

Supplementary Information

Chlorine doped $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ as electrolyte for solid lithium metal batteries

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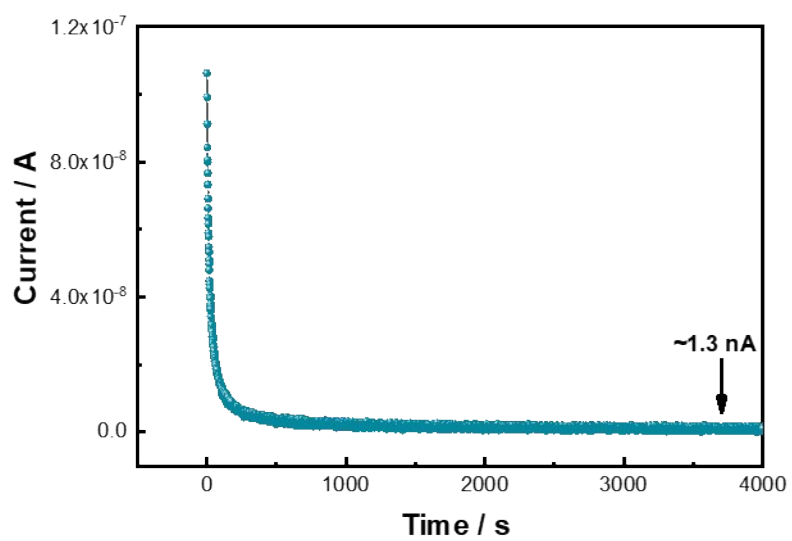


Fig. S1. The polarization current–time curves of the LATP-0.4Cl pellet.

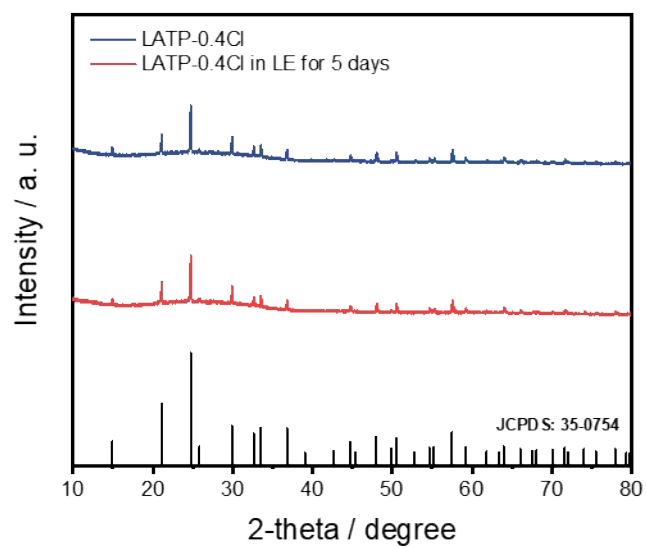


Fig. S2. XRD pattern of LATP-0.4Cl pellet before and after soaking in liquid electrolyte for 5 days.

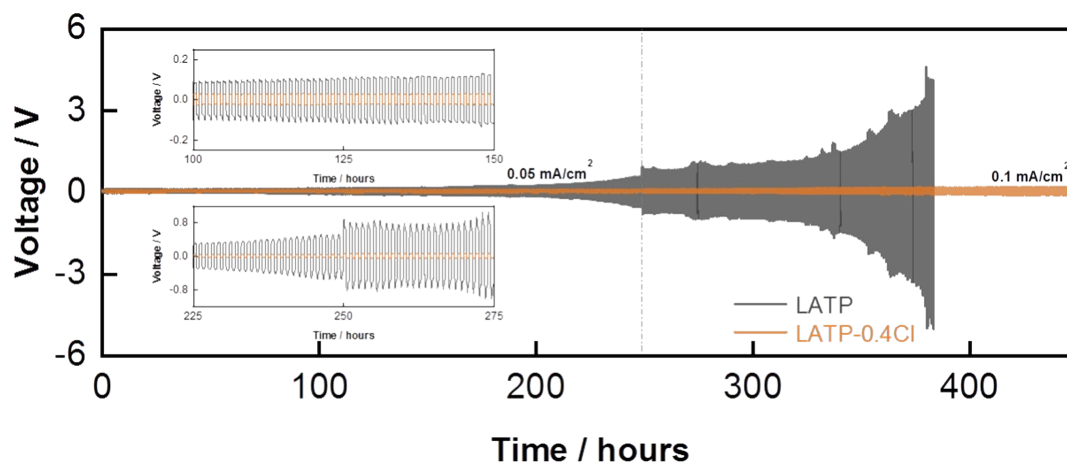


Fig. S3. Voltage profile of the lithium plating/stripping cycling in the symmetrical cell with 5 μ L liquid electrolyte at various current densities.

