

Ether-compatible Sulfurized Polyacrylonitrile Cathode with Excellent Performance Enabled by Fast Kinetics *via* selenium-doping

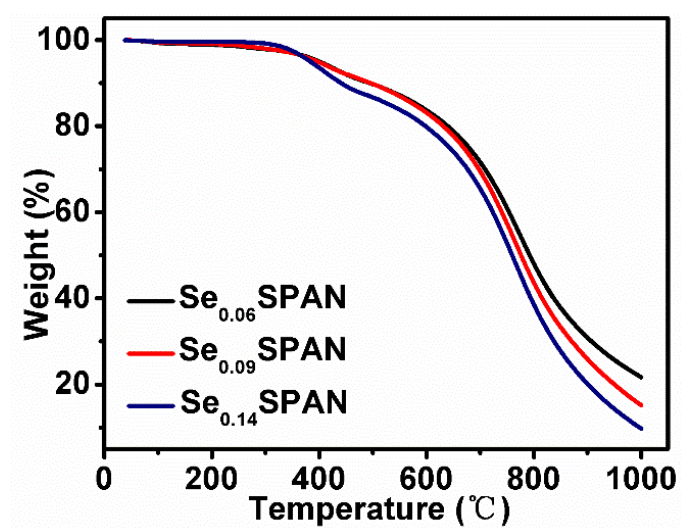
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Supplementary Figure 1. Thermogravimetric analysis of Se_xSPAN . All tests were conducted from 25 to 1000 °C with a rate of 10 °C min⁻¹ in N₂ atmosphere.

Supplementary Table 1. The C, N, S and Se content in the composite based on the elemental analysis.

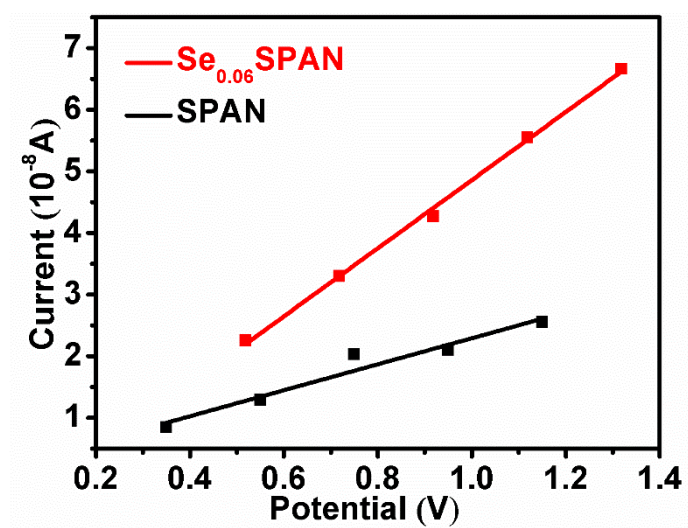
Materials	C (%)	N (%)	S (%)	Se (%)	S&Se (%)	S/Se
Se _{0.06} SPAN	38.5	14.25	40.935	6.315	47.25	1/0.06
Se _{0.09} SPAN	38.01	14.14	38.798	9.052	47.85	1/0.09
Se _{0.14} SPAN	37.3	13.93	35.894	12.876	48.77	1/0.14

Supplementary Table 2. Theoretical capacity of Se_xSPAN composite.

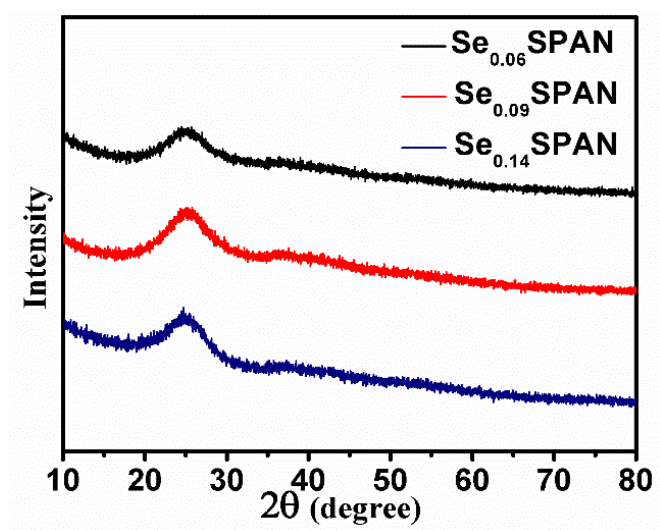
Materials	Se (wt%) /S (wt%)	S&Se (wt%) in composite	Theoretical capacity (mAh g ⁻¹ , based on Se and S)	Theoretical capacity (mAh g ⁻¹ , based on the composite)
Se _{0.06} SPAN	13/87	47.25	1546	726
Se _{0.09} SPAN	19/81	47.85	1485	710
Se _{0.14} SPAN	26/74	48.77	1415	690

