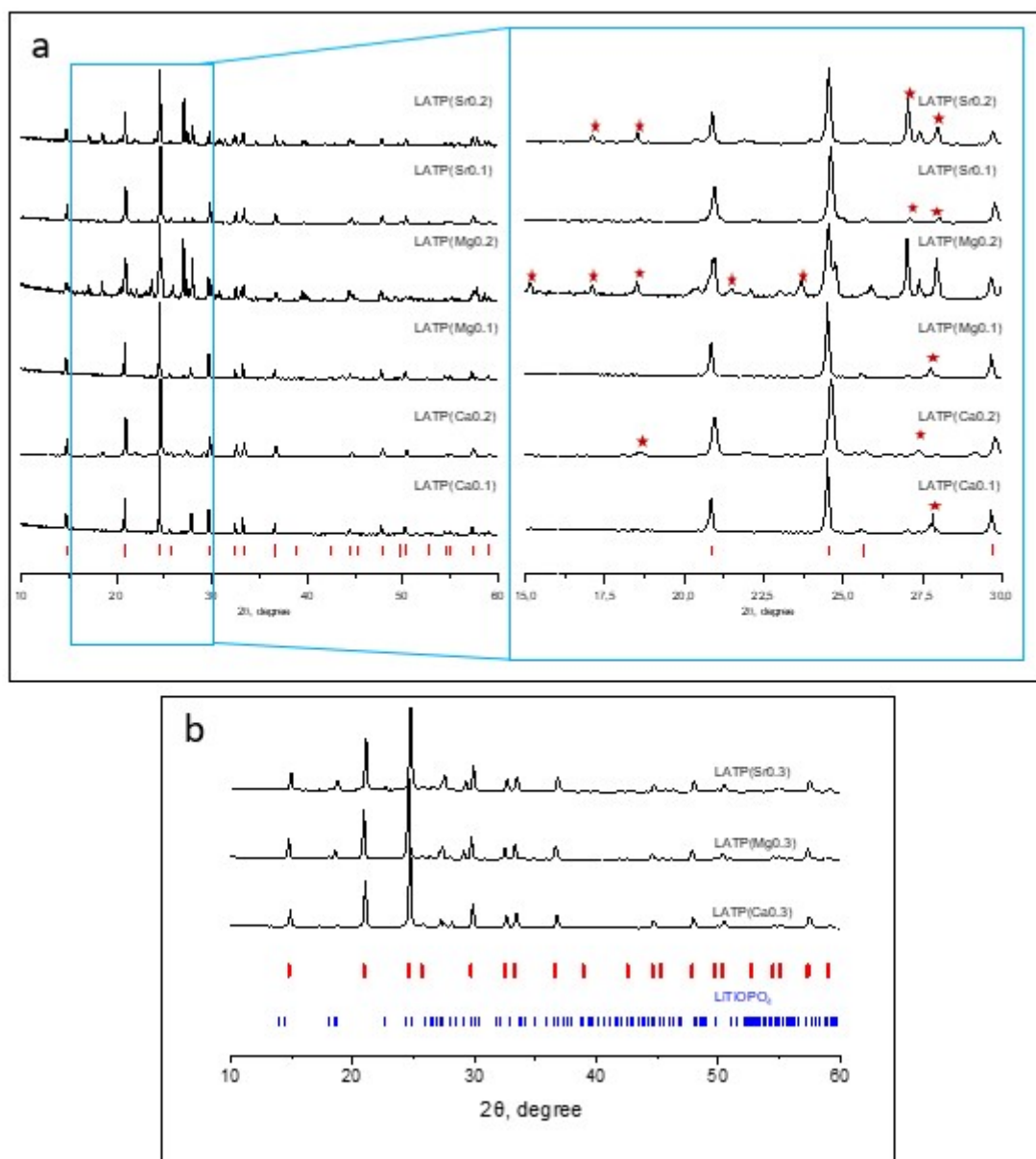


Figure S2. Diffraction patterns of doped LATP samples with divalent cations: (a) synthesized by the molten flux method and (b) doping cation is above 0.2 units per formula with solid-state method. The red ticks indicate the NASICON phase with the spatial group R-3c, the red asterisks the impurity phase belonging to TiP_2O_7

