Supporting Information

A quasi-intercalation reaction for fast sulfur redox kinetics in solidstate lithium-sulfur batteries

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PVDF-HFP+LiFSI+DMF



Figure S1. Schematic representation of the preparation of the PVDF-HFPin-LiFSI (1PVHF1FSI) membrane.



Figure S2. Raman spectra of pure DMF and 1PVHF1FSI. The peak positions for bound and free DMF molecules are 675.9 and 663.3 cm⁻¹, respectively¹. There is no visible 663.3 cm⁻¹ peak in the Raman spectra of 1PVHF1FSI, showing the solid-state property.



Figure S3. CV curves of a Li/1PVHF1FSI/Cu half-cell.



Figure S4. Charge-discharge curves of liquid SPAN at different cycles.



Figure S5. Nyquist plots of (a) liquid SPAN and (b) solid SPAN. (c) the values of R_f (interface resistance from cathode-electrolyte interface and lithium anode-electrolyte interface) at various cycles. The large interfacial resistance of liquid SPAN in the first cycle is due to the native oxide layers and the dendrite Li formation². (d) the values of R_0 (ohmic resistance from electrolyte resistance, contact resistance between the electrode material and the collector, *etc.*) at various cycles. The similar R_0 values at different cycles indicate that there is no shuttling causing electrolyte resistance in both solid SPAN and liquid SPAN.



Figure S6. SEM images of cathodes in (a) solid SBP and (b) solid SPAN before and after 5 cycles.



Figure S7. The configuration of a solid SPAN coin cell used for *in-situ* Raman spectroscopy.



Figure S8. Proposed unstable configuration of SPAN, where the S-S bonds break spontaneously.



Figure S9. (a) Proposed configuration of SPAN and (b) electrical localization of DMF and SPAN through electrical localization function calculations (the darker blue in S atom sites of solid SPAN indicate a stronger C-S bond strength).



Figure S10. FTIR spectra of pure acetone and 1PVHF1FSI (acetone as solvent). The typical peak position (C=N) of pure acetone is 2252 cm⁻¹. There is no visible 2252 cm⁻¹ peak in the FTIR spectra of 1PVHF1FSI (acetone as solvent), showing the acetone was removed completely.



Figure S11. ⁷Li MAS NMR spectra of the SPAN cathodes in solid SPAN without trace DMF after the second discharge/charge.



Figure S12. Possible structures of SPAN and investigation of the origin of irreversible capacity loss during the first discharge process in solid SPAN. Three configurations on the left are possible structures of SPAN and the possible reaction pathways of the first discharge process are shown. The

reaction process leading to irreversible capacity loss needs to be thermodynamically favorable, which means that the change of Gibbs free energy should be sufficiently negative. (a) It is favorable that two nitrogen atoms in SPAN react with one lithium ion with a significantly negative change in the Gibbs free energy. But one nitrogen cannot be further connected with two lithium ions. (b) This process is reversible since the change in Gibbs energy of this reaction is not sufficiently negative, so it does not result in an irreversible capacity loss. (c) This process is thermodynamically unfavorable.



Figure S13. The thermodynamically favorable discharge pathway of solid SPAN batteries highlighted by translucent blue arrows.



Figure S14. The thermodynamically favorable discharge pathway of liquid SPAN batteries highlighted by translucent blue arrows.



Figure S15. The bond lengths of C-S after Li storage in (a) liquid SPAN and (b) solid SPAN.



PP separator 1PVHF1FSI

Figure S16. Comparison of the thermal stabilities of a PP separator and 1PVHF1FSI.

Entry	Electrolyte	Cathode	Capacity (mAh g ⁻¹)		Temperatur	Ref.
				Cycle	e	
					(°C)	
1	AQT@PEO/LiTFSI	Li ₂ S	620/0.1C	60	60	3
2	PEO/LiTFSI	S@C	630/0.05	60	55	4
			mA cm ⁻²			
3	PEO/PIM12%/LiTFSI	S	$\sim 750/0.05C$	30	60	5
4	PEO/LiDFTFSI	S@C	~600/0.1C	30	70	6
5	$Li_{10}GeP_2S_{12}$	S@pPAN	296/0.1C	150	25	7
	$Li_{10}GeP_2S_{12}$	Se _{0.05} S _{0.95} @pPAN	680.4/0.1C	150	25	7
6	Li _{3.25} Ge _{0.25} P _{0.75} S ₄ /PEO/ Pyr _{1,4} TFSI	SPAN	588/0.1C	50	60	8
7	1PVHF1FSI	SPAN	897.4/0.2C	100	25	This
						work

Table S1. Cycling performance comparison of solid-state Li-S batteries.

Reference

1. Fujii, K.; Wakamatsu, H.; Todorov, Y.; Yoshimoto, N.; Morita, M., Structural and electrochemical properties of Li ion solvation complexes in the salt-concentrated electrolytes using an aprotic donor solvent, N,N-dimethylformamide. *The Journal of Physical Chemistry C* **2016**, *120* (31), 17196-17204.

2. Lin, D.; Liu, Y.; Liang, Z.; Lee, H.-W.; Sun, J.; Wang, H.; Yan, K.; Xie, J.; Cui, Y., Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes. *Nature Nanotechnology* **2016**, *11* (7), 626-632.

3. Gao, X.; Zheng, X.; Tsao, Y.; Zhang, P.; Xiao, X.; Ye, Y.; Li, J.; Yang, Y.; Xu, R.; Bao, Z.; Cui, Y., All-solid-state lithium–sulfur batteries enhanced by redox mediators. *Journal of the American Chemical Society* **2021**, *143* (43), 18188-18195.

4. Fang, R.; Xu, H.; Xu, B.; Li, X.; Li, Y.; Goodenough, J. B., Reaction mechanism optimization of solid-state Li–S batteries with a PEO-based electrolyte. *Advanced Functional Materials* **2021**, *31* (2), 2001812.

5. Ji, Y.; Yang, K.; Liu, M.; Chen, S.; Liu, X.; Yang, B.; Wang, Z.; Huang, W.; Song, Z.; Xue, S.; Fu, Y.; Yang, L.; Miller, T. S.; Pan, F., PIM-1 as a multifunctional framework to enable high-performance solid-state lithium–sulfur batteries. *Advanced Functional Materials* **2021**, *31* (47), 2104830.

Zhang, H.; Oteo, U.; Judez, X.; Eshetu, G. G.; Martinez-Ibañez, M.; Carrasco, J.; Li, C.; Armand, M., Designer anion enabling solid-state lithium-sulfur batteries. *Joule* 2019, *3* (7), 1689-1702.
 Zhang, Y.; Sun, Y.; Peng, L.; Yang, J.; Jia, H.; Zhang, Z.; Shan, B.; Xie, J., Se as eutectic accelerator in sulfurized polyacrylonitrile for high performance all-solid-state lithium-sulfur battery. *Energy Storage Materials* 2019, *21*, 287-296.

8. Li, M.; Frerichs, J. E.; Kolek, M.; Sun, W.; Zhou, D.; Huang, C. J.; Hwang, B. J.; Hansen, M. R.; Winter, M.; Bieker, P., Solid-state lithium–sulfur battery enabled by thio-LiSICON/polymer composite electrolyte and sulfurized polyacrylonitrile cathode. *Advanced Functional Materials* **2020**, *30* (14), 1910123.