Supplementary Table 3. Electric conductivity results of SPAN and Se_{0.06}SPAN using direct current (DC) polarization method.

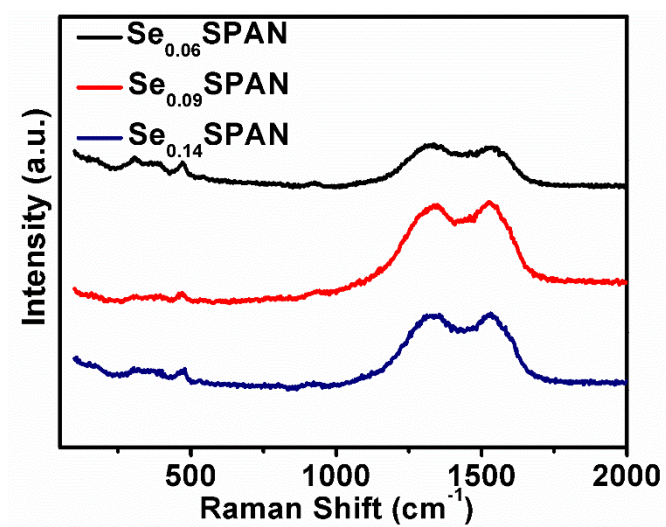
Material	Resistance	Length (cm)	Area (cm ²)	Electric conductivity (S/cm)
SPAN	4.7×10^7	0.089	0.785	2.4×10^{-9}
Se _{0.06} SPAN	1.8×10^7	0.083	0.785	5.8×10^{-9}



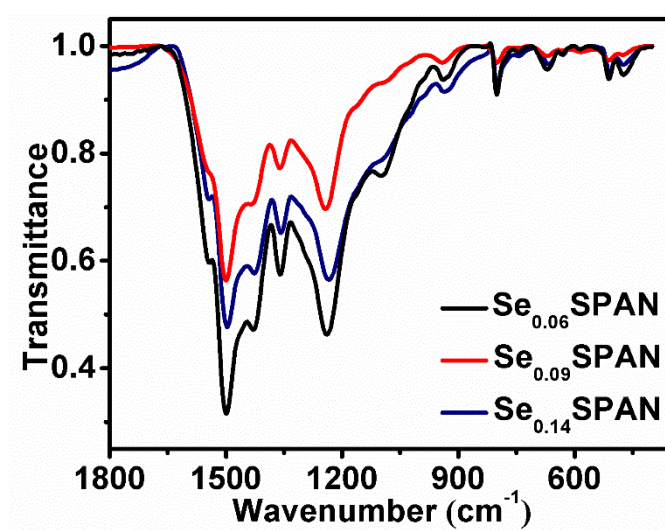
Supplementary Figure 2. Equilibrium current of the $\text{Se}_{0.06}\text{SPAN}$ and SPAN at different set voltages.



Supplementary Figure 3. XRD patterns of Se_xSPAN .



Supplementary Figure 4. Raman analysis. Raman Spectra of Se_xSPAN.



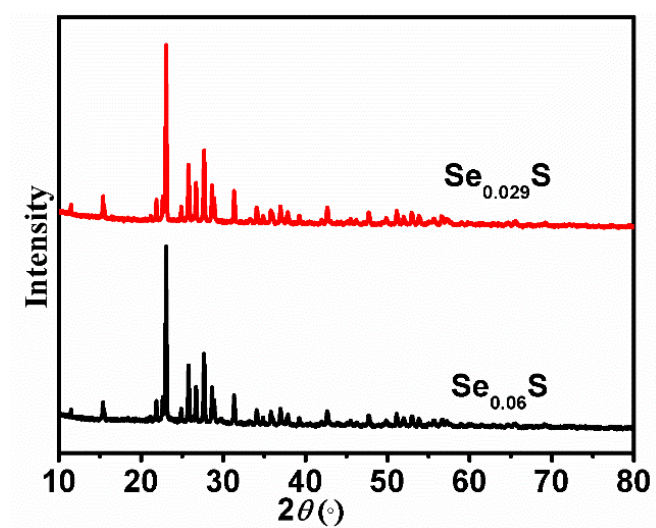
Supplementary Figure 5. FTIR analysis. FTIR Spectras of Se_xSPAN composites.