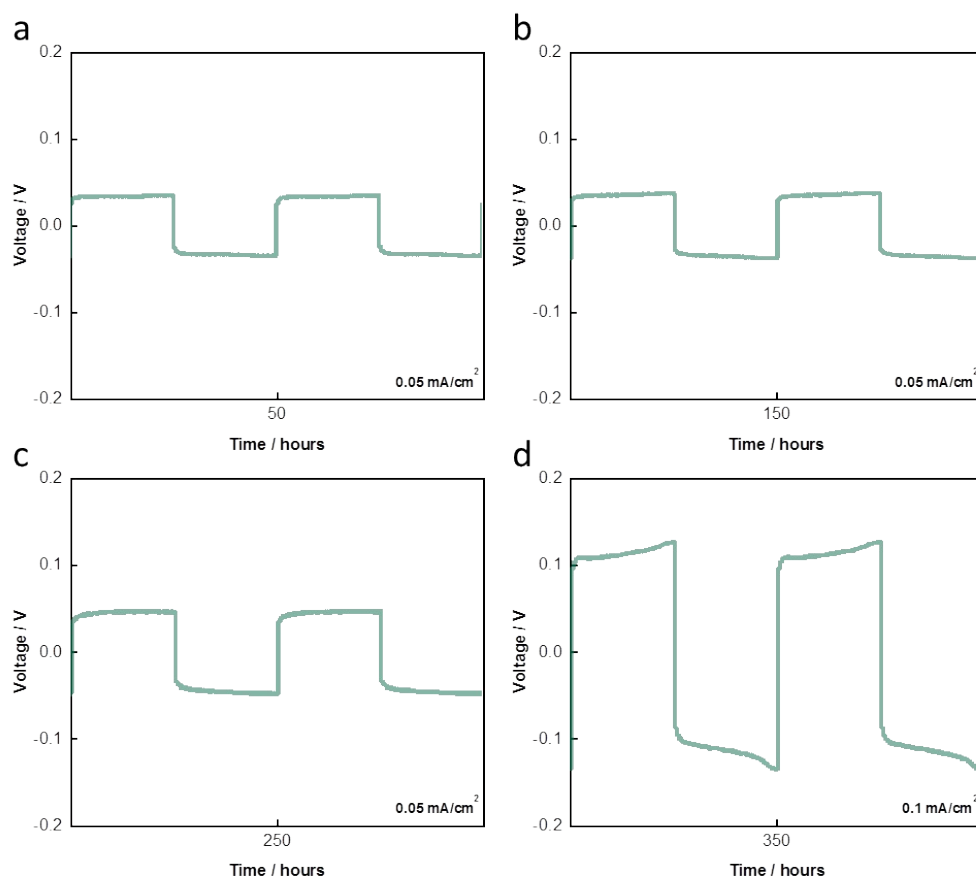


Fig. S4. The voltage profile of the symmetric cells of LATP-0.4Cl with 2 μ L liquid electrolyte at different time: (a) 50 h, (b) 150 h, (c) 250 h, and (d) 350 h.

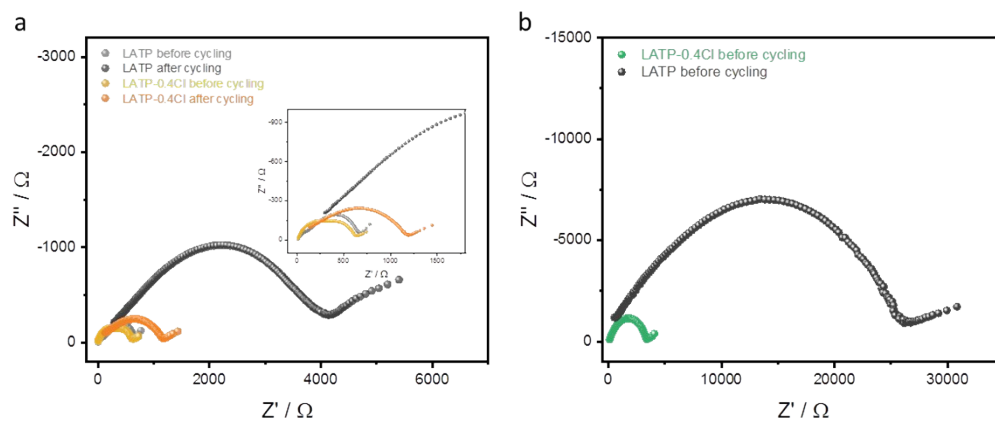


Fig. S5. Electrochemical impedance spectra of the cell (a) with 5 μ L liquid electrolyte and (b) with 2 μ L liquid electrolyte with a structure of Li|LFP.

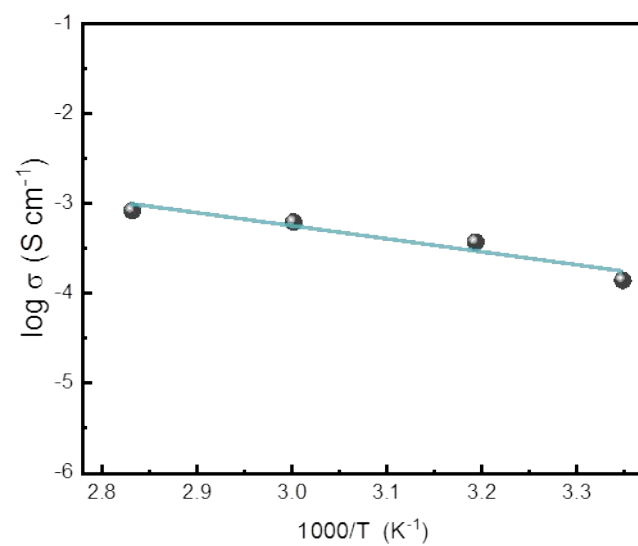


Fig. S6. Temperature dependence of ionic conductivity of LATP.

