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## MATERIALS SCIENCE

# A pyrolyzed polyacrylonitrile/selenium disulfide composite cathode with remarkable lithium and sodium storage performances

Zhen Li, Jintao Zhang, Yan Lu, Xiong Wen (David) Lou\*

As a special class of cathode materials for lithium-sulfur batteries, pyrolyzed polyacrylonitrile/sulfur (pPAN/S) can completely solve the polysulfide dissolution problem and deliver reliable performance. However, the applicable S contents of pPAN/S are usually lower than 50 weight % (wt %), and their capacity utilizations are not sufficient, both of which greatly limit their energy densities for commercial applications. We report a pyrolyzed polyacrylonitrile/selenium disulfide (pPAN/SeS<sub>2</sub>) composite with dramatically enhanced active material content (63 wt %) and superior performances for both lithium and sodium storage. As a result, pPAN/SeS<sub>2</sub> delivers high capacity of >1100 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup> for Li storage with extremely stable cycle life over 2000 cycles at 4.0 A g<sup>-1</sup>. Moreover, when applied in a room temperature Na-SeS<sub>2</sub> battery, pPAN/SeS<sub>2</sub> achieves superior capacity of >900 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and delivers prolonged cycle life over 400 cycles at 1.0 A g<sup>-1</sup>.

## INTRODUCTION

There has been increasing demand for high-energy density and long-cycle life rechargeable batteries to address pressing needs for many emerging applications, such as electric vehicles, portable electronics, and grid energy storage (1). Because of the high theoretical capacity and natural abundance of sulfur, lithium-sulfur (Li-S) batteries present nearly threefold higher energy density and are more cost-effective than the state-of-the-art commercial Li-ion batteries (2). The major problems that hinder the practical applications of Li-S batteries are the insufficient capacity utilization, low energy efficiency, limited cycle life, and fast self-discharge, all of which are mainly caused by the insulating nature of S and the dissolution of long-chain lithium polysulfides (Li<sub>2</sub>S<sub>x</sub>,  $x \geq 4$ , noted as LiPSs) into liquid electrolyte (3). As a resolution, conductive hosts with porous/hollow structures are designed and applied to increase the utilization ratio of S and reduce the dissolution of LiPSs (4–6). Although the electrochemical performance of Li-S batteries can be obviously improved by the rationally designed electrode structures, it must not be ignored that dissolution in organic electrolyte is the intrinsic nature of long-chain LiPSs; thus, the generation and migration of LiPSs could not be ultimately overcome as long as the normal ring-structured S<sub>8</sub> molecule-based cathodes and the ether-based electrolytes are used in the batteries (7, 8).

Fortunately, it is found that, when S molecules are chemically bonded onto polymer backbones or confined within microporous carbons, the LiPS dissolution issue can be entirely eliminated (9–13). On the basis of this special class of cathode materials, the cycling stability of Li-S batteries has been greatly improved (14, 15). Moreover, these cathodes are chemically matched with the industrially used LiPF<sub>6</sub>-carbonate-based electrolytes, so there is a great potential for them to couple with many mature anodes for developing Li-ion batteries with high energy density, low cost, good safety, and reliability (16–18). Compared to microporous carbon materials, which usually require multistep preparation, polyacrylonitrile (PAN) has been thought as a much better precursor for composing with sulfur species. Because of the easiness to dehydrogenate and cyclize into conjugated backbones, the pyrolyzed

PAN/sulfur (pPAN/S) composite can be prepared through a facile one-step reaction of PAN with commercial S powder at elevated temperature (19, 20). Previous studies have successfully revealed the electrochemical reaction mechanisms of pPAN/S for lithium storage (15, 21–24) and introduced conductive additives into the pPAN/S composites to further enhance their capacity utilizations (25–28). However, the S content of pPAN/S is usually less than 50 weight % (wt %), which leads to an obvious lower energy density compared to the normal S<sub>8</sub>-based composite cathodes with the loading of  $\geq 60$  wt % of S (19). Because the concentration of functional groups in pPAN backbones is limited, it seems not possible to bond more S in the pPAN/S composite.

Besides the low S content issue, another challenge is the relatively low capacity utilization of the pPAN/S cathode because of the insulating nature of S and the polymer backbones. Therefore, to make the pPAN-supported cathodes more practical, it is of great importance to explore new-concept cathode materials with higher content of active materials and better reaction kinetics. Similar with S, selenium (Se) can be applied as the cathode for Li and Na storage via alloying reactions, but with much enhanced kinetics because of its orders of magnitude higher conductivity (29, 30). Moreover, Li/Na-Se batteries could readily achieve prolonged cycle life without shuttle effect in carbonate electrolyte (31–33). Some recently reported Se-based composites have shown excellent electrochemical performances accompanied with high volumetric energy density (34–37). However, the theoretical gravimetric energy density of Se is not high, and the material cost of Se is much higher than S, both of which limit the application potential of pure Se-based cathode materials. Therefore, it might be a more rational approach to use Se<sub>x</sub>S<sub>y</sub> solid solution as the active material for energy storage (38–41).

Here, we report a novel pyrolyzed PAN/selenium disulfide (pPAN/SeS<sub>2</sub>) composite as a cathode material for lithium and sodium storage. Benefiting from the novel multichannel structure and the relatively higher density of SeS<sub>2</sub>, the active material content of pPAN/SeS<sub>2</sub> reaches 63 wt %. Because of the better conductivity of SeS<sub>2</sub> than S, the electrochemical reaction kinetics of pPAN/SeS<sub>2</sub> are remarkably boosted. As a result, the Li-SeS<sub>2</sub> battery based on the pPAN/SeS<sub>2</sub> cathode delivers high capacity, excellent C-rate property, and extremely stable cycle life over 2000 cycles. When applied in a room temperature Na-SeS<sub>2</sub> (RT Na-SeS<sub>2</sub>) battery, the pPAN/SeS<sub>2</sub> cathode shows superior capacity

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of  $>900 \text{ mAh g}^{-1}$  at a current density of  $0.1 \text{ A g}^{-1}$  and delivers prolonged cycle life over 400 cycles.