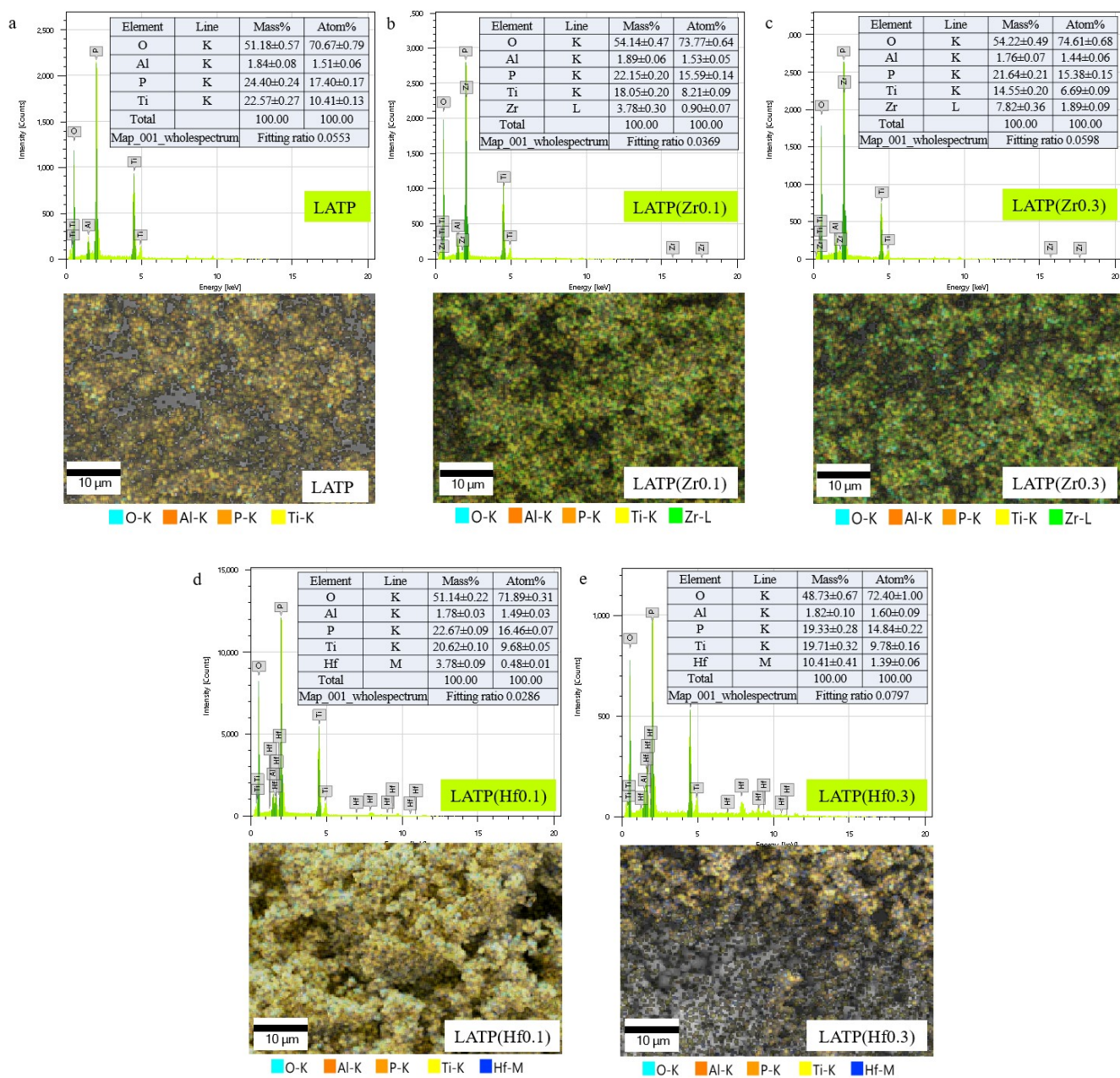


Figure S3. EDS spectra of electrolytes: (a) LATP, (b) LATP(Zr0.1), (c) LATP(Zr0.3), (d) LATP(Hf0.1), (e) LATP(Hf0.3)