Supplementary Table 4. Raman shifts (cm^{-1}) and assignments for Se_xSPAN .

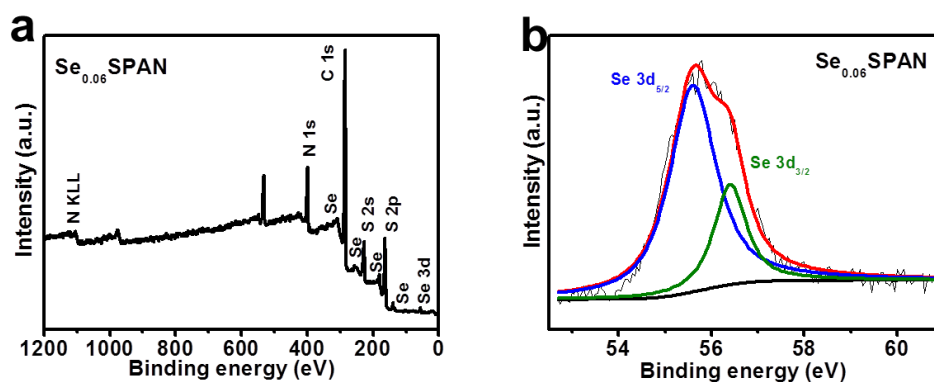
Se_xSPAN	Assignments
307	C-S in plane bending
470	S-S
926	Ring (containing S-S bond) Stretch
1325	D Band
1532	G Band

Supplementary Table 5. FTIR wavenumbers (cm^{-1}) and assignments for Se_xSPAN .

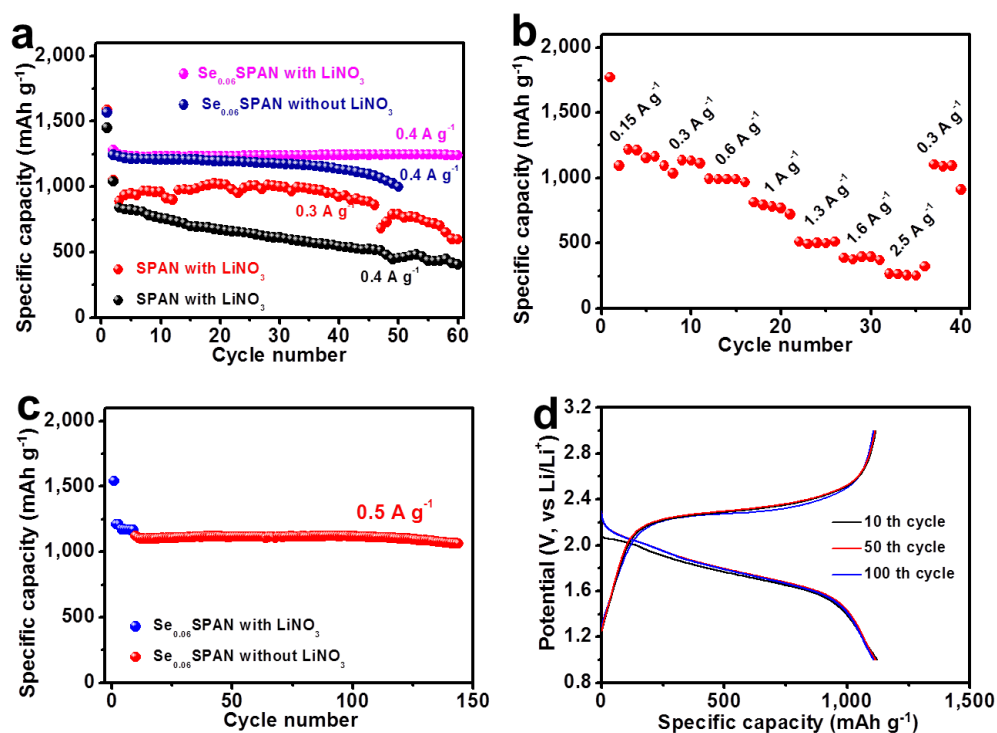
Se_xSPAN	Assignments
1543	C=C Asymmetric Stretch
1498	C=C Symmetric Stretch
1430	C=N Asymmetric Stretch
1357	C-C Deformation
1237	C=N Symmetric Stretch
940	Ring Breath (Side-chain Containing S-S)
801	Ring Breath (Main-chain Hexahydric-ring)
668	C-S Stretch
511	S-S Stretch
479	S-S