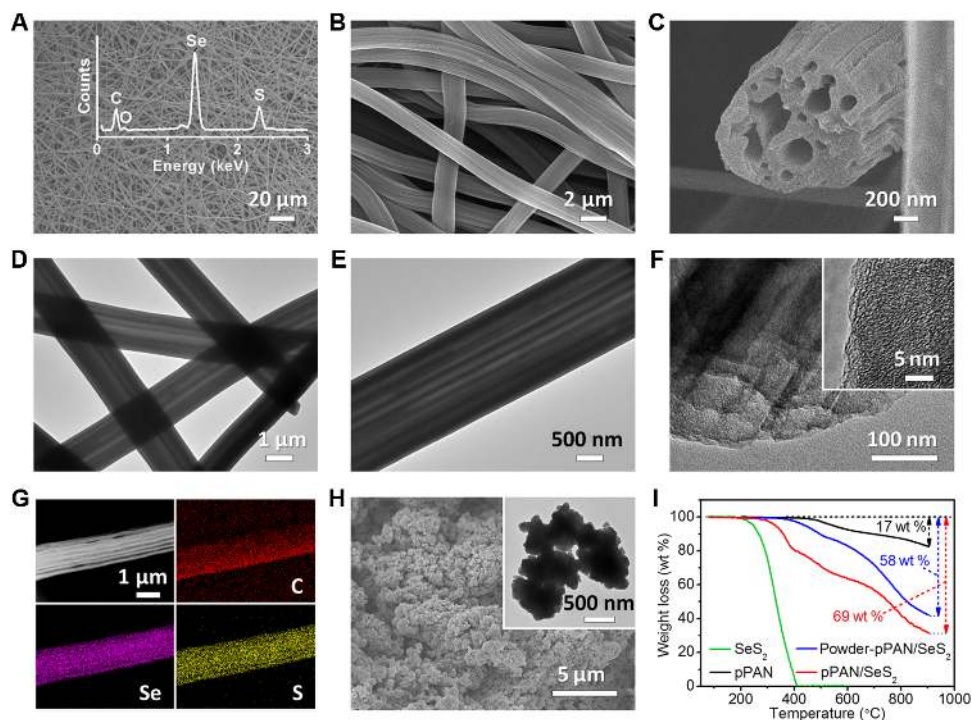
## RESULTS

### Materials synthesis and characterization

The pPAN/Se<sub>2</sub> composite cathode is prepared by a facile strategy, which involves a simple heating treatment of the mixture of the PAN/PS fibers and commercial Se<sub>2</sub> powder (fig. S1). The precursor of PAN/PS fibers was prepared by an electrospinning method reported by our group elsewhere (42). During the heating process, PAN reacts with gasified Se<sub>2</sub>, and the PS component would decompose and generate a series of paralleled channels inside the composite fibers. The as-prepared pPAN/Se<sub>2</sub> product well maintains the one-dimensional (1D) morphology with large aspect ratio, and the diameters of the fibers are in the range of 1.4 to 2  $\mu\text{m}$  (Fig. 1, A and B). A cross-section image directly shows the unique multichannel structure of pPAN/Se<sub>2</sub> (Fig. 1C). The highly paralleled channels are uniformly running through every pPAN/Se<sub>2</sub> fiber (Fig. 1, D and E). Compared to solid particles, the hollow channels inside pPAN/Se<sub>2</sub> will be beneficial for better infiltration of electrolyte and then achieve superior ion conductivity accordingly. No additional Se<sub>2</sub> particles can be observed on the surface or inside the channels of the pPAN framework, and the pPAN/Se<sub>2</sub> composite shows an amorphous phase without any crystal lattice image in its structure (Fig. 1F). These observations indicate that Se<sub>2</sub> is well composed with pPAN after the heat treatment. Elemental mappings further confirm that Se and S are uniformly distributed within the pPAN framework (Fig. 1G and fig. S2). The compact density of the pPAN/Se<sub>2</sub> composite is measured to be  $0.78 \text{ g cm}^{-3}$ . To verify the structural advantage of the multichannel design for increasing the SeSe<sub>2</sub> content, a

control sample of powder-pPAN/Se<sub>2</sub> is prepared (Fig. 1H). Thermogravimetric analysis (TGA) results show that these multichannel pPAN/Se<sub>2</sub> fibers can be loaded with 63 wt % of SeSe<sub>2</sub> within the framework, which is obviously higher than that of the powder-pPAN/Se<sub>2</sub> composite (49 wt %) (Fig. 1I). It is proposed that, compared to solid particles, the multichannel framework can provide more surface area of PAN to directly contact and fully react with SeSe<sub>2</sub> (fig. S3). In addition, there might be some small pores generated by PS (42), which can firmly trap part of SeSe<sub>2</sub> even after an additional treatment at 300°C for 4 hours in flowing N<sub>2</sub> atmosphere. Another two samples of pPAN/S and pPAN/Se are prepared by the same method as control groups. The morphologies of these two control samples are the same with pPAN/Se<sub>2</sub> (fig. S4), and the mass ratios of S and Se in pPAN/S and pPAN/Se are 52 and 65 wt %, respectively (fig. S5). The differences on active material contents are mainly caused by the different molar mass of S, SeSe<sub>2</sub>, and Se. When the same molar quantity of S, SeSe<sub>2</sub>, and Se molecules is bonded onto the polymer backbones, the heavier element might gain higher mass loading content in the final composite. It is noteworthy that the SeSe<sub>2</sub> content of multichannel pPAN/Se<sub>2</sub> is higher than previously reported similar composites (19, 43), which further confirms the structural and componential advantages of our design for increasing the active material ratio (fig. S6).

After the heat treatment, the derived pPAN/Se<sub>2</sub> shows an amorphous phase without any signal of pristine SeSe<sub>2</sub> (Fig. 2A), which is consistent with the high-resolution TEM observation. Fourier transform infrared (FTIR) spectra show the changes of organic functional groups from PAN to pPAN/Se<sub>2</sub> (Fig. 2, B and C). After reacting with SeSe<sub>2</sub> at an elevated temperature (380°C), the  $-\text{CH}$ ,  $-\text{CH}_2$ , and  $-\text{CN}$  groups on PAN vanish, while some new bonds/groups of  $\text{C}=\text{C}$  ( $1485 \text{ cm}^{-1}$ ),  $-\text{CH}$  ( $1356 \text{ cm}^{-1}$ ), and cyclic structure ( $1436$  and  $802 \text{ cm}^{-1}$ ) emerge,



**Fig. 1. Morphology and structure characterizations of pPAN/Se<sub>2</sub>.** (A to C) Scanning electron microscopy (SEM) images, (D to F) transmission electron microscopy (TEM) images, (G) dark-field TEM image, and corresponding elemental mappings of pPAN/Se<sub>2</sub>. (H) SEM and TEM images of powder-pPAN/Se<sub>2</sub>. (I) TGA curves of Se<sub>2</sub>, pPAN, pPAN/Se<sub>2</sub>, and powder-pPAN/Se<sub>2</sub>. Inset of (A) shows the energy-dispersive x-ray (EDX) plot of pPAN/Se<sub>2</sub>.

