Ultrafast solid-state lithium ion conductor through alloying induced lattice softening of Li_6PS_5Cl

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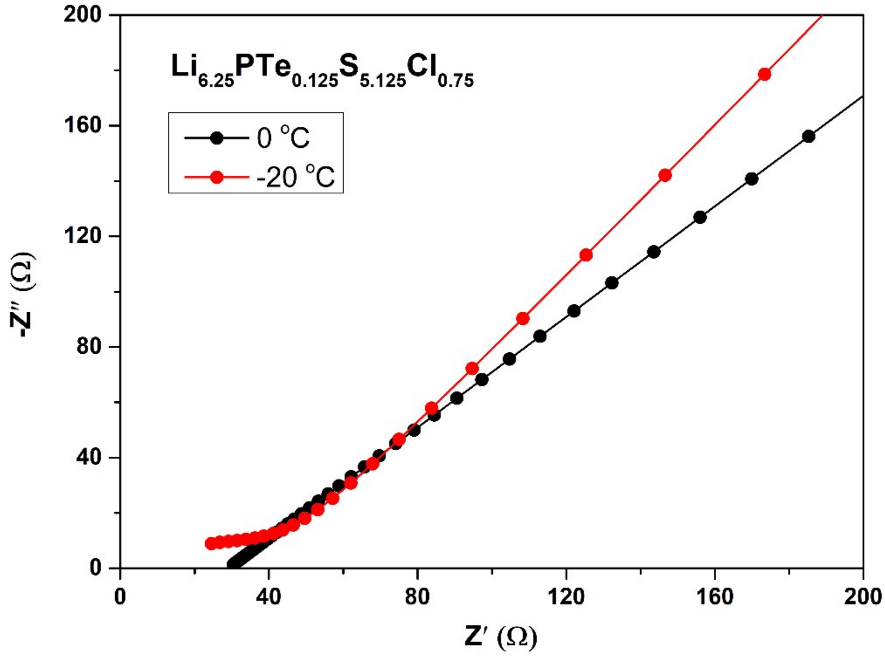

Fig. S1 Temperature dependence of impedance for the $Li_{6.25}PTe_{0.125}S_{5.125}Cl_{0.75}$ alloy, at -20 and 0 ^{0}C.

Preparation of all-solid-state cell

The whole preparation process was carried out under an argon atmosphere inside a glove box. The flow delay coating method was used to prepare cathode and electrolyte separator of the all-solid-state cell. Thin plates of lithium were used as anode.

The preparation of cathode coating:

The cathode consisted of $LiFePO_4$ powder, acetylene black powder and a certain amount of poly(vinylidene fluoride) (PVDF) as an organic binder in a 70:20:10 (wt%) ratio. These materials were mixed in a ball miller with N-methyl-2-pyrrolidone (NMP) solvent. Then the slurry was coated on the aluminum foil with a thickness of 40μm, which was then heated at 120 ℃ to remove NMP.

Preparation of electrolyte separator coating:

Electrolyte separator consisted of $Li_{6.25}PTe_{0.125}S_{5.125}Cl_{0.75}$ and PVDF in a 90:10 (wt%) ratio. The mixture was mixed in a ball miller with NMP solvent. Then the slurry was coated on the cathode coating with the thickness of 20μm.

The preparation of all-solid-state cell:

The aluminum foil with cathode and electrolyte coatings were pressed together and then punched into a disc with a diameter of 19 mm, which was then stacked with a lithium plate under pressure to make a CR2025 cell.

Charge and discharge measurements

The charge and discharge experiments of the all-solid-state cells ($LiFePO_4$ loading: 4.5 mg/cm2) were conducted between 2.5 and 3.8 V. The cycling characteristics at 25℃ were examined at a current density of 0.02 mAcm^{-2} (0.026C) at the first cycle and then 0.08 mAcm^{-2} (0.1C) for later cycles. The electrochemical properties of the cells were determined using a battery-testing instrument (LAND CT2001A), with results plotted in Fig. S2.

