

Improving electrochemical performance of Li₂S cathode based on point defect control with cation/anion dual doping

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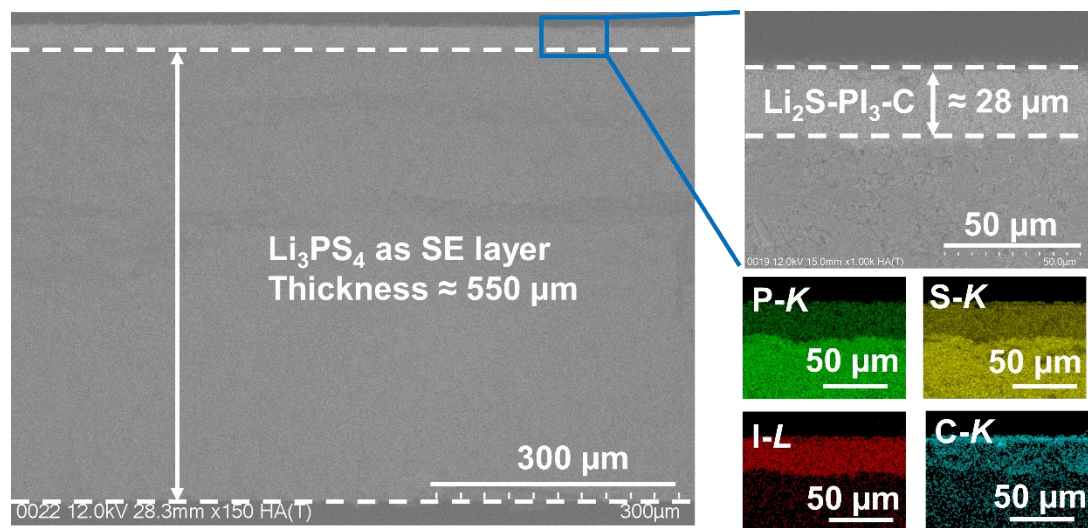


Fig. S1 The cross-section SEM with EDS mapping of $\text{Li}_2\text{S-PI}_3\text{-C/Li}_3\text{PS}_4$ pellet.