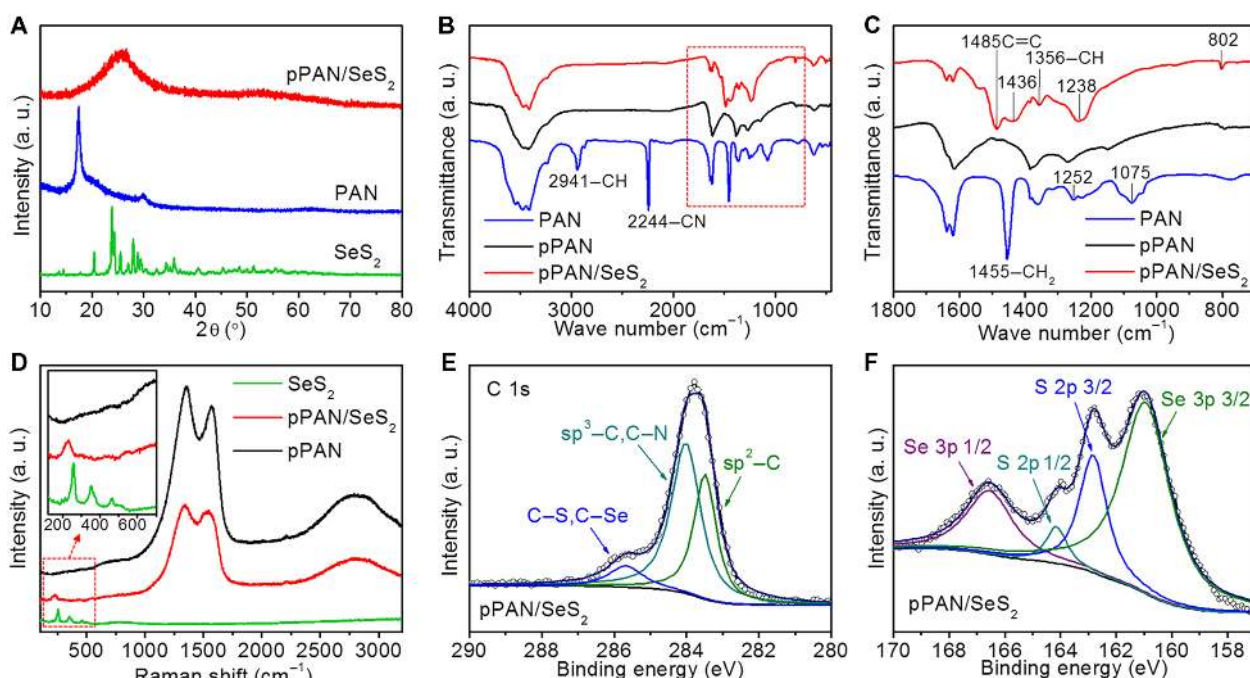
indicating the formation of heterocyclic compounds during the dehydrogenation reaction with  $\text{SeS}_2$  (23, 44). During this dehydrogenation process, Se-S chains are chemically bonded to the polymer backbones simultaneously. Raman spectra are collected to further determine the structure of  $\text{SeS}_2$  in the composite (Fig. 2D). After composing with PAN, three characteristic peaks of bare  $\text{SeS}_2$  are replaced with one peak in pPAN/ $\text{SeS}_2$ , and its position shifts to  $228\text{ cm}^{-1}$ . This suggests that the ring-structured  $\text{SeS}_2$  molecules have been transformed to chain-like  $\text{Se}_x\text{S}_y$  molecules, which is similar with the S chains covalently bonded onto the polymer backbones (23). XPS spectrum of C 1s reveals the chemical bonds between Se/S and C (Fig. 2E), and the spectrum of S 2p and Se 3p shows the strong interaction between Se and S (Fig. 2F), reflecting that Se and S are bonded simultaneously in the chain-like Se-S molecules (43, 45).

### The electrochemical performances

To show the differences on electrochemical behaviors of pPAN/ $\text{SeS}_2$ , pPAN/S, and pPAN/Se, coin cells of three samples are prepared in the same way using Li metal as the anode. By comparing the electrochemical impedance spectroscopy (EIS) plots of three samples, it can be seen that the conductivity of the active material has direct effects on the interfacial resistance of the derived electrode films (fig. S7). Compared to pPAN/S, pPAN/ $\text{SeS}_2$  shows obviously reduced interfacial resistance of the electrode. Figure 3A compares the typical galvanostatic discharge-charge voltage profiles at  $0.5\text{ A g}^{-1}$ . The pPAN/ $\text{SeS}_2$  cathode delivers a specific capacity of  $1031\text{ mAh g}^{-1}$  and an average discharge voltage plateau of  $1.76\text{ V}$  at 50% depth of discharge, both of which are higher than that of the pPAN/S and pPAN/Se cathodes. Although the theoretical capacity of S ( $1672\text{ mAh g}^{-1}$ ) is higher than that of  $\text{SeS}_2$  ( $1123\text{ mAh g}^{-1}$ ), the insulating nature of S greatly affects the reaction kinetics of the pPAN/S cathode, which increases the polarization during the redox reaction and limits the capacity utilization.

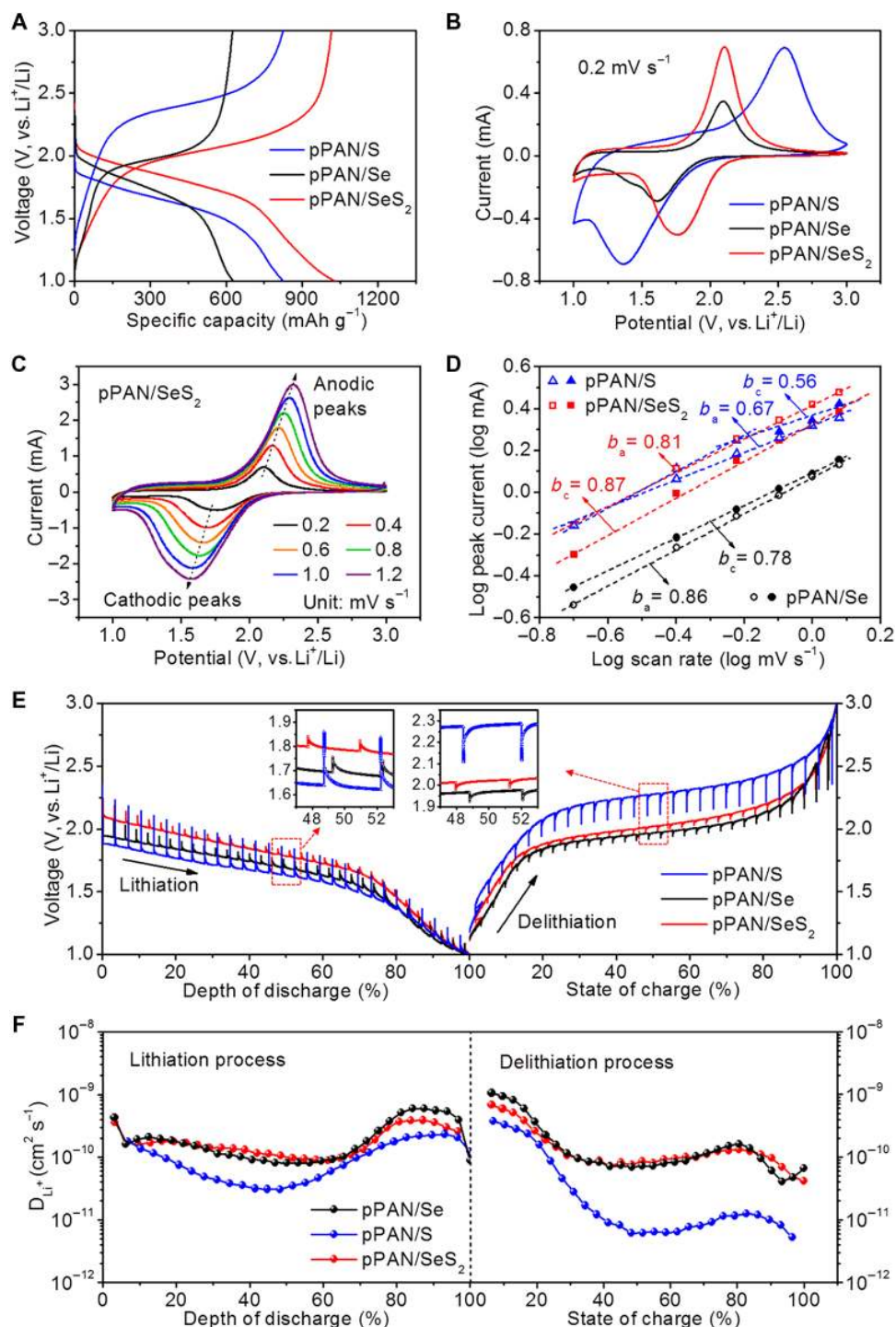
Because of the good conductivity of Se, the pPAN/Se electrode delivers a capacity of  $629\text{ mAh g}^{-1}$ , corresponding to an excellent utilization ratio (93%) to its theoretical capacity ( $678\text{ mAh g}^{-1}$ ). However, the pPAN/Se cathode provides the lowest energy density among all three cathodes because of its much lower capacity (fig. S8). The comparison of cyclic voltammetry (CV) curves at  $0.2\text{ mV s}^{-1}$  shows differences on the cathodic/anodic peak positions and areas, which indicates that pPAN/ $\text{SeS}_2$  has a better balance on reaction kinetics and capacity releasing compared to pPAN/S and pPAN/Se (Fig. 3B).