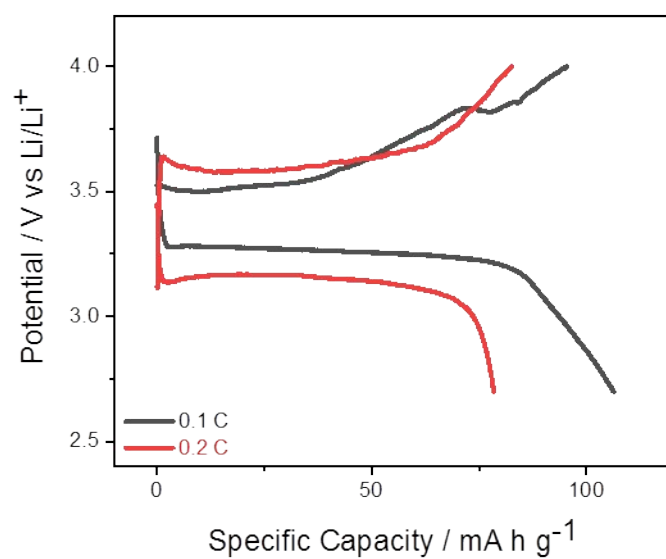


Fig. S7. Charge/discharge voltage profiles of the cell with Li anode, LATP electrolyte and LFP cathode. 2 μ L liquid electrolyte was modified between LATP electrolyte and LFP cathode, tested at 52°C.

Table S1. Rietveld refinements result of LATP at room temperature

LATP		Chemical Formula (Derived from Refinement): $\text{Li}_{1.30}\text{Al}_{0.31}\text{Ti}_{1.69}(\text{PO}_4)_3$			
<i>S. G.</i> $R\bar{3}c$, $Z = 6$		$a = 8.481(1) \text{ \AA}$, $c = 20.772(4) \text{ \AA}$, $V = 1293.85(4) \text{ \AA}^3$			
$R_{\text{exp}} = 1.68$, $R_{\text{Bragg}} = 1.68$, $\chi^2 = 6.43$		Weight Percentage: 94.7(2)%			
Element	Site	x	y	z	Occupancy
Li	$6b$	0	0	0	0.774(1)
	$36f$	0.0594(8)	0.2847(8)	0.0921(9)	0.088(1)
Al	$12c$	0	0	0.1403(2)	0.156(1)
Ti					0.844(1)
P	$18e$	0.2874(3)	0	0.25	1
O	$36f^*$	0.1836(5)	0.9932(5)	0.1898(6)	1
	$36f^\wedge$	0.1899(5)	0.1649(5)	0.0812(6)	1

Note:

① The impurity is LiTiPO_5 , with *S.G.* $Pnma$ and lattice parameters: $a = 7.390(1) \text{ \AA}$, $b = 6.371(1) \text{ \AA}$, $c = 7.224(1) \text{ \AA}$.

② O occupies two different $36f$ sites marked with * and ^.

Table S2. Rietveld refinement results of LATP-0.4Cl at room temperature

LATP-Cl		Chemical Formula (Derived from Refinement):			
		$\text{Li}_{1.30}\text{Al}_{0.30}\text{Ti}_{1.41}(\text{PO}_{3.61}\text{Cl}_{0.39})_3$			
S. G. $R\bar{3}c$, $Z = 6$		$a = 8.483(2) \text{ \AA}$, $c = 20.758(4) \text{ \AA}$, $V = 1293.80(4) \text{ \AA}^3$			
$R_{\text{exp}} = 1.70$, $R_{\text{Bragg}} = 3.99$, $\chi^2 = 6.83$		Weight Percentage: 90.8(4)%			
Element	Site	x	y	z	Occupancy
Li	$6b$	0	0	0	0.795(1)
	$36f$	0.1011(8)	0.2643(8)	0.0849(9)	0.084(1)
Al	$12c$	0	0	0.1393(2)	0.150(1)
Ti					0.705(1)
P	$18e$	0.2871(1)	0	0.25	1
O	$36f^*$	0.1866(5)	0.9948(5)	0.1901(6)	0.877(1)
	$36f^\wedge$	0.1872(6)	0.1645(6)	0.0811(6)	0.928(1)
Cl	$36f^*$	0.1866(5)	0.9948(5)	0.1901(6)	0.123(1)
	$36f^\wedge$	0.1872(6)	0.1645(6)	0.0811(6)	0.072(1)

Note:

① The impurity is LiTiPO_5 , with S.G. $Pnma$ and lattice parameters: $a = 7.398(1) \text{ \AA}$, $b = 6.363(1) \text{ \AA}$, $c = 7.241(1) \text{ \AA}$.

② Cl and O share the two $36f$ sites marked with * and ^.