

Supporting Information

Insight into Sulfur Rich Selenium Sulfide/Pyrolyzed Polyacrylonitrile Cathodes for Li-S Batteries

Wei Zhang^a, Shuping Li^a, Lihui Wang^{a, b}, Xumin Wang^{a, b}, Jia Xie^{a*}

^aState Key Laboratory of Advanced Electromagnetic Engineering and Technology, School of Electrical and Electronic Engineering, Huazhong University of Science and Technology, Wuhan 430074, P. R. China.

^bState Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China

*Corresponding Author:

Email: xiejia@hust.edu.cn

Table S1. Elemental analysis results of the $\text{Se}_x\text{S}_{1-x}$ @pPAN composites.

Materials	C (wt%)	N (wt%)	S (wt%)	Se (wt%)	$\text{Se}_x\text{S}_{1-x}$ (wt%)	S Cap.	Se Cap.	$\text{Se}_x\text{S}_{1-x}$ Cap.	$\text{Se}_x\text{S}_{1-x}$ Cap.
						(based on composites) (mAh g ⁻¹)	(based on composites) (mAh g ⁻¹)	(based on composites) (mAh g ⁻¹)	(based on $\text{Se}_x\text{S}_{1-x}$) (mAh g ⁻¹)
$\text{Se}_{0.35}\text{S}_{0.65}$ @pPAN-350°C	24.73	9.01	27.90	38.04	65.94	467	258	725	1099
$\text{Se}_{0.38}\text{S}_{0.62}$ @pPAN-450°C	32.67	12.11	21.56	33.23	54.79	361	225	586	1071
$\text{Se}_{0.44}\text{S}_{0.56}$ @pPAN-550°C	37.04	13.95	16.48	31.90	48.38	276	216	492	1018
$\text{Se}_{0.48}\text{S}_{0.52}$ @pPAN-650°C	42.36	15.44	12.48	28.99	41.47	209	197	406	978

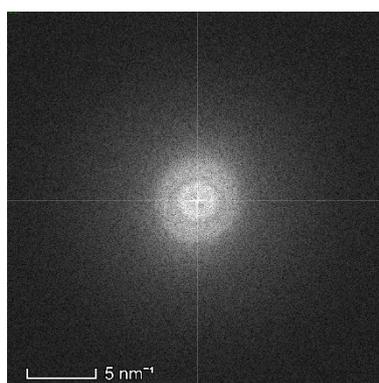
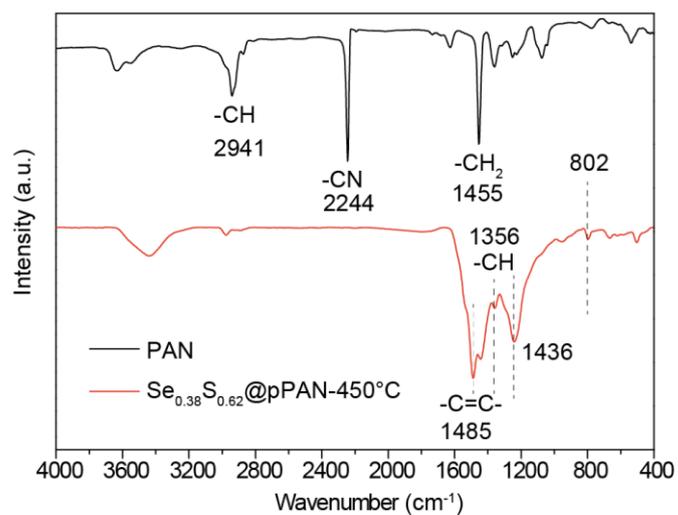
**Figure S1.** Selected area electron diffraction pattern of the $\text{Se}_{0.38}\text{S}_{0.62}$ @pPAN-450 °C.**Figure S2.** FT-IR spectra of the PAN and $\text{Se}_{0.38}\text{S}_{0.62}$ @pPAN-450 °C.

Table S2. The ratio of I_G/I_D in the Raman spectra for the $Se_xS_{1-x}@pPAN$ composites.