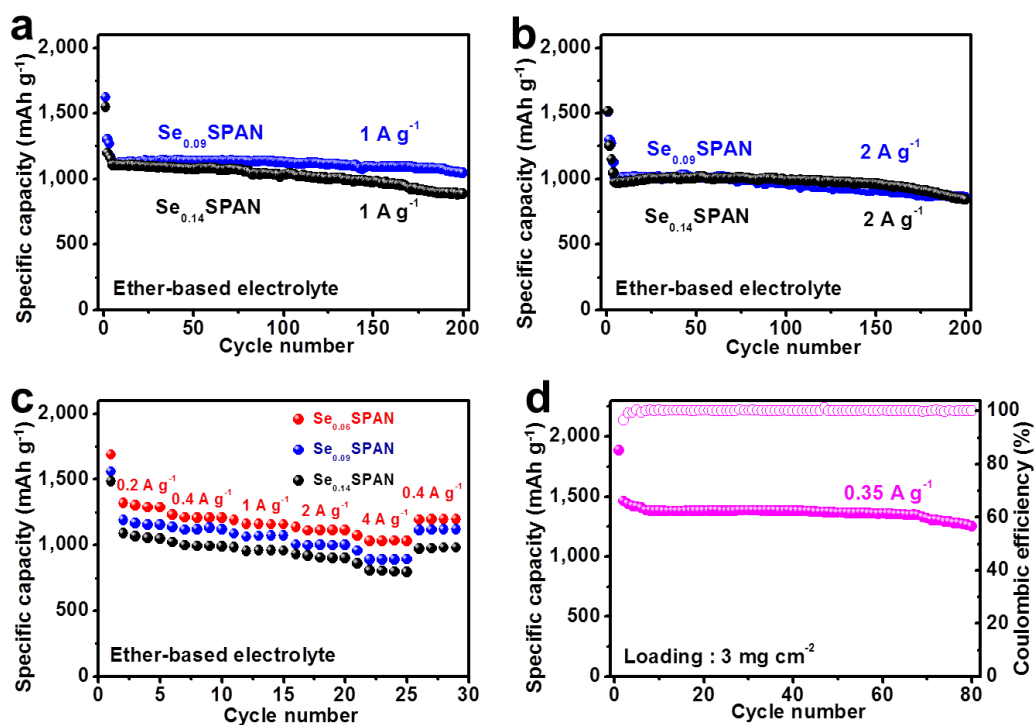
Supplementary Figure 6. XRD patterns of $\text{Se}_{0.029}\text{S}$ and $\text{Se}_{0.06}\text{S}$ composites.



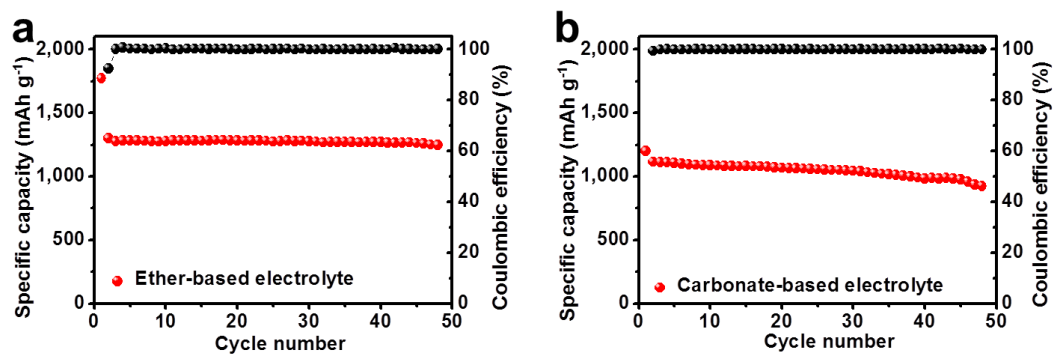
Supplementary Figure 7. XPS spectra. (a) Survey XPS spectrum of $\text{Se}_{0.06}\text{SPAN}$, and (b) Se 3d XPS spectrum.