The reaction kinetics of pPAN/ $\text{SeS}_2$ , pPAN/S, and pPAN/Se is further analyzed based on CV measurements at various scan rates (Fig. 3C and fig. S9). The results show that, for all groups, both the peak current and the potential polarization increase with the scan rate. Because the current changes with respect to the sweep rate can be expressed as  $i = a \cdot v^b$  (where  $i$  is the peak current,  $v$  is the scan rate, and  $a$  and  $b$  are the adjustable constants), it is possible to mathematically analyze the reaction kinetics by comparing the  $b$  values of various groups (35, 46). The  $b$  values of pPAN/ $\text{SeS}_2$  in both cathodic ( $b_c$ ) and anodic ( $b_a$ ) processes are similar with pPAN/Se and much higher than that of pPAN/S, demonstrating that the introduction of Se can effectively improve reaction kinetics of the electrode material (Fig. 3D). The  $\text{Li}^+$ -ion diffusion coefficients of three groups are calculated via the galvanostatic intermittent titration technique (GITT) during discharge/charge processes (Fig. 3, E and F). The results show that the  $\text{Li}^+$ -ion diffusion coefficients of pPAN/ $\text{SeS}_2$  and pPAN/Se are nearly one order of magnitude higher than that of pPAN/S, which reveals that the  $\text{Li}^+$ -ion diffusion in the redox reactions is greatly improved benefiting from the presence of Se. On the basis of the above results, it can be concluded that, when a certain content of Se is introduced into the pPAN/S composite, both the electronic conductivity and the ionic diffusion efficiency in the cathode material can be effectively enhanced.



**Fig. 2. Characterizations of pPAN/ $\text{SeS}_2$  and the control samples.** (A) X-ray diffraction (XRD) patterns, (B and C) FTIR, and (D) Raman spectra of pPAN/ $\text{SeS}_2$  and the control samples ( $\text{SeS}_2$ , PAN, and pPAN). X-ray photoelectron spectroscopy (XPS) spectra of (E) C 1s and (F) S 2p/Se 3p for pPAN/ $\text{SeS}_2$ . a.u., arbitrary units.





**Fig. 3. Electrochemical evaluation of pPAN/SeS<sub>2</sub>, pPAN/S, and pPAN/Se.** Comparisons of (A) typical voltage profiles at 0.5 A g<sup>-1</sup>, and (B) CV curves at 0.2 mV s<sup>-1</sup> of pPAN/SeS<sub>2</sub>, pPAN/S, and pPAN/Se. (C) CV curves of pPAN/SeS<sub>2</sub> from 0.2 to 1.2 mV s<sup>-1</sup>. (D) Comparison of *b* values in the cathodic (*b<sub>c</sub>*) and anodic (*b<sub>a</sub>*) scans from 0.2 to 1.2 mV s<sup>-1</sup> of different groups. *b*-value determination based on logarithmic peak currents versus scan rate. Voltage profiles (E) and the Li-ion diffusion coefficients (F) of pPAN/SeS<sub>2</sub>, pPAN/S, and pPAN/Se obtained via the GITT technique during discharge/charge processes.