Materials	$Se_{0.35}S_{0.65}$ @pPAN-350°C	$Se_{0.38}S_{0.62}$ @ pPAN-450°C	$Se_{0.44}S_{0.56}$ @ pPAN-550°C	$Se_{0.48}S_{0.52}$ @ pPAN-650°C
I_G/I_D	0.34	0.46	0.51	0.59

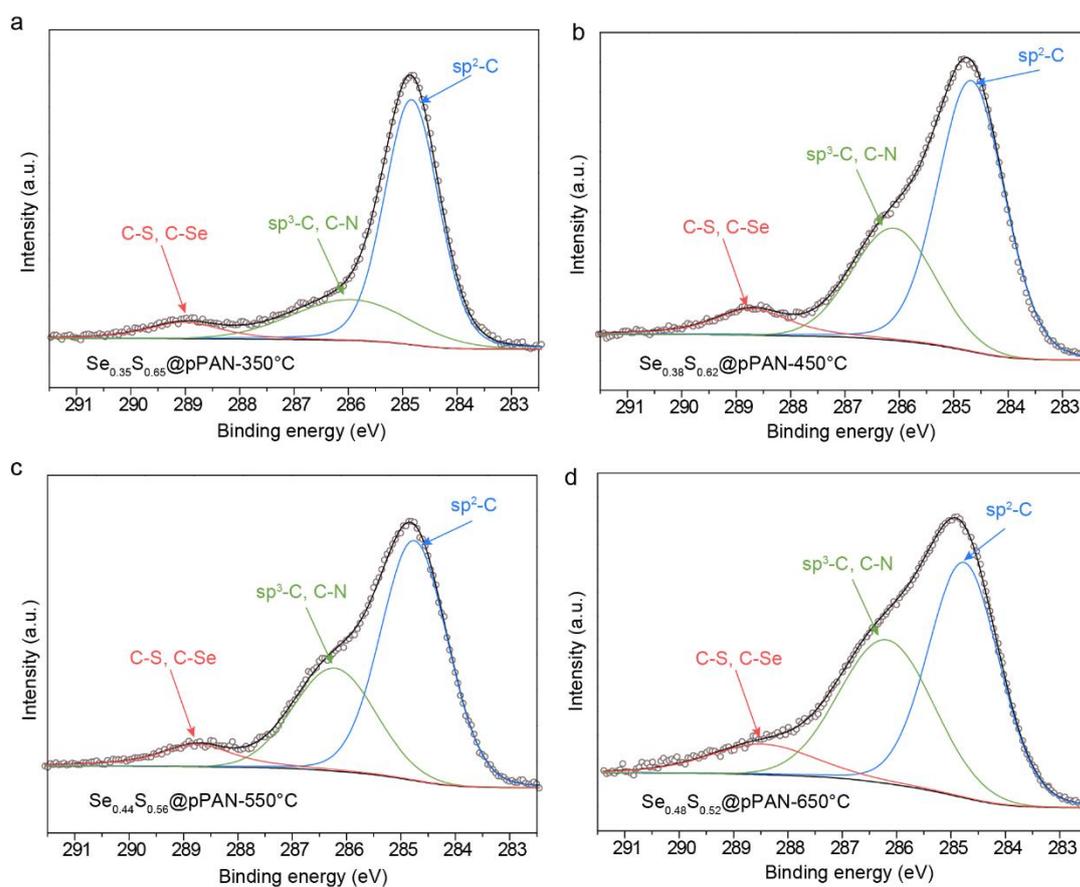


Figure S3. XPS spectra of $Se_xS_{1-x}@pPAN$ composites. C 1s for $Se_xS_{1-x}@pPAN$.