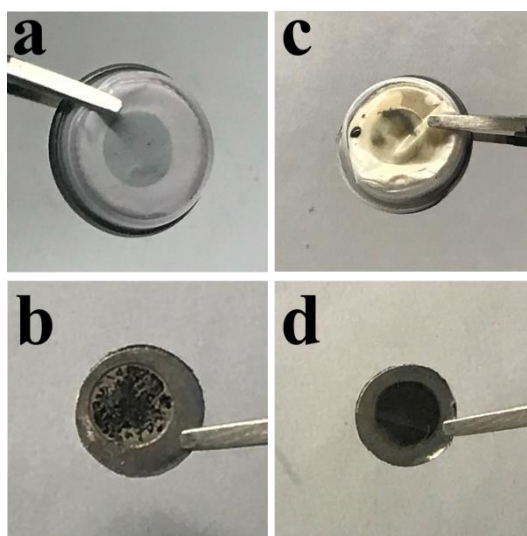
Supplementary Figure 8. Electrochemical performance of the Li-S batteries. (a) Cycle performance of the Se_xSPAN cathodes using ether-based electrolyte with and without LiNO₃, and SPAN cathode with LiNO₃ in ether-based electrolyte. (b) Rate performance of SPAN in the ether-based electrolyte. (c) Cycle performance of the Se_xSPAN cathode using ether-based electrolyte, which is firstly cycled for 10 cycles with LiNO₃ and subsequently cycled without LiNO₃. (d) The corresponding electrochemical discharge and charge profiles of Se_{0.06}SPAN at various cycles.



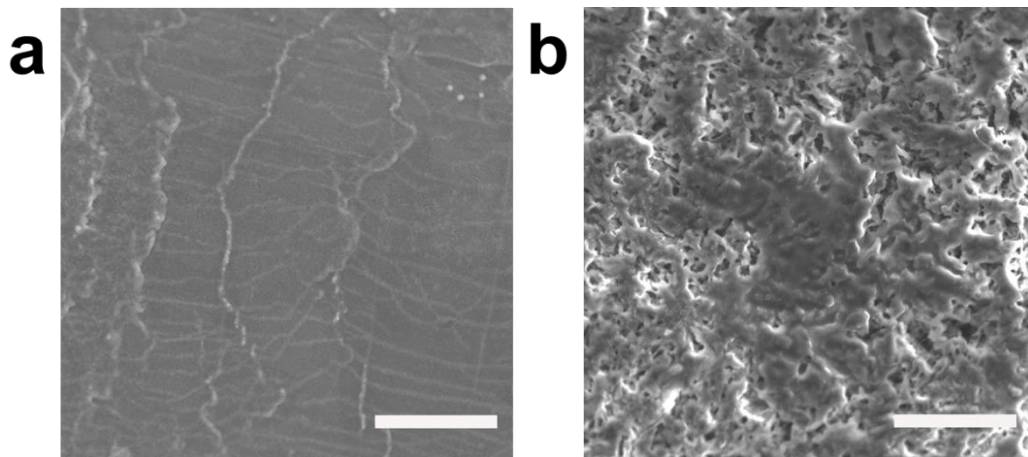
Supplementary Figure 9. Electrochemical performance of the Li-S batteries. (a) Cycle performance of $\text{Se}_{0.09}\text{SPAN}$ and $\text{Se}_{0.14}\text{SPAN}$ cathodes at 1 A g^{-1} . (b) Cycle performance of $\text{Se}_{0.09}\text{SPAN}$ and $\text{Se}_{0.14}\text{SPAN}$ cathodes at 2 A g^{-1} . (c) Rate performance of Se_xSPAN composite cathodes at various current densities. (d) Cycle performance of $\text{Se}_{0.06}\text{SPAN}$ composite cathode with 3 mg cm^{-2} based on the mass of S and Se in the ether-based electrolyte.



