

Sulfurized Polyacrylonitrile Impregnated Delignified Wood-Based 3D Carbon Framework for High-Performance Lithium–Sulfur Batteries

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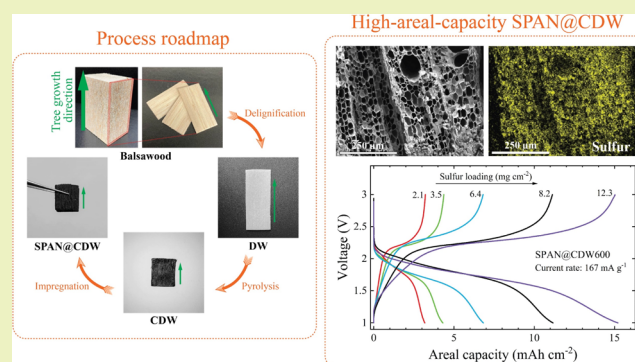
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ABSTRACT: Sulfurized polyacrylonitrile (SPAN) is a promising cathode active material capable of suppressing lithium polysulfide dissolution in lithium–sulfur (Li–S) batteries. However, due to the low S content in SPAN, achieving a high SPAN areal loading without compromising specific capacity and cycling stability would be required. To address this challenge, we took advantage of the inherent porous structure of natural wood and engineered carbonized delignified wood (CDW) frameworks using a delignification/low-temperature pyrolysis approach. The unique design of the SPAN-impregnated CDW (SPAN@CDW) electrode, wherein the interconnected pathways run in three dimensions, ensures effective electron and ion transport within the electrode. Biomass-derived SPAN@CDW cathodes exhibited an excellent rate capability compared to the popular synthetic 3D scaffolds, such as graphene foam cathodes, with discharge capacities >1000 mA h g_s^{-1} at 1 C (1672 mA g_s^{-1}). Electrodes with CDW pyrolyzed at 600 °C, and a S areal loading of ~ 2 mg cm^{-2} exhibited a high specific capacity of ~ 1350 mA h g_s^{-1} after 500 cycles at 0.1 C, indicating good cycling stability. We also demonstrated the sustainable fabrication of SPAN@CDW electrodes with high SPAN loadings up to ~ 35 mg cm^{-2} , which could deliver a high areal capacity of ~ 15.1 mA h cm^{-2} at 0.1 C.

KEYWORDS: sulfurized polyacrylonitrile, Li–S batteries, natural wood, delignification, low-temperature pyrolysis, CDW framework, biomass



INTRODUCTION

Strong interest in renewable energy, electric vehicles, and portable electronics has led researchers to develop environmentally friendly, safe, and high-energy-density energy storage devices. The lithium–sulfur (Li–S) battery is one of the most promising rechargeable battery systems due to its high theoretical specific capacity (1672 mA h g^{-1}), high theoretical specific energy (2567 W h kg^{-1}), and abundant availability of sulfur.^{1–3} However, several challenges have hindered the optimization of Li–S batteries. Due to the poor conductivity of S, a significant internal resistance leads to high cell polarization and limits S utilization.⁴ Significant volume change of S during the cycling process also causes mechanical cracking and poor electrical connectivity with the conductive substrate and electrode.⁵ Moreover, the uncontrolled growth of dendrites due to the uneven deposition of Li^+ ions on the surface of Li anodes causes detrimental effects such as the evolution of dead Li and the formation of unstable solid–electrolyte interphase (SEI) layer, increased polarization, and safety concerns for the Li–S batteries.^{6–9} Last, the shuttle effect caused by the

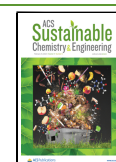
dissolution of intermediate Li polysulfides in the electrolyte leads to irreversible S loss and, thus, a lower discharge capacity and Coulombic efficiency (CE).^{10–12}

To date, researchers have employed various approaches to alleviating these challenges, including but not limited to (i) utilizing carbon additives and conductive polymers for improving electrical conductivity,^{13,14} (ii) designing three-dimensional (3D) cathode architectures for accommodating volume changes,^{15–17} (iii) optimizing the electrolyte composition for controlling dendrite growth and stabilizing the SEI layer,^{18,19} and (iv) encapsulating S particles in conductive polymers, hollow particles, activated carbons, carbon nanotubes/nanofibers, graphene, or other 3D porous media for