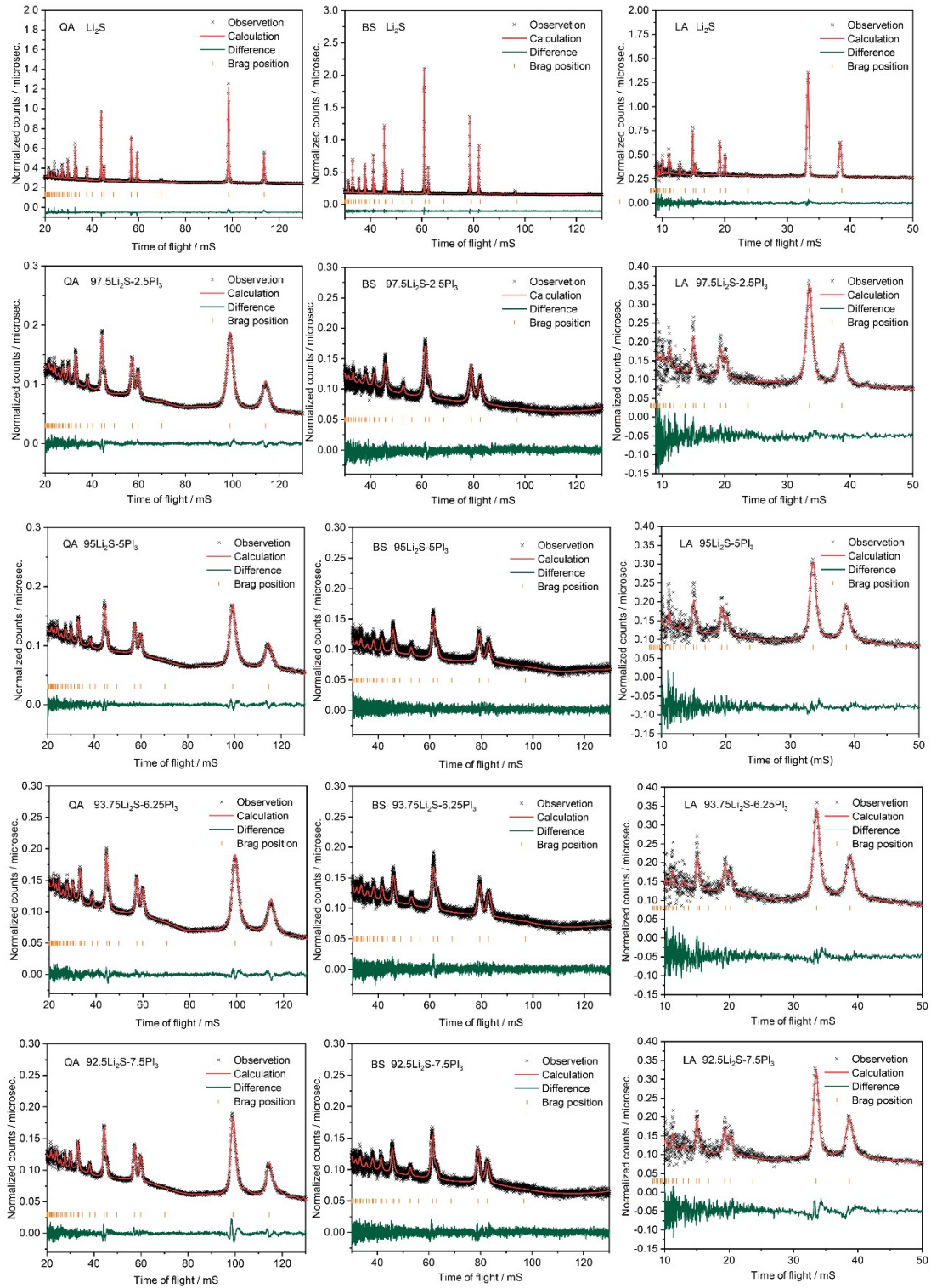


Fig. S2 Rietveld refinement results performed with TOF neutron diffraction data using all of QA, BS and LA detectors to determine the structural parameters more precisely for Li_2S , $97.5\text{Li}_2\text{S}-2.5\text{PI}_3$, $95\text{Li}_2\text{S}-5\text{PI}_3$, $93.75\text{Li}_2\text{S}-6.25\text{PI}_3$, $92.5\text{Li}_2\text{S}-7.5\text{PI}_3$.