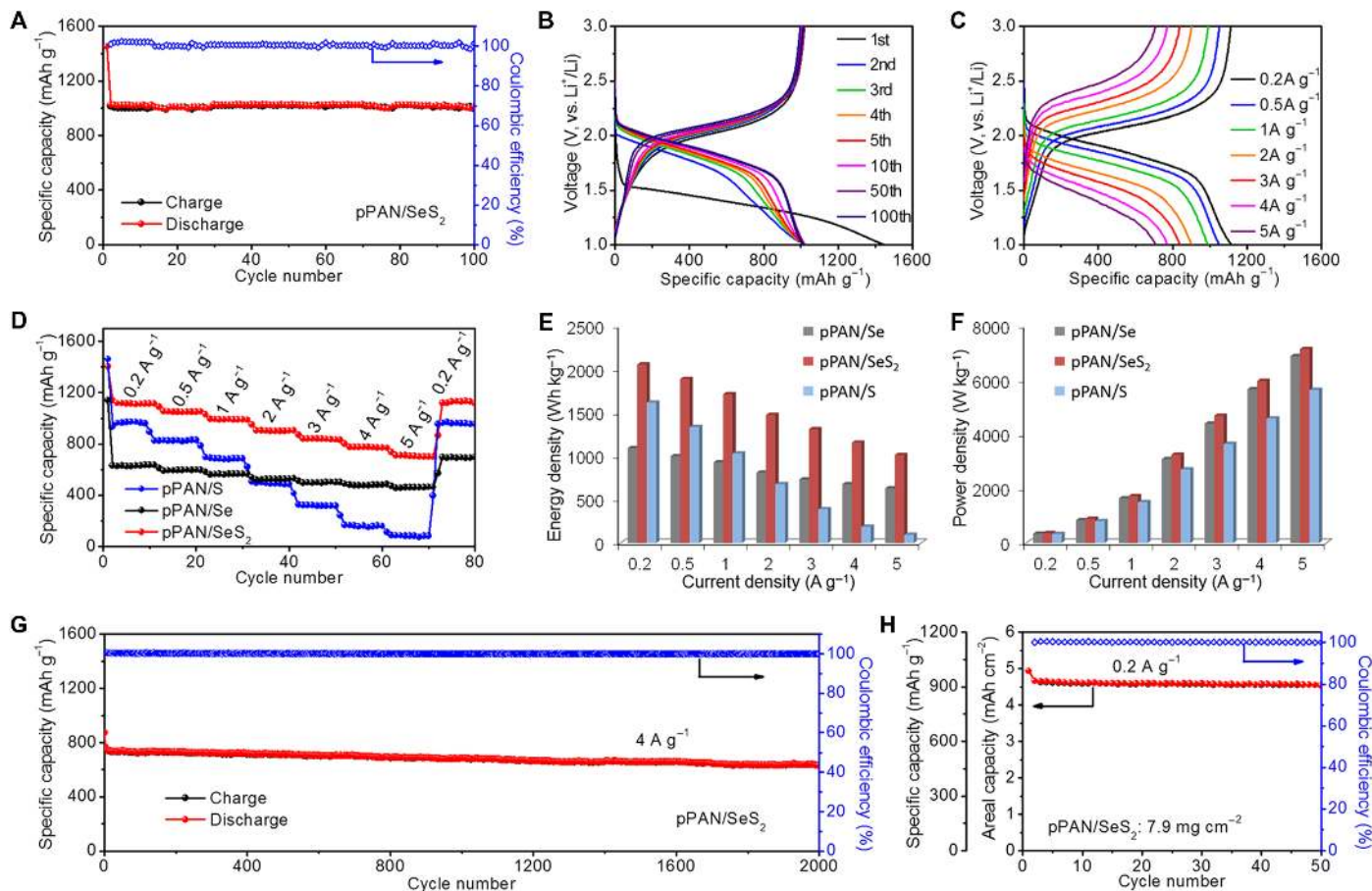
The pPAN/SeS<sub>2</sub> cathode exhibits superior cycling stability similar to as previously reported pPAN-supported S-based cathodes (9, 15, 21). When cycled at 0.5 A g<sup>-1</sup>, the pPAN/SeS<sub>2</sub> cathode delivers a capacity of 1451 mAh g<sup>-1</sup> in the initial discharge, and then the capacities stabilize

at around 1020 mAh g<sup>-1</sup> in subsequent cycles with Coulombic efficiency of nearly 100% (Fig. 4A). The lower discharge plateaus and the irreversible capacity in the first discharge are mainly caused by the reduction of electrolyte solvents on the fresh surface of electrode materials for the

formation of solid electrolyte interface (43, 47, 48). Although the released capacity is very stable even in the first 10 cycles, it is observed that the discharge voltage plateaus gradually increase with the cycle times, indicating that there is an electrochemical activation process in the cathode (Fig. 4B). Similar phenomena are also observed in the pPAN-supported Se or S-based cathodes in previous studies (44, 45). After that, the discharge plateaus are stabilized, and the typical voltage profiles of the 50th and 100th cycles are well matched with each other, demonstrating very good stability of the pPAN/SeS<sub>2</sub> cathode. The comparison of high-rate capabilities further supports the superiority of pPAN/SeS<sub>2</sub> over pPAN/S and pPAN/Se (Fig. 4, C and D). Upon cycling at current densities of 0.2, 0.5, 1, 2, 3, 4, and 5 A g<sup>-1</sup>, the pPAN/SeS<sub>2</sub> cathode delivers reversible capacities of 1117, 1053, 992, 904, 839, 774, and 709 mAh g<sup>-1</sup>, respectively (Fig. 4D). When the rate is reduced back to 0.2 A g<sup>-1</sup>, the capacity of pPAN/SeS<sub>2</sub> regains 1115 mAh g<sup>-1</sup>, indicating excellent electrochemical stability of the cathode material. In contrast, the pPAN/S cathode delivers lower discharge capacities at various current densities (fig. S10). When the current density is increased to 5 A g<sup>-1</sup>, the pPAN/S cathode only delivers a capacity of 85 mAh g<sup>-1</sup>, corresponding to a poor retention ratio of 9% versus the early capacity of 971 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup>. The relatively poor performance of pPAN/S compared to some previously reported pPAN/S composites might be caused by the higher S content (52 wt %),

which may easily lead to a higher polarization and decrease the capacity utilization.

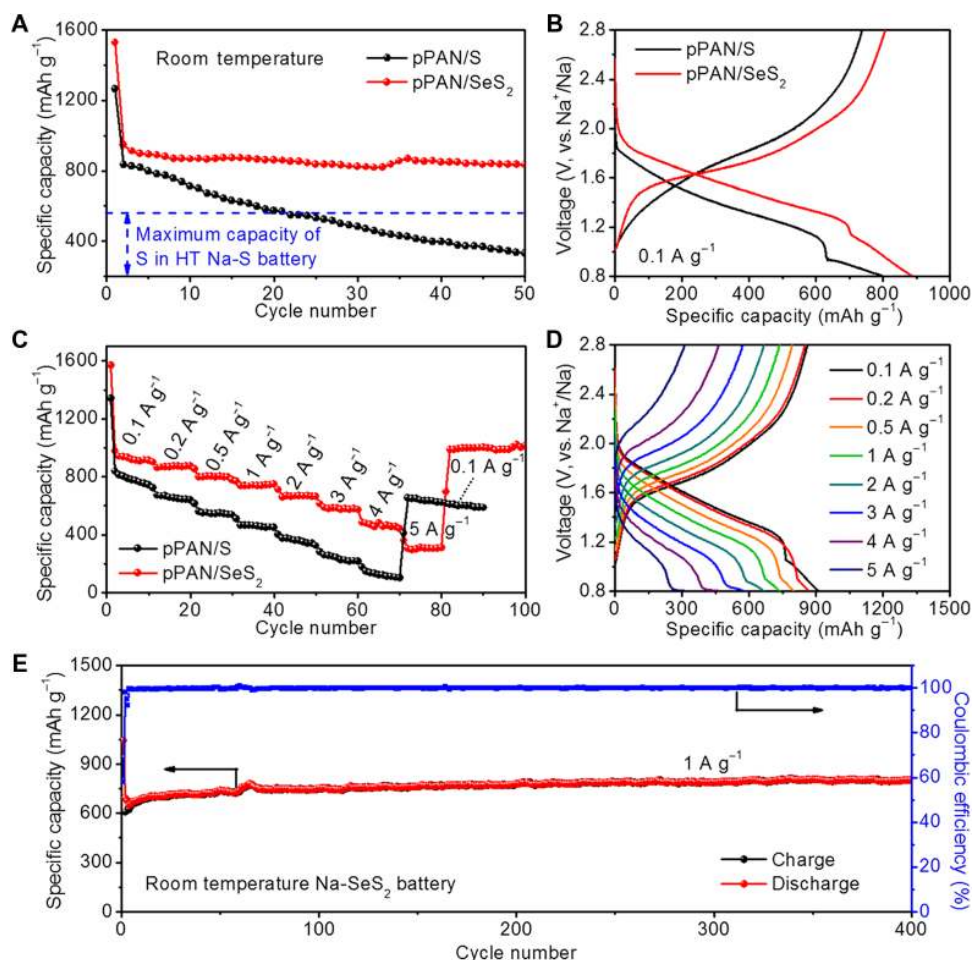
It is noted that pPAN/Se achieves the best capacity retention ratios in the C-rate tests among three groups (fig. S11), demonstrating that Se is a good constituent material for enhancing the reaction kinetics of the cathode materials. However, limited by the low theoretical capacity of Se, the specific capacities of pPAN/Se are much lower than those of pPAN/SeS<sub>2</sub>, which affect the gravimetric/power energy densities of the Li-Se battery (Fig. 4, E and F). Therefore, the pPAN/SeS<sub>2</sub> composite cathode might be a more rational choice for Li storage because it inherits advantages of both pPAN/Se and pPAN/S. Moreover, the pPAN/SeS<sub>2</sub> cathode promises extremely stable cycle life (Fig. 4G). After an activation process of three cycles at 0.2 A g<sup>-1</sup>, the pPAN/SeS<sub>2</sub> cathode is cycled at a higher current density for 2000 cycles. The pPAN/SeS<sub>2</sub> cathode delivers a capacity of 871 mAh g<sup>-1</sup> when first discharged at 4 A g<sup>-1</sup>, and it keeps a discharge capacity of 633 mAh g<sup>-1</sup> at the end of the test, corresponding to a very low capacity decay rate of 0.014% per cycle. To reveal the commercial application potential of pPAN/SeS<sub>2</sub>, a thick electrode with pPAN/SeS<sub>2</sub> loading of 7.9 mg cm<sup>-2</sup> is further evaluated (Fig. 4H). Over 50 cycles at 0.2 A g<sup>-1</sup>, the specific capacity of SeS<sub>2</sub> is remarkably stable at >900 mAh g<sup>-1</sup>, corresponding to a high areal capacity of >4.5 mA cm<sup>-2</sup>.