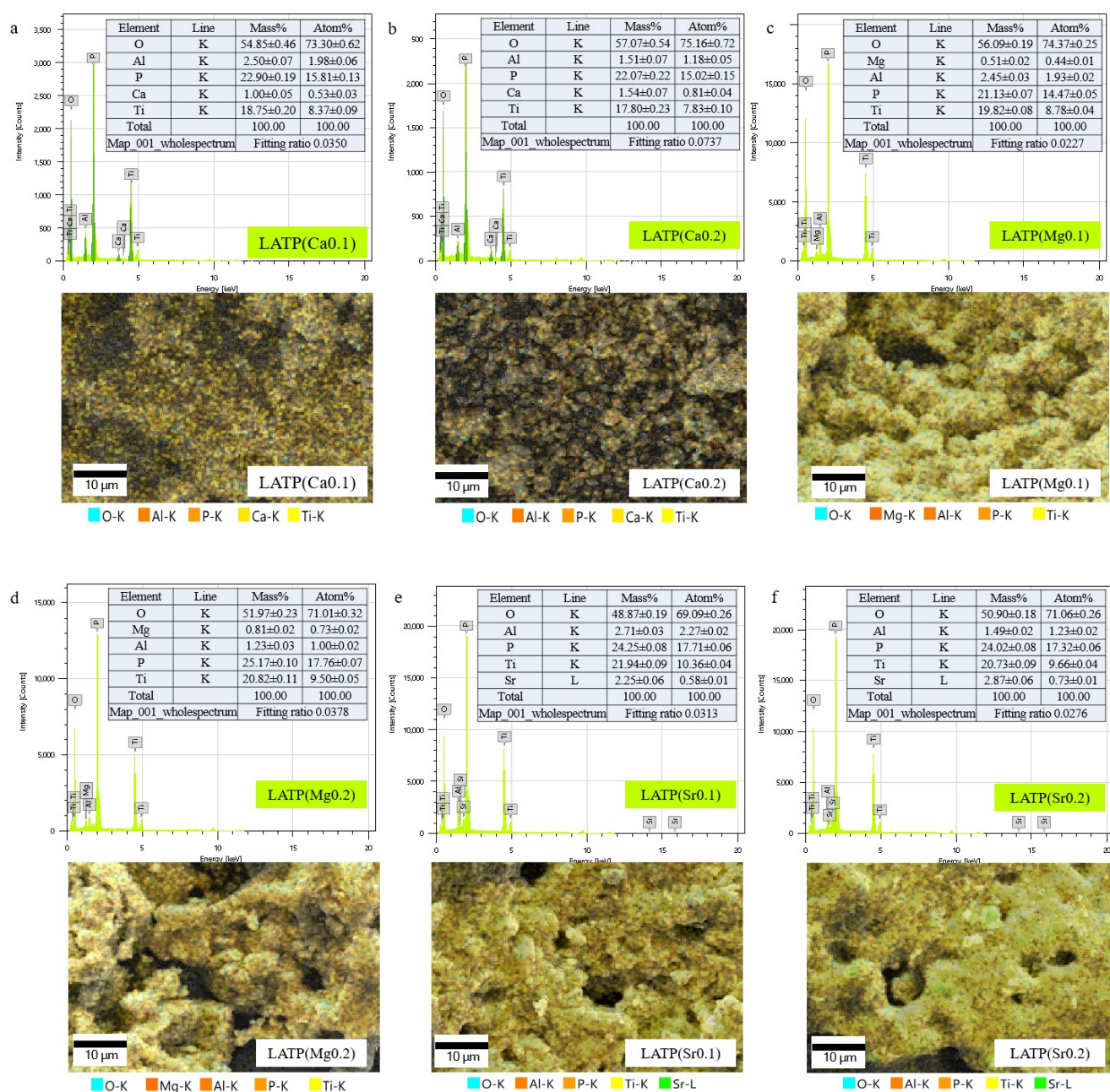


Figure S4. EDS spectra of electrolytes: (a) LATP(Ca0.1), (b) LATP(Ca0.2), (c) LATP(Mg0.1), (d) LATP(Mg0.2), (e) LATP(Sr0.1), (f) LATP(Sr0.2)