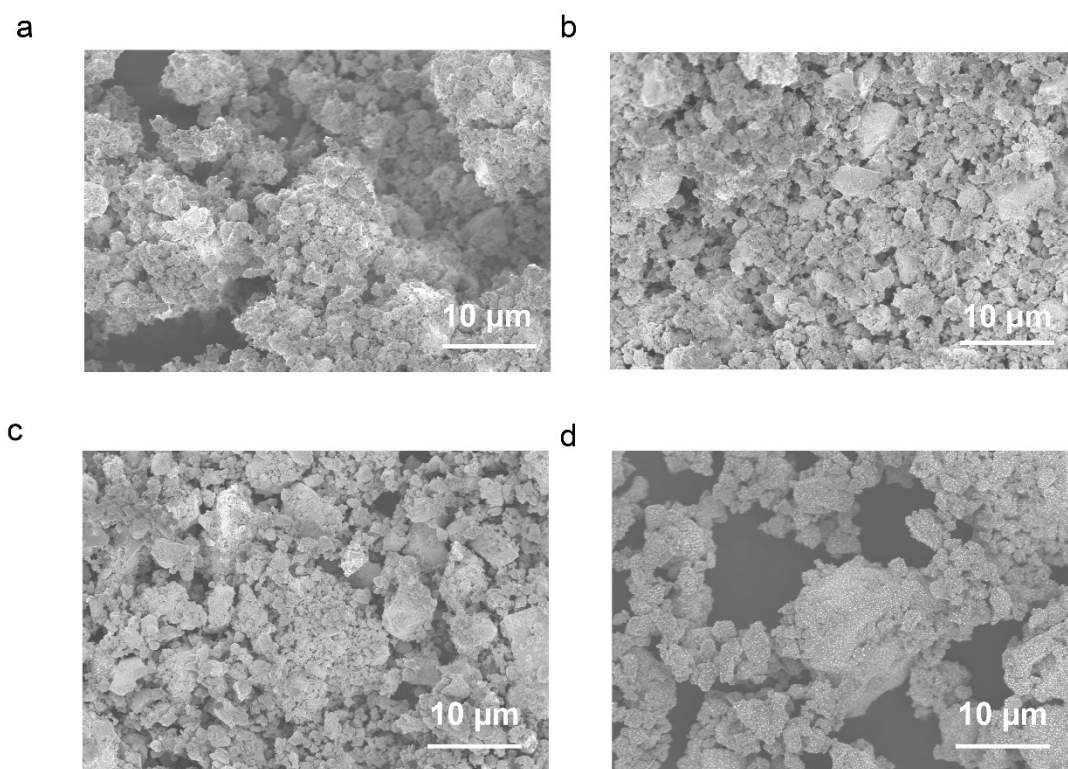


Fig. S3 SEM images of (a) $97.5\text{Li}_2\text{S}-2.5\text{PI}_3$ (b) $95\text{Li}_2\text{S}-5\text{PI}_3$ (c) $93.75\text{Li}_2\text{S}-6.25\text{PI}_3$ (d) $92.5\text{Li}_2\text{S}-7.5\text{PI}_3$.

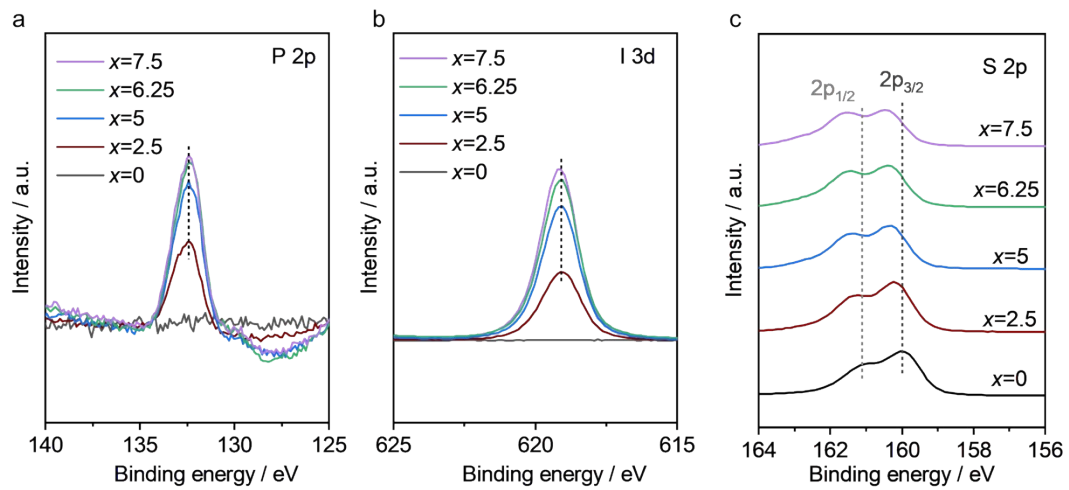


Fig. S4 XPS P 2p, I 3d and S 2p for $(100-x) \text{Li}_2\text{S}-x \text{PI}_3$ ($x=0, 2.5, 5, 6.25, 7.5$).