**Fig. 4. Electrochemical performance of Li-SeS<sub>2</sub> battery.** (A) Cycle property at 0.5 A g<sup>-1</sup>. (B) Voltage profiles during cycle test. (C) Voltage profiles at various current densities from 0.2 to 5 A g<sup>-1</sup> of pPAN/SeS<sub>2</sub>. Comparisons of (D) rate performance from 0.2 to 5 A g<sup>-1</sup>, (E) energy density, and (F) power density of pPAN/Se, pPAN/SeS<sub>2</sub>, and pPAN/S. (G) Prolonged cycle life at 4 A g<sup>-1</sup>, and (H) cycling property at 0.2 A g<sup>-1</sup> with high areal mass loading of pPAN/SeS<sub>2</sub> for Li storage.

Recently, the room temperature sodium-sulfur (RT Na-S) battery has attracted much attention in view of its tremendous potential for reducing the cost and improving the safety of traditional high-temperature Na-S battery systems (47, 49–52). However, because of the poor electronic and ionic conductivity of S and Na<sub>2</sub>S, the reaction kinetics of RT Na-S batteries could not be easily improved. It is still a big challenge to further enhance the capacity utilization of RT Na-S batteries. Here, because pPAN/SeS<sub>2</sub> shows much higher reactivity than pPAN/S for Li storage, it is thus anticipated that the pPAN/SeS<sub>2</sub> composite could give better Na-storage performance than previous S-based cathodes. When evaluated as a cathode material for Na storage, the CV curves and voltage profiles of pPAN/SeS<sub>2</sub> show very similar electrochemical features with the Li-SeS<sub>2</sub> battery (fig. S12). After an initial activation, the RT Na-SeS<sub>2</sub> battery shows two discharging plateaus in voltage ranges of 2.8 to 1.2 and 1.2 to 0.8 V. The lower-voltage plateaus may be caused by a stepped reduction reaction between SeS<sub>2</sub> and Na (35, 37, 47). Figure 5A shows the comparison of cycling properties between pPAN/SeS<sub>2</sub> and pPAN/S for Na storage. By using pPAN/SeS<sub>2</sub> as the cathode, the RT Na-SeS<sub>2</sub> battery delivers a high capacity of 1530 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> in the first discharge, and then its capacity stabilizes at 944 mAh g<sup>-1</sup> at the second cycle. After 50 cycles, pPAN/SeS<sub>2</sub> still maintains a high capacity of 835 mAh g<sup>-1</sup>, which is much

higher than the specific capacity of S in high-temperature Na-S batteries (53). On the contrary, although pPAN/S gains a high initial capacity of 1264 mAh g<sup>-1</sup>, the capacity decreases rapidly to 331 mAh g<sup>-1</sup> after 50 cycles. Moreover, the average discharge plateau of pPAN/SeS<sub>2</sub> is obviously higher than that of pPAN/S (Fig. 5B), demonstrating that the pPAN/SeS<sub>2</sub> cathode is beneficial to achieve a higher energy density than pPAN/S for Na storage. pPAN/SeS<sub>2</sub> exhibits excellent Na storage capabilities at various current densities. The RT Na-SeS<sub>2</sub> battery maintains a capacity of 938 mAh g<sup>-1</sup> at 0.1 A g<sup>-1</sup> and then delivers 869, 802, 736, 634, 583, 471, and 302 mAh g<sup>-1</sup> when the current density is successively increased from 0.2 to 0.5, 1, 2, 3, 4, and 5 A g<sup>-1</sup>, respectively (Fig. 5, C and D). For the RT Na-S battery, the pPAN/S cathode shows a reversible capacity of 813 mAh g<sup>-1</sup> when first cycled at 0.1 A g<sup>-1</sup>. Subsequent cycling at different current densities from 0.2 to 4 A g<sup>-1</sup> reveals that the rate capabilities of pPAN/S are inferior to those of pPAN/SeS<sub>2</sub>. When the current density is abruptly turned back to 0.1 A g<sup>-1</sup> from 4 A g<sup>-1</sup>, the pPAN/SeS<sub>2</sub> cathode recovers all of the original capacity, indicating the superior robustness and reversibility of the electrode. Prolonged cycle life of the RT Na-SeS<sub>2</sub> battery is evaluated under 1 A g<sup>-1</sup> (Fig. 5E). The pPAN/SeS<sub>2</sub> cathode delivers a high initial capacity of 1043 mAh g<sup>-1</sup> and maintains a reversible capacity of 800 mAh g<sup>-1</sup> after 400 cycles, indicating an extremely stable cycle life. Compared



**Fig. 5. Electrochemical performance of RT Na-SeS<sub>2</sub> battery.** Comparisons of (A) cycle stabilities at 0.1 A g<sup>-1</sup>, (B) typical voltage profiles, (C) and rate performances between pPAN/S and pPAN/SeS<sub>2</sub>. (D) Voltage profiles at various current densities from 0.1 to 5 A g<sup>-1</sup>. (E) Prolonged cycle life of pPAN/SeS<sub>2</sub> for Na storage.