Supplementary Figure 10. Cycle performance of the Li-S batteries. Se_{0.06}SPAN composite cathodes with 2.3 mg cm⁻² cycle (a) in the ether-based electrolyte and (b) in the carbonate-based electrolyte after 50 cycles for subsequent tests.



Supplementary Figure 11. Digital graph of separators and Li metals. The cycled coin cells were taken in a glovebox after 50 cycles: (a, b) in ether-based electrolyte and (c, d) in carbonate-based electrolyte.



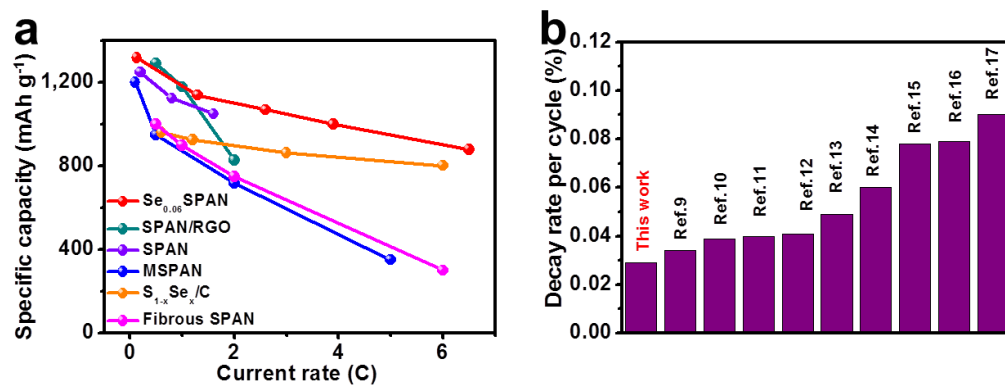
Supplementary Figure 12. Characterization of the cycled Li metal. SEM image of Li metal after 50 cycles: (a) in ether-based electrolyte and (b) in carbonate-based electrolyte. Scale bars, 20 μm (a, b).

Supplementary Table 6 The performance comparison of this work with some similar composite.

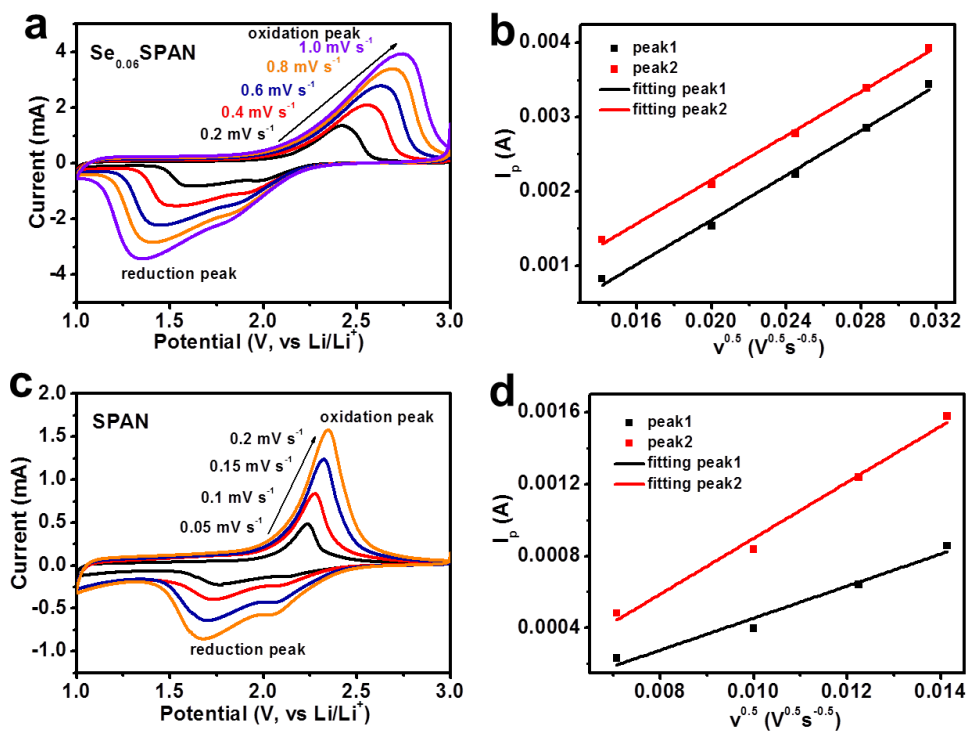
Materials ^{Reference}	Ratio of Active material	Areal loading (mg cm ⁻²)	Capacity Retention (mAh g ⁻¹)	Rate capacity mAh g ⁻¹
pPAN-S/GNS ¹	47%	N/A	1200 (0.1 C, 100 cycles)	800 (6 C)
S/PAN/Mg _{0.6} Ni _{0.4} O ₂ ²	38.5%	1.23	1223 (0.1 C, 100 cycles)	887 (0.5 C); 710 (0.7 C) 445 (1 C)
SPAN/RGO ³	44 %	2-2.8	1100 (0.1 C, 200 cycles)	1292 (0.5 C); 1180 (1 C); 828 (2 C)
SPAN ⁴	45.6%	~0.38	~1000 (0.4 C, 1000 cycles)	1250 (0.2 C); 1125 (0.8 C); 1050 (1.6 C)
NiS ₂ -SPAN ⁵	46%	1.15	1533 (0.2 A/g, 100 cycles)	1180 (2 A g ⁻¹ , 1.2 C)
MSPAN ⁶	45.87%,	2.45	755 (1 C, 200 cycles)	1202 (0.1 C); 949 (0.5 C); 717 (2 C); 350 (5 C)
Fibrous SPAN ⁷	43.6%	0.672	N/A	1000 (0.5 C); 900 (1 C); 750 (2 C); 300 (6 C);
S _{1-x} Se _x /C ⁸	50%,	0.8-1.5	910 (1 A g ⁻¹ , 500 cycles)	961 (1 A g ⁻¹ , 0.6 C) 926 (2 A g ⁻¹ , 1.2 C) 863 (5 A g ⁻¹ , 3 C) 802 (10 A g ⁻¹ , 6 C)
Se _{0.06} SPAN (This work)	47.25%	1-3	880 (0.4 A g ⁻¹ , 800 cycles)	1320 (0.2 A g ⁻¹ , 0.13 C) 1140 (2 A g ⁻¹ , 1.3 C) 1070 (4 A g ⁻¹ , 2.6 C) 1000 (6 A g ⁻¹ , 3.9 C) 900 (10 A g ⁻¹ , 6.5 C)