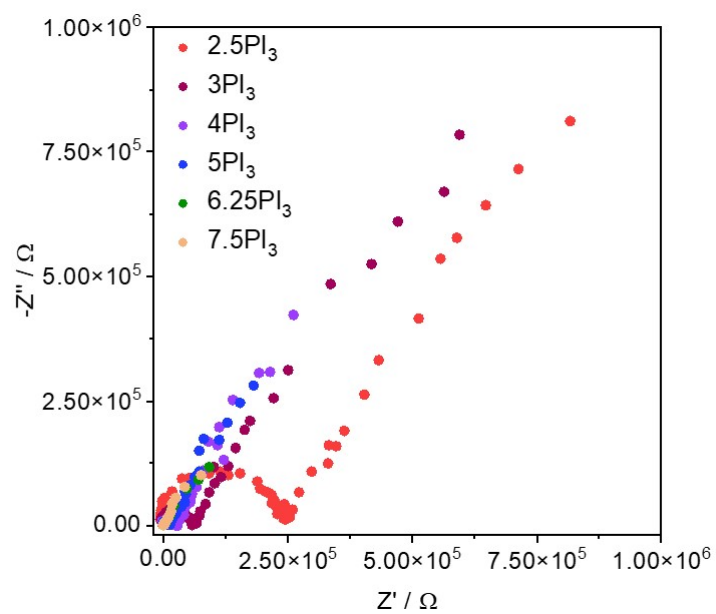


Fig. S5 The Nyquist plots of $(100-x)\text{Li}_2\text{S}-x\text{PI}_3$ ($x=2.5, 3, 4, 5, 6.25, 7.5$).

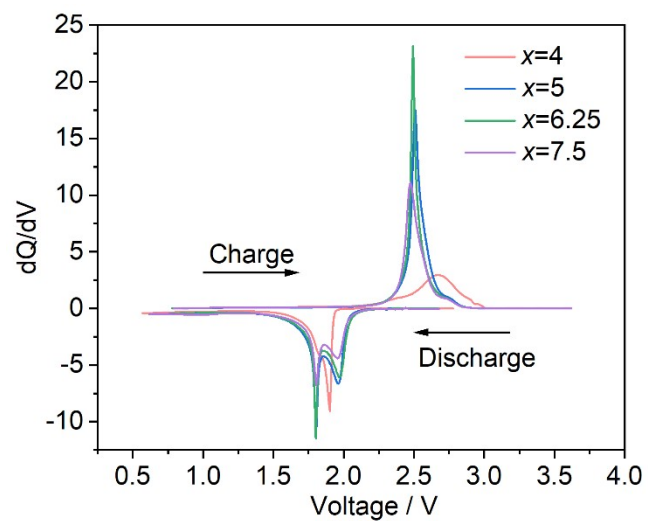


Fig. S6 The differential capacity (dQ/dV) plot of $(1-x) \text{Li}_2\text{S}-x\text{PI}_3$ ($x=4-7.5$).

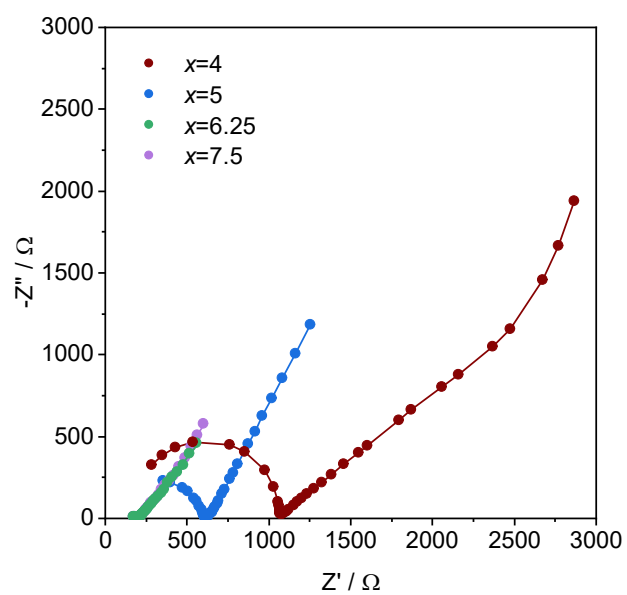


Fig. S7 The EIS and the fitting results by equivalent circuit model for the batteries with $(100-x)\text{Li}_2\text{S}-x\text{PI}_3\text{-C}$ ($x=4, 5, 6.25$ and 7.5) as cathode at pristine state.