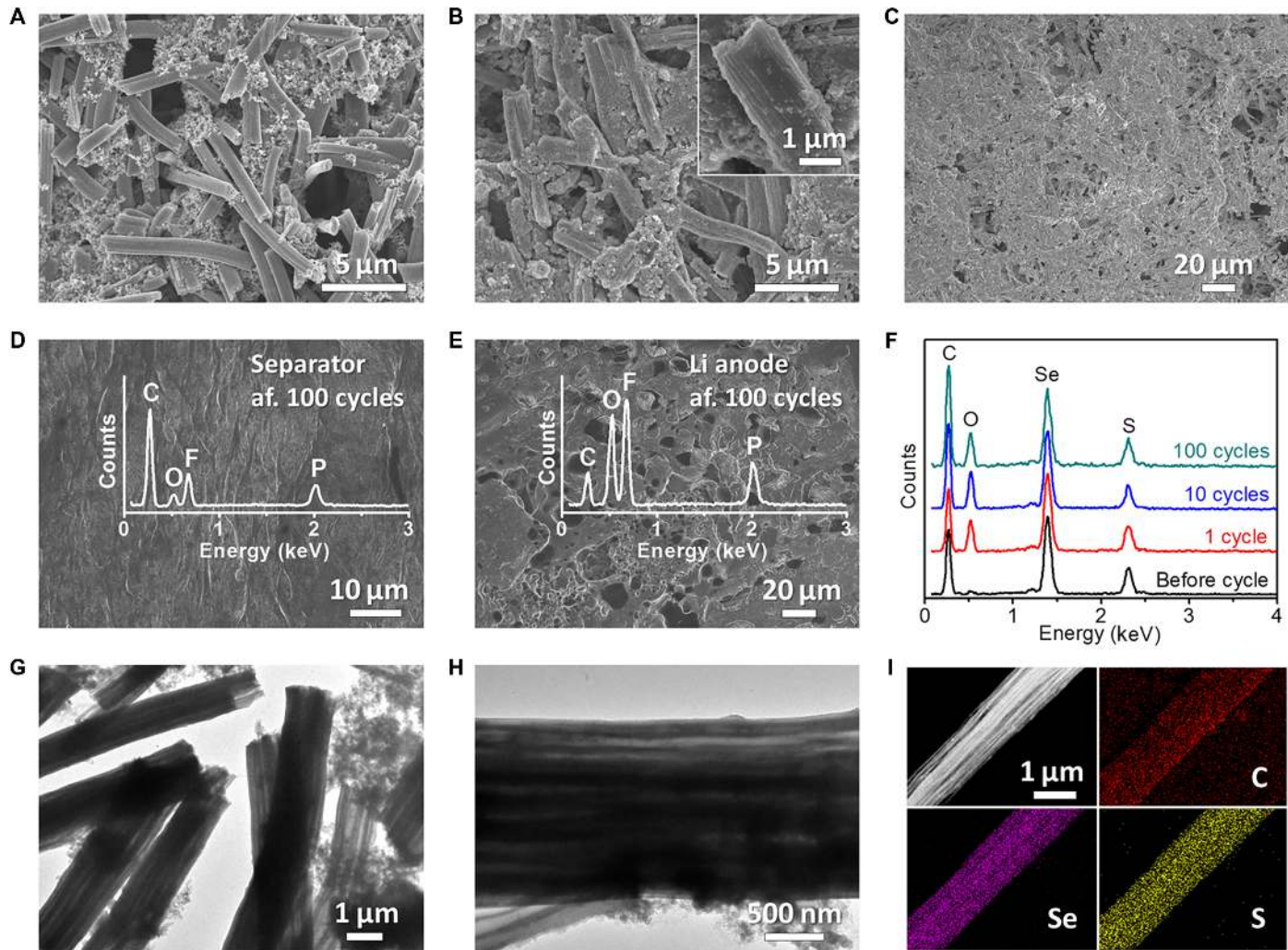


to previously reported RT Na-S batteries, our RT Na-SeS<sub>2</sub> battery shows significant advantages on both active materials content and overall capacities of the composite cathodes (fig. S13).

## DISCUSSION

Many spectroscopic characterizations have consistently identified that sulfur molecules in the sulfurized PAN exist in the form of short -S<sub>x</sub>- chains covalently bonded to the cyclized and dehydrogenated PAN backbones through C-S bonds (21, 23, 24). It can be speculated that, in the pPAN/SeS<sub>2</sub> composite, there might be short -Se<sub>x</sub>S<sub>y</sub>- chains covalently bonded to PAN backbones through C-S and/or C-Se bonds. Because the mole fraction of Se is as high as one-third, it is highly possible that Se may be present in every active short chain. Because of the excellent reaction kinetics of Se, the presence of Se in the short -Se<sub>x</sub>S<sub>y</sub>- chains will greatly enhance the reactivity of the electrode material. Thus, the diffusivity and voltage profile of pPAN/SeS<sub>2</sub> are akin to the pure Se-based pPAN/Se cathode rather than pPAN/S.

To reveal the structural and chemical stability of pPAN/SeS<sub>2</sub>, the Li-SeS<sub>2</sub> coin cells have been disassembled for further characterization. After cycling for 100 cycles, the pPAN/SeS<sub>2</sub> electrode film maintains similar morphology with the fresh electrode film (Fig. 6, A and B), and the cathode material is still strongly adhered on the current collector without any visible cracking (Fig. 6C), proving that the electrode film is robust enough to endure the electrochemical tests. The separator disassembled from the cycled coin cell well maintains its original morphology, and the porous structure can be observed as before (Fig. 6D), while the surface of the Li metal anode becomes rough because of many cycles of Li plating/stripping (Fig. 6E). Besides the morphological observations, it is more remarkable that no Se or S can be detected on the surfaces of both the separator and the Li metal anode (insets of Fig. 6, D and E), which implies that the dissolution of polysulfides/polyselenides is completely avoided in the pPAN/SeS<sub>2</sub>-based battery system. Meanwhile, the EDX results show that the chemical compositions of the pPAN/SeS<sub>2</sub> electrode films are almost the same with each other during the cycling process (Fig. 6F), thus directly confirming the good chemical stability of pPAN/SeS<sub>2</sub>.



**Fig. 6. Characterizations of pPAN/SeS<sub>2</sub> after cycling tests.** SEM images of (A) fresh and (B and C) 100 times cycled pPAN/SeS<sub>2</sub> electrode films. SEM images of (D) separator and (E) Li anode disassembled from the pPAN/SeS<sub>2</sub> cells after 100 cycles. Insets of (D), (E), and (F) are EDX plots of separator, Li anode, and cathode films, respectively. (G and H) TEM images and (I) elemental mappings of pPAN/SeS<sub>2</sub> after 100 cycles for Li storage.



In addition, the 1D morphology of the pPAN/SeS<sub>2</sub> fibers is well preserved (Fig. 6G), and the internal channels can still be observed (Fig. 6H), revealing the robust and reliable feature of the multichannel structure. The elemental mappings show the uniform distributions of Se and S in the pPAN polymer backbones (Fig. 6I), further confirming the good chemical stability of pPAN/SeS<sub>2</sub>.