Supplementary Table 7 Long-term cycling stability of representative cathodes for Li-S batteries.

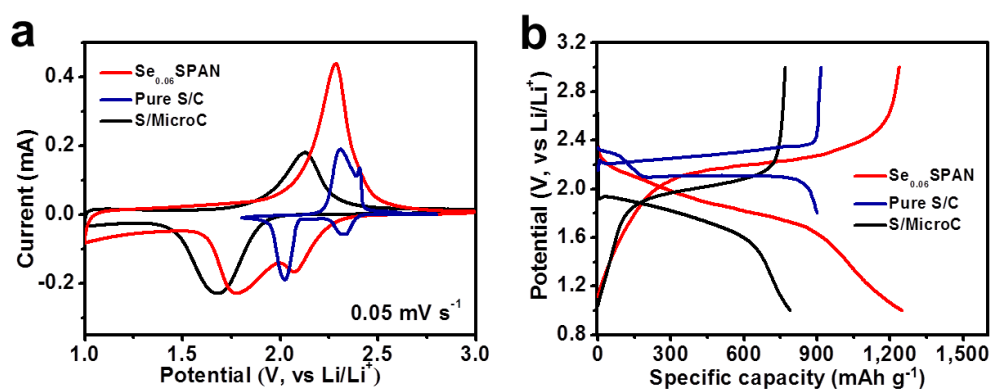
Materials ^{Reference}	Initial Capacity (mAh g ⁻¹)	Capacity Retention (mAh g ⁻¹)	Decay rate per cycle (%)
CoS ₂ ⁹	1003 (2 C)	321 (2000 cycles)	0.034
MnO ₂ ¹⁰	934 (2 C)	315 (1700 cycles)	0.039
PEDOT:PSS-graphene ¹¹	1008 (1 C)	806 (500 cycles)	0.04
Co ₉ S ₈ /C ¹²	950 (2 C)	560 (1000 cycles)	0.041
CC@Co ₃ O ₄ ¹³	612 (2 C)	476 (500 cycles)	0.049
Ti ₄ O ₇ ¹⁴	850 (2 C)	595 (500 cycles)	0.06
N,S-codoped graphene ¹⁵	878 (0.5 C)	550 (500 cycles)	0.078
ACNF/Co ₃ S ₄ /S ¹⁶	953 (1 C)	610 (450 cycles)	0.079
S@Co-N-GC ¹⁷	1150 (1 C)	625 (500 cycles)	0.09
Se _{0.06} SPAN (This work)	1230 (0.4 A g ⁻¹)	880 (800 cycles)	0.029