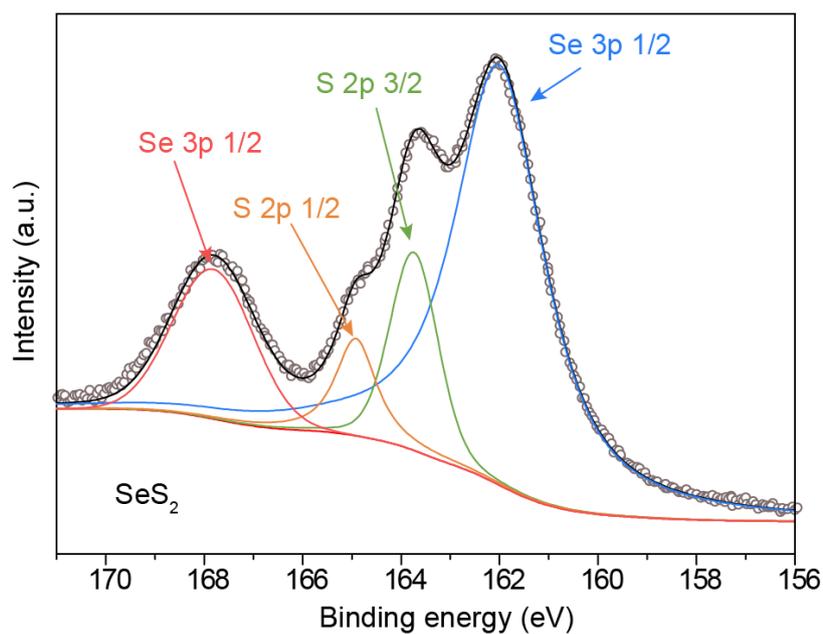


Figure S4. XPS spectra of SeS₂, S 2p and Se 3p

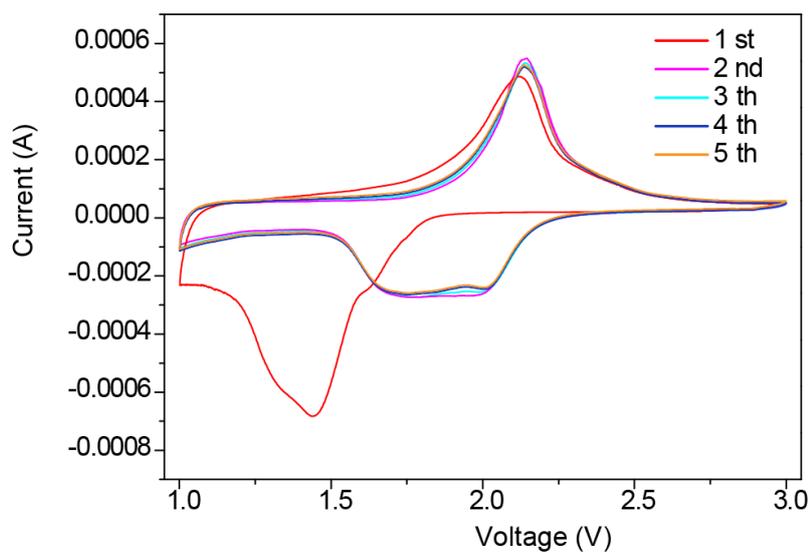


Figure S5. Cyclic voltammograms of the Se_{0.38}S_{0.62}@pPAN-450 °C electrode at a scan rate of 0.1 mV/s over a potential window of 1.0-3.0 V (vs. Li⁺/Li) in carbonate electrolyte.