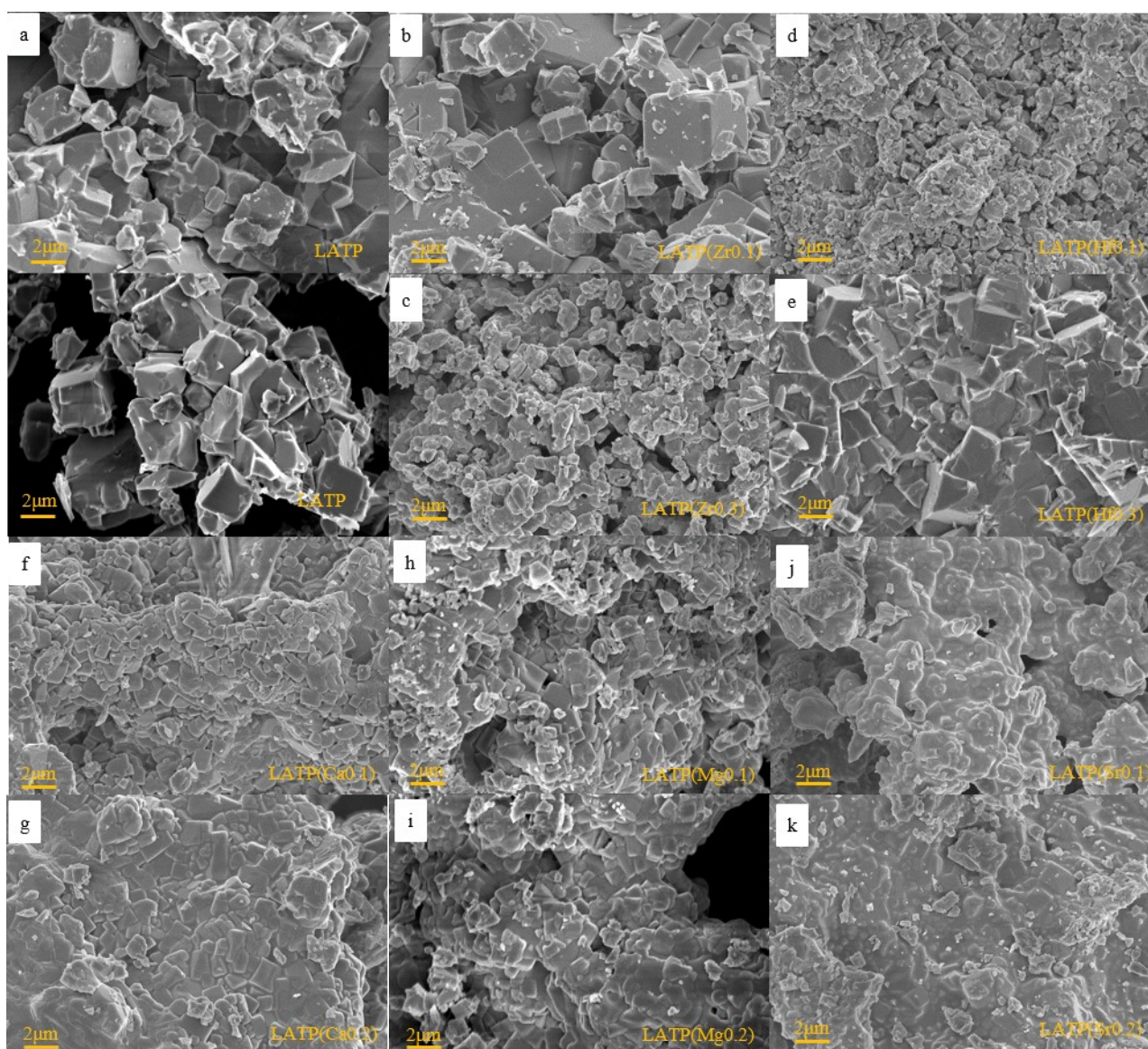


Figure S5. SEM images of doped LATP electrolytes: (a) LATP, (b) LATP(Zr0.1), (c) LATP(Zr0.3), (d) LATP(Hf0.1), (e) LATP(Hf0.3), (f) LATP(Ca0.1), (g) LATP(Ca0.2), (h) LATP(Mg0.1), (i) LATP(Mg0.2), (j) LATP(Sr0.1), (k) LATP(Sr0.2)