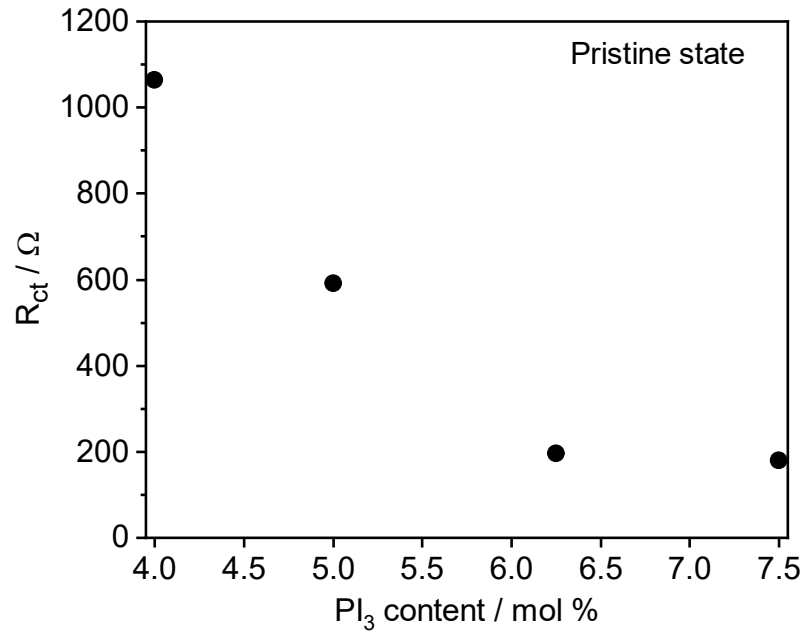


Fig. S8 The R_{ct} obtained by equivalent circuit model for the batteries with $(100-x)\text{Li}_2\text{S}-x\text{PI}_3\text{-C}$ ($x=4, 5, 6.25$ and 7.5) as cathode at pristine state.

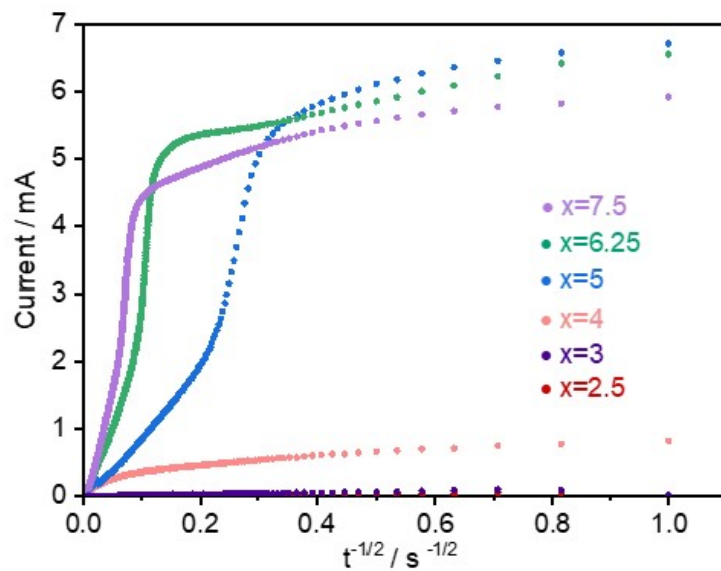


Fig. S9 The Cottrell plots of $(100-x)\text{Li}_2\text{S}-x\text{PI}_3\text{-C}$ ($x=2.5, 3, 4, 5, 6.25, 7.5$).

Table S1 The structure information obtained by Rietveld refinement of TOF neutron diffraction.