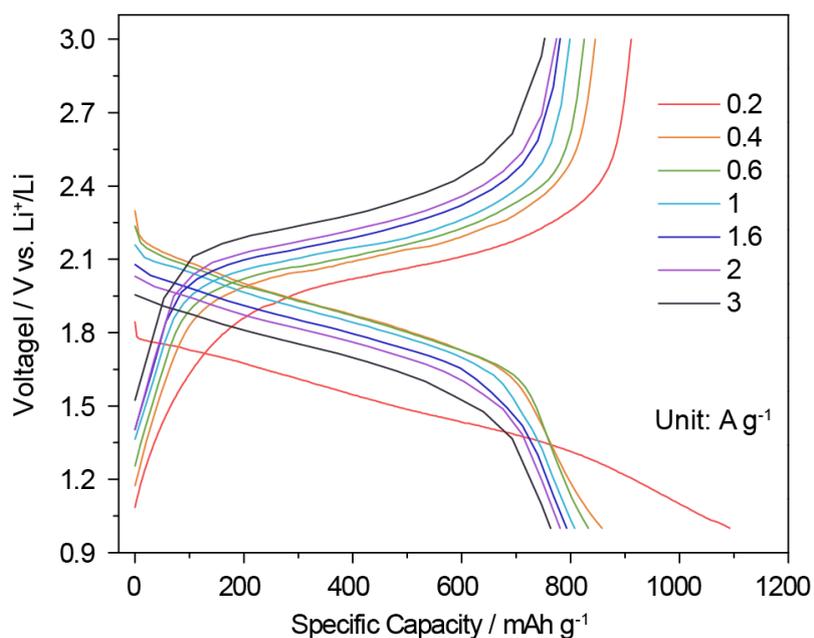


Figure S6. The discharge-charge profiles of the $\text{Se}_{0.38}\text{S}_{0.62}@p\text{PAN}$ -450 °C electrode at various current densities from 1.0 to 3.0 V (vs. Li^+/Li) in carbonate electrolyte.

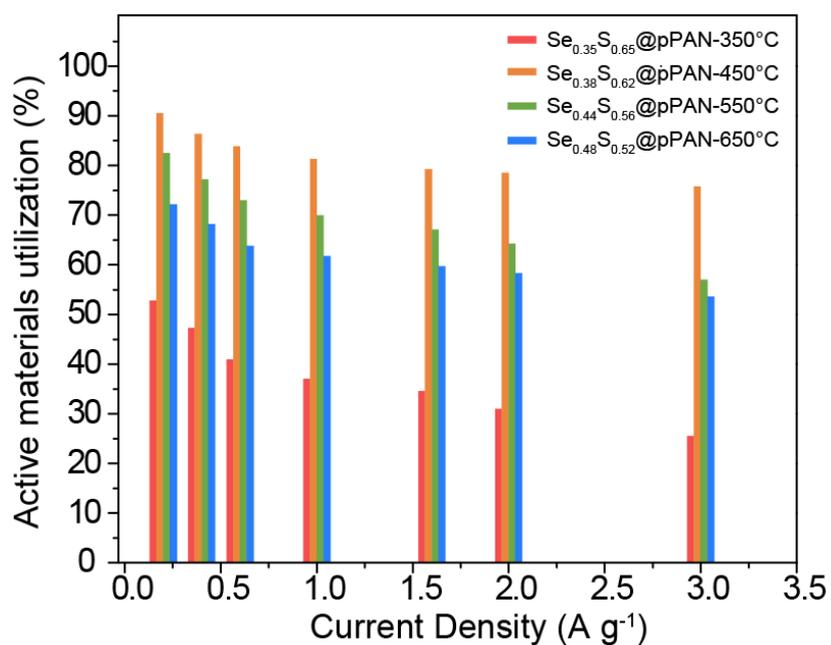


Figure S7. The active material utilization of $\text{Se}_x\text{S}_{1-x}@p\text{PAN}$ electrodes at various current density in carbonate electrolyte.

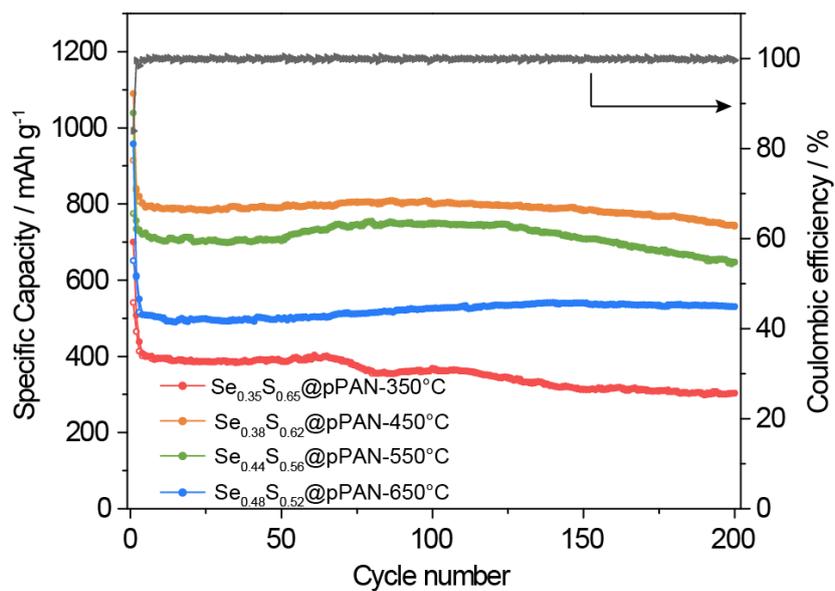


Figure S8. Cycling performances of the Se_xS_{1-x}@pPAN electrodes at 1 A g⁻¹ in ether electrolyte.