Table S1 Experimental data of XPS peaks

Sample	Ion	Peak BE	Height CPS	FWHM eV	Area	Ti ratio, %	Sample	Ionic conductivity at 25 °C, S·cm ⁻¹	Ion	Peak BE	Height CPS	FWHM eV	Area	Ti ratio, %
LATP	Ti ⁴⁺ _{1/2}	459,83	21212	1,71	42558	100%	LATP-Li	7.86·10 ⁻⁵	Ti ⁴⁺ _{1/2}	459,98	45742	1,22	65552	56%
	Ti ⁴⁺ _{3/2}	465,53	8357	2,55	24978				Ti ⁴⁺ _{3/2}	465,83	13545	1,61	25604	
	Ti ³⁺ _{1/2}	0	0	0	0	0%			Ti ³⁺ _{1/2}	457,73	15215	2,23	39814	44%
	Ti ³⁺ _{3/2}	0	0	0	0				Ti ³⁺ _{3/2}	463,79	8099	3,5	33256	
LATP(Zr0.1)	Ti ⁴⁺ _{1/2}	459,05	62802	1,67	122900	100%	LATP(Zr0.1)-Li	4.7·10 ⁻⁵	Ti ⁴⁺ _{1/2}	460,1	11643	1,53	21899	60%
	Ti ⁴⁺ _{3/2}	464,8	22937	2,39	64297				Ti ⁴⁺ _{3/2}	465,91	4488	2,05	9774	
	Ti ³⁺ _{1/2}	0	0	0	0	0%			Ti ³⁺ _{1/2}	459,33	4725	2,73	14128	40%
	Ti ³⁺ _{3/2}	0	0	0	0				Ti ³⁺ _{3/2}	464,73	2292	3,5	7012	
LATP(Hf0.1)	Ti ⁴⁺ _{1/2}	459,78	11171	1,55	37562	100%	LATP(Hf0.1)-Li	2.41·10 ⁻⁵	Ti ⁴⁺ _{1/2}	460,19	11607	1,53	20834	67%
	Ti ⁴⁺ _{3/2}	465,58	4595	2,26	22505				Ti ⁴⁺ _{3/2}	465,84	6061	2,38	16910	
	Ti ³⁺ _{1/2}	0	0	0	0	0%			Ti ³⁺ _{1/2}	459,44	4734	2,78	15458	33%
	Ti ³⁺ _{3/2}	0	0	0	0				Ti ³⁺ _{3/2}	463,59	1120	2,27	2976	
LATP(Ca0.1)	Ti ⁴⁺ _{1/2}	459,35	62772	1,66	122074	100%	LATP(Ca0.1)-Li	9.02·10 ⁻⁵	Ti ⁴⁺ _{1/2}	459,87	8762	1,77	18205	45%
	Ti ⁴⁺ _{3/2}	465,11	23017	2,42	65312				Ti ⁴⁺ _{3/2}	465,62	4277	2,19	10998	
	Ti ³⁺ _{1/2}	0	0	0	0	0%			Ti ³⁺ _{1/2}	458,38	6807	3,11	24866	55%
	Ti ³⁺ _{3/2}	0	0	0	0				Ti ³⁺ _{3/2}	463,74	3017	2,89	10238	
LATP(Mg0.1)	Ti ⁴⁺ _{1/2}	459,74	73804	1,26	109327	100%	LATP(Mg0.1)-Li	3.01·10 ⁻⁶	Ti ⁴⁺ _{1/2}	460,18	43139	1,22	61842	78%
	Ti ⁴⁺ _{3/2}	465,56	25646	2,03	61000				Ti ⁴⁺ _{3/2}	465,98	14095	1,86	30786	
	Ti ³⁺ _{1/2}	0	0	0	0	0%			Ti ³⁺ _{1/2}	458,93	6441	1,49	11282	22%
	Ti ³⁺ _{3/2}	0	0	0	0				Ti ³⁺ _{3/2}	464,27	3484	3,5	14306	
LATP(Sr0.1)	Ti ⁴⁺ _{1/2}	459,38	64171	1,62	122232	100%	LATP(Sr0.1)-Li	6.91·10 ⁻⁵	Ti ⁴⁺ _{1/2}	459,67	25205	2,09	61845	51%
	Ti ⁴⁺ _{3/2}	465,14	23548	2,4	66276				Ti ⁴⁺ _{3/2}	465,54	9442	2,19	24300	
	Ti ³⁺ _{1/2}	0	0	0	0	0%			Ti ³⁺ _{1/2}	457,86	25057	1,82	53330	49%
	Ti ³⁺ _{3/2}	0	0	0	0				Ti ³⁺ _{3/2}	463,7	11262	2,34	30909	