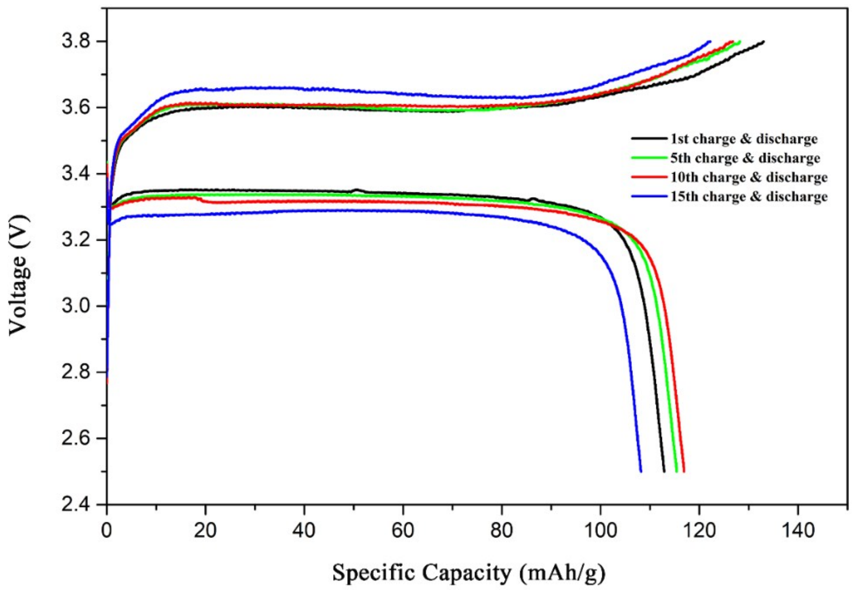

Fig. S2 Charge-discharge performance of $LiFePO_4/Li_{6.25}PTe_{0.125}S_{5.125}Cl_{0.75}$ /Li cell.

Table S1 Key parameters corresponding to each element in the equivalent circuits shown in Fig. 6.

Material	Equivalent Circuit	Element	Value	σ_{total} at 25℃ (mS cm^{-1})
Li_6PS_5Cl	$R_0(R_1Q_1)W_0$	R_0	6.2	0.28
		T_{Q1}	3.066×10^{-6}	
		P_{Q1}	0.8969	
		R_1	260	
		R_{W0}	282.4	
		T_{W0}	0.16816	
		P_{W0}	0.43663	
		R_{total}	**266.2**	
$Li_{6.25}PS_{5.25}Cl_{0.75}$	$R_0(R_1Q_1)$ W_0	R_0	14.5	1.03
		T_{Q1}	6.23×10^{-6}	
		P_{Q1}	0.61314	
		R_1	58	
		R_{W0}	19.2	
		T_{W0}	1.476×10^{-4}	
		P_{W0}	0.27911	
		R_{total}	**72.5**	
$Li_{6.25}PTe_{0.125}S_{5.125}Cl_{0.75}$	R_0W_0	R_0	16.56	4.5
		R_{W0}	265	
		T_{W0}	0.0025	
		P_{W0}	0.3504	
		R_{total}	**16.56**	

Impedance for constant phase element (Q) and Warburg element (W) are expressed as:

$$Z_Q=\frac{1}{T\times(j\omega)^P}$$

$$Z_W=\frac{R\times ctnh[(jT\omega)^P]}{(jT\omega)^P}$$

Table S2 Derived electrical properties for $Li_{6.25}PS_{5.25}Cl_{0.75}$ and $Li_{6.25}PTe_{0.125}S_{5.125}Cl_{0.75}$.

$Li_{6.25}PS_{5.25}Cl_{0.75}$			$Li_{6.25}PTe_{0.125}S_{5.125}Cl_{0.75}$		
Temperature（℃）	R_{total}	σ_{total} (mS cm^{-1}）	Temperature（℃）	R_{total}	σ_{total} (mS cm^{-1}）
---	---	---	-20	46.3	1.6
---	---	---	0	30.5	2.45
25	72.5	1.03	25	16.56	4.5
50	56.3	1.33	40	13.91	5.37
60	45	1.66	60	11.81	6.32
80	37.5	1.99	80	7.71	9.68
100	30	2.99	100	6.33	11.7
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VIDEO

The video presented the ionic trajectories of $Li_{6.25}PTeS_{4.25}Cl_{0.75}$ by AIMD at 1000K, in which Li^{+}, P^{5+}, Te^{2-}, S^{2-}, and Cl^{-} ions are indicated by white, red, orange, yellow, and blue balls, correspondingly.