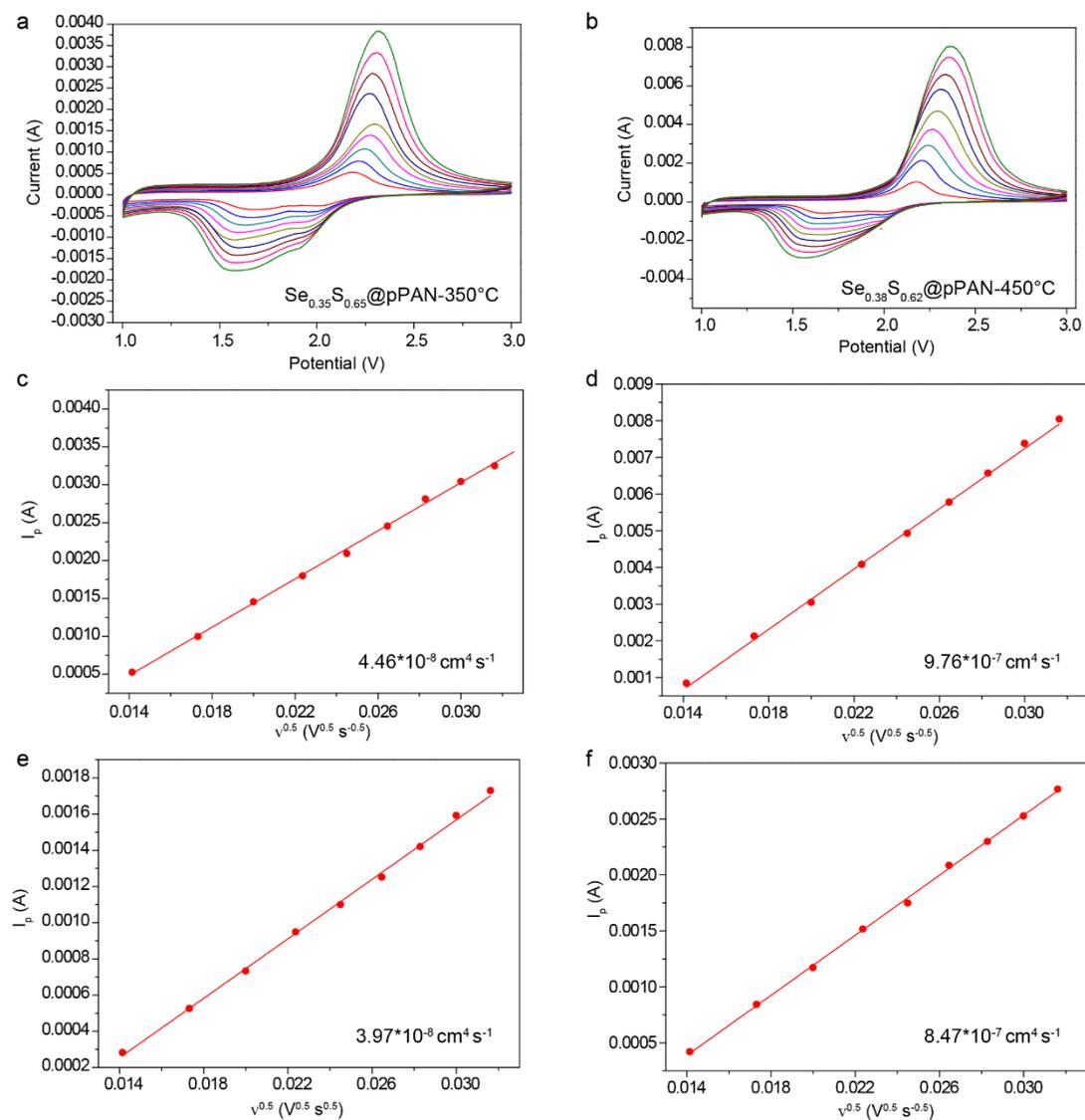


Figure S9. CV curves and peak currents versus square root of scan rates of $\text{Se}_x\text{S}_{1-x}@p\text{PAN}$ electrodes in carbonate electrolyte. (a), (c) and (e) are for $\text{Se}_{0.35}\text{S}_{0.65}@p\text{PAN}-350^\circ\text{C}$; and (b), (d) and (f) are for $\text{Se}_{0.38}\text{S}_{0.62}@p\text{PAN}-450^\circ\text{C}$.