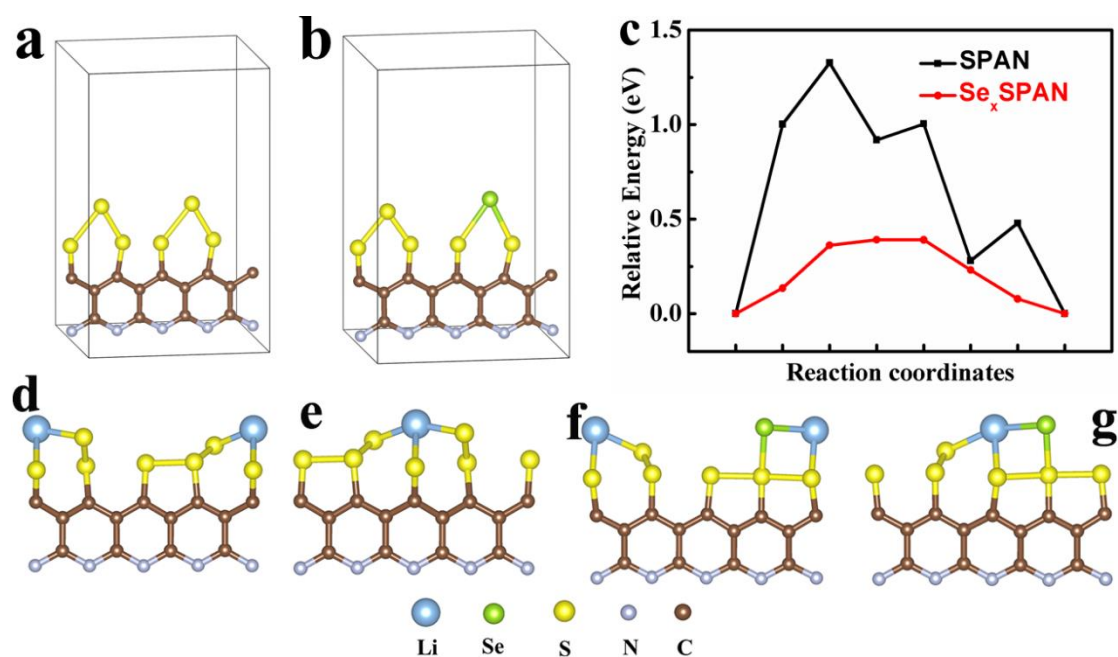
Supplementary Figure 13. Electrochemical performance comparisons. (a) Specific capacity and (b) Cyclic life of Se_{0.06}SPAN electrodes compared with various SPAN and S based cathode materials.



Supplementary Figure 14. CV tests and plots of CV peak current at various scan rates. CV curves and peak currents versus square root of scan rates of (a, b) the $\text{Se}_{0.06}\text{SPAN}$ and (c, d) SPAN electrodes.



Supplementary Figure 15. Comparison of CV curves and voltage profiles. (a) the CV curves and (b) voltage profiles at 0.1 C of Se_xSPAN , Pure S/C and S/microC.



Supplementary Figure 16. DFT simulation of Li migration behavior. The model for Li⁺ migration energy barriers employing DFT calculation on (a) SPAN and (b) Se_xSPAN. Li, Se, S, N and C atoms are represented by blue, green, yellow, purple and brown spheres, respectively. c) The corresponding energy barriers profiles. Throughout the diffusion path, the Li⁺ migration energy barriers on Se_xSPAN is apparently lower than that on SPAN; (d-e) Schematically shows the migration occurs through the following step: Li atom sitting on a S top site passes through a vacant site and to a new S top site. (f-g) Schematically shows the migration occurs through the following step: Li atom sitting on a S top site passes through a vacant site and to a Se top site.

Supplementary References

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