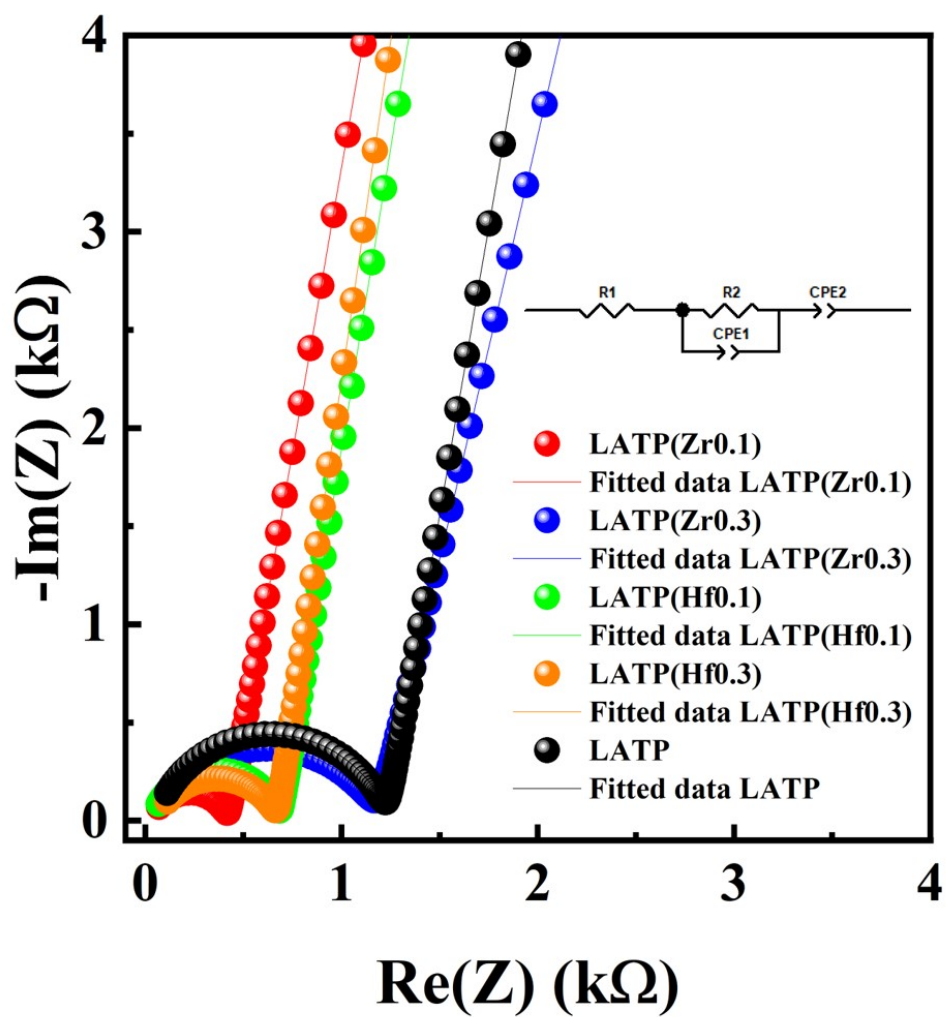


Figure S6. Fitted EIS results of pure and doped LATP electrolytes