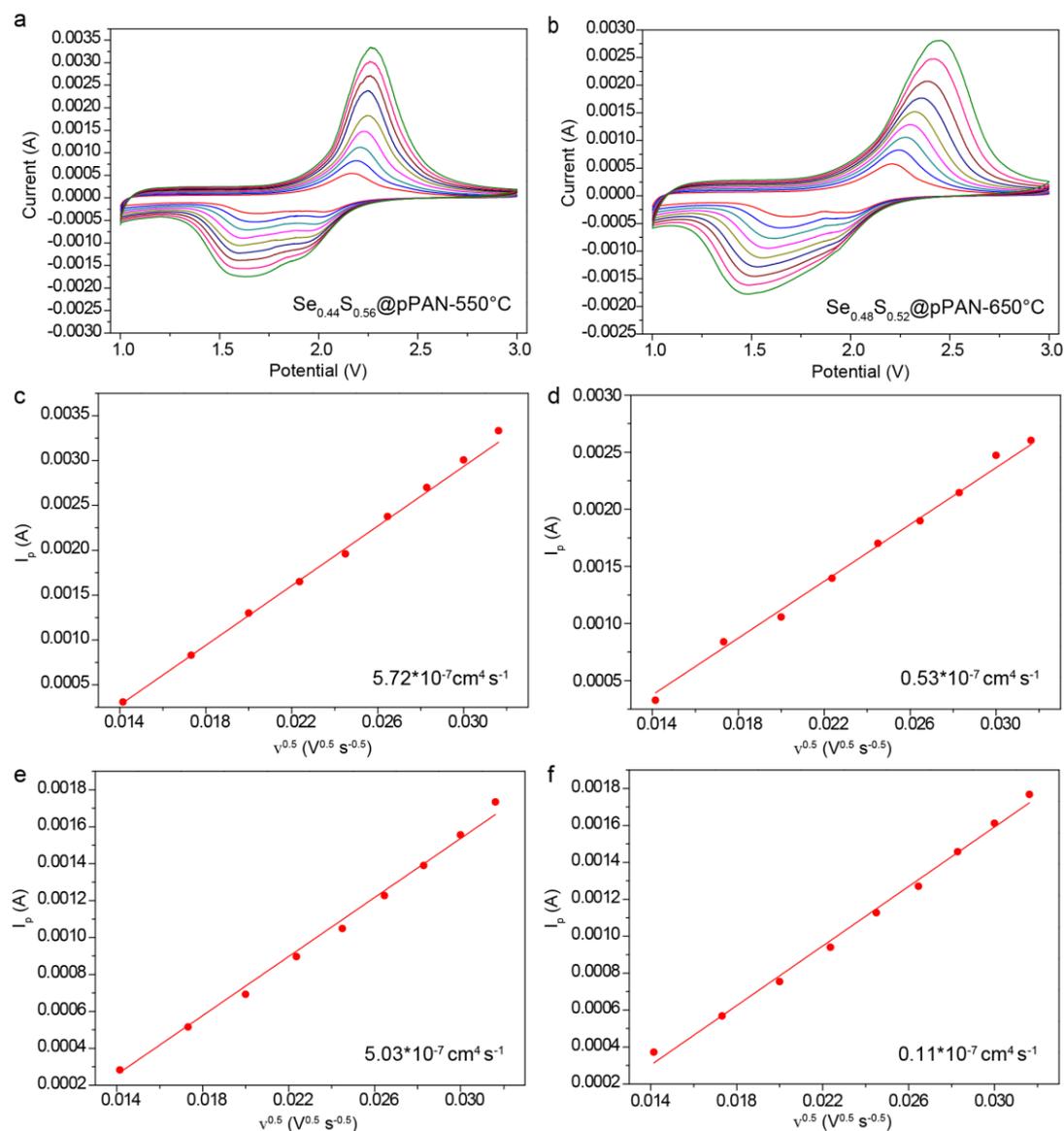


Figure S10. CV curves and peak currents versus square root of scan rates of SeS_2 @pPAN electrodes in carbonate electrolyte. (a), (c) and (e) are for $\text{Se}_{0.44}\text{S}_{0.56}$ @pPAN-550 °C; and (b), (d) and (f) are for $\text{Se}_{0.48}\text{S}_{0.52}$ @pPAN-650 °C.

Table S3. Comparison of the results in this work with that of some previously reported cycling performance of S/Se cathodes for Li-S batteries.

Material	Electrolyte	Current Density (A g ⁻¹)	Cycle number	Capacity retention (mAh g ⁻¹)	Ref.
Se _x S _{1-x} /pPAN	Carbonate	0.2	200	857.4	This work
	Ether	0.4	200	806.1	
	Ether	1	500	574.5	
Se _x /cPAN	Carbonate	0.6	1200	780	1
pPAN/SeS ₂	Carbonate	4	2000	633	2
S _{0.87} Se _{0.13} /CPAN	Carbonate	0.3	200	989	3
Se _x S _y /mesoporous carbon microsphere	Ether	0.5C	100	796.4	4
SeS ₂ /double-layered hollow carbon sphere	Carbonate	1C	900	610	5
S-rich S _{1-x} Se _x /C	Carbonate	1	500	910	6
Se ₂ S ₅ confined in micro/mesoporous carbon	Ether	0.5C	100	430.2	7
Se _n S _{8-n} Molecules Confined in Nitrogen-Doped Mesoporous Carbons	Ether	0.25	200	780	8
S _{22.2} Se/Ketjenblack	HFE-based	1C	250	660	9
NiCo ₂ S ₄ @NC-SeS ₂	Ether	1C	800	580	10
CMK-3/SeS ₂ @PDA	Ether	2	500	350	11
CoS ₂ @LRC/SeS ₂	Ether	0.5	400	470	12
S _{0.6} Se _{0.4} @CNFs	Carbonate	1	1000	346	13
Co-N-C/SeS ₂	Ether	0.2C	200	970.2	14
HMC@TiN/SeS ₂	Ether	0.2C	200	690	15
S/Se@CB@NNH	Ether	0.2	500	915	16

Reference:

- [1] C. Luo, Y. J. Zhu, Y. Wen, J. J. Wang, C. S. Wang, Carbonized Polyacrylonitrile-Stabilized SeS_x Cathodes for Long Cycle Life and High Power Density Lithium Ion Batteries, *Adv. Funct. Mater.* 24 (26) (2014) 4082-4089.
- [2] Z. Li, J. T. Zhang, Y. Lu, X. W. Lou, A pyrolyzed polyacrylonitrile/selenium disulfide composite cathode with remarkable lithium and sodium storage performances, *Sci. Adv.* 4 (6) (2018) 1687.
- [3] T. C. Zhu, Y. Pang, Y. G. Wang, C. X. Wang, Y. Y. Xia, $\text{S}_{0.87}\text{Se}_{0.13}/\text{CPAN}$ composites as high capacity and stable cycling performance cathode for lithium sulfur battery, *Electrochimica Acta* 281 (2018) 789-795.
- [4] Y. J. Wei, Y. Q. Tao, Z. K. Kong, L. Liu, J. T. Wang, W. N. Qiao, L. C. Ling, D. H. Long, Unique electrochemical behavior of heterocyclic selenium–sulfur cathode materials in ether-based electrolytes for rechargeable lithium batteries, *Energy Storage Materials* 5 (2016) 171-179.
- [5] H. W. Zhang, L. Zhou, X. D. Huang, H. Song, C. Z. Yu, Encapsulation of selenium sulfide in double-layered hollow carbon spheres as advanced electrode material for lithium storage, *Nano Research* 9(12) (2016) 3725-3734.
- [6] X. N. Li, J. W. Liang, K. L. Zhang, Z. G. Hou, W. Q. Zhang, Y. C. Zhu, Y. T. Qian, Amorphous S-rich $\text{S}_{1-x}\text{Se}_x/\text{C}$ ($x \leq 0.1$) composites promise better lithium-sulfur batteries in a carbonate-based electrolyte, *Energy Environ. Sci.* 8(11) (2015) 3181-3186.