In summary, pPAN/SeS<sub>2</sub> fibers with the multichannel structure have been designed and prepared by a facile method. This nanocomposite successfully inherits advantages of both pPAN/S and pPAN/Se and avoids their drawbacks. The active material content of the pPAN-supported composites has been elevated to a new level. When applied as cathode materials for Li and Na storage, pPAN/SeS<sub>2</sub> fibers show excellent reaction kinetics, high capacity utilizations, robust material structure, and remarkable electrochemical stability. Besides, it should be pointed out that although the molar ratio of Se/S (1:2) has given a much better balance on reaction kinetics and capacity than bare S and Se, there might be more space for optimizing the S-to-Se ratio for gaining specific cost/performance balance for different applications. It is thus believed that the composite cathode material reported here might have a great potential for building better batteries beyond traditional lithium ion batteries.

## MATERIALS AND METHODS

### Synthesis

One gram of PAN and 0.8 g of polystyrene (PS) were dissolved in 10 ml of *N,N*-dimethylformamide with vigorous stirring at 60°C overnight. Then, the PAN/PS composite nanofibers were prepared by the electrospinning method. A high voltage of 17 kV was applied with a flow rate of 1 ml h<sup>-1</sup>, and the distance between the syringe and the collector was 15 cm. Then, the derived PAN/PS fibers and the commercial SeS<sub>2</sub> powder (1:4, w/w) were sealed in a glass vessel and heated at 380°C for 8 hours in N<sub>2</sub> atmosphere. To remove extra SeS<sub>2</sub>, the sample was put in a porcelain boat and heated at 300°C for 4 hours in flowing N<sub>2</sub> atmosphere. After the temperature is decreased below 50°C, pPAN/SeS<sub>2</sub> was gained. Similarly, both pPAN/S and pPAN/Se were prepared by the same method, only using S or Se instead of SeS<sub>2</sub> for the reaction, respectively. A control sample of powder-pPAN/SeS<sub>2</sub> was prepared by heating the mixture of commercial PAN powder and SeS<sub>2</sub> in a sealed glass vessel at 380°C for 8 hours in N<sub>2</sub> atmosphere, and then the product was put in a porcelain boat and heated at 300°C for 4 hours in a flowing N<sub>2</sub> atmosphere. The pure pPAN was prepared by heating PAN/PS at 380°C for 8 hours in an N<sub>2</sub> atmosphere.

### Materials characterization

SEM (JEOL-6700F) and TEM (JEOL, JEM-2010) were used to characterize the morphologies and structures of the samples. Elemental mappings were recorded by EDX spectroscopy attached to TEM (JEOL, JEM-2100F). Compositions of electrode films, separator, and Li anode were measured by EDX spectroscopy attached to the SEM instrument. The XRD patterns were measured by a Bruker D2 phaser (Cu K $\alpha$  radiation  $\lambda = 1.5406 \text{ \AA}$ ). Raman spectra were examined by a Renishaw System 1000 micro-Raman spectroscope with 514-nm excitation source. FTIR spectra were collected with Bruker MPA NearIR. Active material contents were determined by TGA (Shimadzu DRG-60) in N<sub>2</sub> flow. XPS was carried out on a Thermo Fisher Scientific ESCALAB 250Xi. The nitrogen sorption isotherms were collected by a Quantachrome Autosorb AS-6B system at liquid-nitrogen temperature. To determine the compact density of the material, pPAN/SeS<sub>2</sub> was pressed into pellets

at 10 MPa, and then the compact density was calculated based on the mass and volume of the pellets.

### Electrochemical measurements

The electrode film of pPAN/SeS<sub>2</sub> was prepared by mixing pPAN/SeS<sub>2</sub>, Super-P, carboxymethylcellulose, and styrene butadiene rubber with a mass ratio of 8:1:0.5:0.5 in deionized water, and then the slurry was casted on the Al foil and dried at 70°C overnight. The areal mass loading of pPAN/SeS<sub>2</sub> was around 2.0 mg cm<sup>-2</sup>. High-mass loading electrode films were prepared by coating the same slurry on carbon papers. CR2032 coin cells were assembled in an Ar-filled glove box. For Li-SeS<sub>2</sub> batteries, Li metal was applied as the anode, and Celgard 2400 membrane was applied as the separator. The electrolyte was 1.0 M LiPF<sub>6</sub> in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v). The SeS<sub>2</sub>/electrolyte ratio is around 1 mg/50  $\mu$ l. For RT Na-SeS<sub>2</sub> batteries, Na metal was applied as the anode and Whatman glass fiber membrane as the separator. The electrolyte was 1.0 M NaClO<sub>4</sub> in EC and DMC (1:1, v/v) with 5 wt % fluoroethylene carbonate. The control cells of pPAN/S and pPAN/Se were prepared by the same method. The CV plots were recorded on an electrochemical workstation (CHI614b). Galvanostatic discharge-charge tests were measured on a Land battery measurement system (China). GITT was performed by discharging the cells for 10 min at  $1/30$  C based on the stabilized capacity followed by a 5-min relaxation. For all electrochemical tests, the voltage range of Li-SeS<sub>2</sub> batteries is between 3.0 and 1.0 V versus Li/Li<sup>+</sup>, while for RT Na-SeS<sub>2</sub> batteries the voltage range is 2.8 to 0.8 V versus Na/Na<sup>+</sup>. The high loading Li-SeS<sub>2</sub> batteries were first cycled two times at 0.05 A g<sup>-1</sup> for activation and then cycled at 0.2 A g<sup>-1</sup>. The specific capacities and current densities of all cells were calculated based on the mass of SeS<sub>2</sub>, S, or Se. The Nyquist plots were obtained at 5-mV ac oscillation amplitude from 100 kHz to 1 Hz.

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/6/eaat1687/DC1>

- fig. S1. Schematic illustrations of the chemical structure and synthesis method.
- fig. S2. EDX mappings of pPAN/SeS<sub>2</sub>.
- fig. S3. N<sub>2</sub> sorption isotherms of multichannel pPAN/SeS<sub>2</sub> fibers and pPAN/SeS<sub>2</sub> powder.
- fig. S4. Morphology characterizations.
- fig. S5. TGA curves of pPAN/S and pPAN/Se.
- fig. S6. The active material contents of various PAN-supported or microporous carbon-supported composites for Li-S or Li-Se/S batteries.
- fig. S7. EIS of pPAN/S, pPAN/SeS<sub>2</sub>, and pPAN/Se.
- fig. S8. Comparisons of capacity utilization and energy density for Li storage.
- fig. S9. CV curves from 0.2 to 1.2 mV s<sup>-1</sup>.
- fig. S10. Rate performances.
- fig. S11. Comparison of normalized capacities.
- fig. S12. CV curves and voltage profiles of pPAN/SeS<sub>2</sub> for Na storage.
- fig. S13. Comparisons of RT Na-S and Na-Se/S batteries.

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