(a) The space group of Li_2S is $Fm\bar{3}m$. Standard deviations are shown in parentheses.

The final R factors and lattice parameters are $R_p=5.20\%$ $wR_p=4.83\%$, $RF_{obs}=8.96\%$ and $RF_{wobs}=5.98\%$. $a=b=c=5.7130(3)$ Å.

Atom	Site	g	x	y	z	B (Å ²)
Li/P	$8c$	0.998/0	1/4	1/4	1/4	1.50(10)
S/I	$4a$	0.998/0.002(1)	0	0	0	1.26(8)

(b) The space group of $97.5\text{Li}_2\text{S}-2.5\text{PI}_3$ is $Fm\bar{3}m$. Standard deviations are shown in

parentheses. The final R factors and lattice parameters are $R_p=5.19\%$ $wR_p=4.56\%$, $RF_{obs}=7.81\%$ and $RF_{wobs}=5.62\%$. $a=b=c=5.7395(2)$ Å.

Atom	Site	g	x	y	z	B (Å ²)
Li/P	$8c$	0.979/0.004	1/4	1/4	1/4	1.59(5)
S/I	$4a$	0.979/0.021(1)	0	0	0	1.17(4)

(c) The space group of $95\text{Li}_2\text{S}-5\text{PI}_3$ is $Fm\bar{3}m$. Standard deviations are shown in

parentheses. The final R factors and lattice parameters are $R_p=2.67\%$ $wR_p=2.64\%$, $RF_{obs}=4.06\%$ and $RF_{wobs}=2.84\%$. $a=b=c=5.7605(7)$ Å.

Atom	Site	g	x	y	z	B (Å ²)
Li/P	$8c$	0.962/0.006	1/4	1/4	1/4	1.58(2)
S/I	$4a$	0.962/0.038(1)	0	0	0	0.98(5)

(d) The space group of $93.75\text{Li}_2\text{S}-6.25\text{PI}_3$ is $Fm\bar{3}m$. Standard deviations are shown in

parentheses. The final R factors and lattice parameters are $R_p=2.60\%$ $wR_p=2.60\%$, $RF_{obs}=3.85\%$ and $RF_{wobs}=2.99\%$. $a=b=c=5.7689(2)$ Å.

Atom	Site	g	x	y	z	B (Å ²)
Li/P	$8c$	0.952/0.008	1/4	1/4	1/4	1.28(6)
S/I	$4a$	0.952/0.048(1)	0	0	0	0.68(3)

(e) The space group of $92.5\text{Li}_2\text{S}-7.5\text{PI}_3$ is $Fm\bar{3}m$. Standard deviations are shown in parentheses. The final R factors and lattice parameters are $R_p=4.26\%$, $wR_p=5.16\%$, $RF_{obs}=5.46\%$ and $RF_{wobs}=4.45\%$. $a=b=c=5.7723(2)$ Å.

Atom	Site	g	x	y	z	B (Å ²)
Li/P	$8c$	0.947/0.009	1/4	1/4	1/4	1.21(6)
S/I	$4a$	0.947/0.053(1)	0	0	0	1.12(7)

Table S2. The parameters of EIS fitting by equivalent circuit model for the batteries with $(100-x)\text{Li}_2\text{S}-x\text{PI}_3\text{-C}$ ($x=4, 5, 6.25$ and 7.5) as cathode at pristine state.

PI ₃ content	4	5	6.25	7.5
R ₁ (Ω)	9.89	10.02	9.93	10.04
CPE-T	1.53×10^{-9}	2.52×10^{-9}	5.78×10^{-9}	6.18×10^{-9}
CPE-P	0.785	0.857	0.862	0.804
R _{ct} (Ω)	1063.3	590.2	195.4	180.1
W-R	143.4	120.5	113.4	111.5
W-T	0.008	0.016	0.018	0.019
W-P	0.309	0.288	0.342	0.345
C (μF)	1.050	14.36	40.34	42.52