- [7] G. L. Xu, T. Y. Ma, C. J. Sun, C. Lou, L. Cheng, Z. H. Chen, K. Amine, et al. Insight into the capacity fading mechanism of amorphous Se_2S_5 confined in micro/mesoporous carbon matrix in ether-based electrolytes, *Nano letters* 16(4) (2016) 2663-2673.
- [8] F. G. Sun, H. Y. Cheng, J. Z. Chen, N. Zheng, Y. S. Li, J. L. Shi, Heteroatomic $\text{Se}_n\text{S}_{8-n}$ Molecules Confined in Nitrogen-Doped Mesoporous Carbons as Reversible Cathode Materials for High-Performance Lithium Batteries, *ACS Nano* 10(9) (2016) 8289-8298.
- [9] G. L. Xu, H. Sun, C. Luo, L. Estevez, M. Hao, et al. Solid-State Lithium/Selenium-Sulfur Chemistry Enabled via a Robust Solid-Electrolyte Interphase, *Adv. Energy Mater.* 9(2) (2019) 1802235.
- [10] B. S. Guo, T. T. Yang, W. Y. Du, Q. R. Ma, L. Z. Zhang, S. J. Bao, X. Y. Li, Y. M. Chen, M. W. Xu, Double-walled N-doped carbon@ NiCo_2S_4 hollow capsules as SeS_2 hosts for advanced Li- SeS_2 batteries, *J. Mater. Chem. A* 7(19) (2019) 12276-12282.
- [11] Z. Li, J. T. Zhang, H. B. Wu, X. W. Lou, An improved Li- SeS_2 battery with high energy density and long cycle life, *Adv. Energy Mater.* 7(15) (2017) 1700281.
- [12] J. T. Zhang, Z. Li, X. W. Lou, A Freestanding Selenium Disulfide Cathode Based on Cobalt Disulfide-Decorated Multichannel Carbon Fibers with Enhanced Lithium Storage Performance, *Angew. Chem. Int. Ed.* 56(45) (2017) 14107-14112.

- [13] Y. Yao, L. C. Zeng, S. H. Hu, Y. Jiang, B. B. Yuan, Y. Yu, Binding $S_{0.6}Se_{0.4}$ in 1D Carbon Nanofiber with C-S Bonding for High-Performance Flexible Li-S Batteries and Na-S Batteries, *Small* 13(19) (2017) 1603513.
- [14] J. R. He, W. Q. Lv, Y. F. Chen, J. Xiong, K. C. Wen, C. Xu, W. L. Zhang, Y. R. Li, W. Qin, W. D. He, Direct impregnation of SeS_2 into a MOF-derived 3D nanoporous Co-N-C architecture towards superior rechargeable lithium batteries, *J. Mater. Chem. A* 6(22) (2018) 10466-10473.
- [15] Z. Li, J. T. Zhang, B. Y. Guan, X. W. Lou, Mesoporous Carbon@titanium nitride hollow spheres as an efficient SeS_2 host for advanced Li- SeS_2 batteries, *Angew. Chem. Int. Ed.* 56(50) (2017) 16003-16007.
- [16] T. Meng, Y. N. Liu, L. P. Li, J. H. Zhu, J. C. Gao, H. Zhang, L. Ma, C. M. Li, J. Jiang, Smart Merit Combination of Sulfur, Selenium and Electrode Engineering to Build Better Sustainable Li-Storage Batteries, *ACS Sustainable Chem. Eng.* 7(1) (2018) 802-809.