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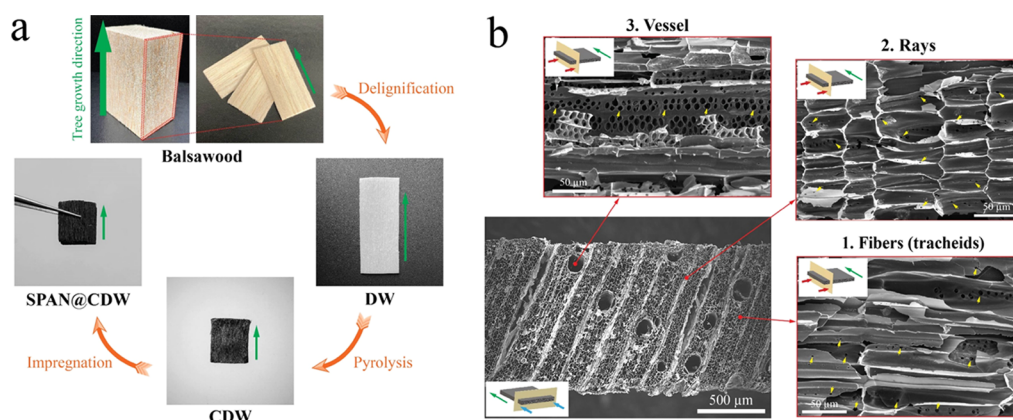


Figure 1. (a) Process roadmap for freestanding SPAN@CDW electrodes from natural wood. This work used one block to minimize the effect of variations in density and cellular geometry. Balsa wood was sliced into thin sheets parallel to the tree's growth direction (green arrow), delignified, pyrolyzed, and impregnated with a SPAN slurry under vacuum. (b) Transverse cross-sectional view of a CDW scaffold and higher-magnification radial images of major structural features showing high porosity (yellow arrows).

boosting the cycle life of Li–S batteries.^{20–25} Sulfurized polyacrylonitrile (SPAN) is an alternative sulfur cathode material for practical applications in Li–S batteries because of its ability to mitigate the shuttle of high-order lithium polysulfides in comparison with elemental sulfur cathodes.²⁶ Since its development by Wang et al.,²⁷ SPAN has attracted considerable attention because of its high active material utilization (with almost 100% CE), excellent reversibility and cycle stability, good compatibility with carbonate-based electrolytes, and adaptability to industrial manufacturing processes of current rechargeable batteries.^{28,29}

It has been proposed that the areal capacity of Li–S batteries must reach higher than 5 mA h cm^{-2} to compete with state-of-the-art lithium-ion batteries (LIBs).^{30,31} Assuming a S utilization of $\sim 60\%$ (corresponding to the specific capacity of $\sim 1000 \text{ mA h g}_s^{-1}$), this requirement translates to a S areal loading of 5 mg cm^{-2} . On the other hand, there is an upper limit of the mass percentage for S covalently bonded in SPAN ($\sim 44 \text{ wt } \%$).^{32–34} This is due to the inherent structure of PAN that restricts the supply of enough S storage sites for covalent bonding to the PAN backbone.³⁵ Thus, a SPAN areal loading of $>11 \text{ mg cm}^{-2}$ would be required for SPAN-based Li–S batteries to displace commercial LIBs. Achieving such a high SPAN areal loading on commercial metallic current collectors (e.g., aluminum foil) without compromising specific capacity and cycling stability is practically unrealistic, primarily due to restricted charge transfer and delamination/cracking of the coating layer in thick electrodes.³⁵ Through the use of synthetic materials (e.g., graphene foam,³⁶ graphene aerogel,³⁷ metal–organic framework³⁸), 3D electrode architectures with high SPAN loading and efficient electron- and ion-conductive pathways have been constructed. However, preparing these 3D electrodes mainly involves synthetic raw materials, which necessitate using toxic/harsh chemicals and a costly fabrication setup. As a result, synthetic 3D scaffolds cannot be considered sustainable and environmental-friendly sources for developing high-areal-capacity Li–S batteries. Porous carbon frameworks derived from biomass, which are often referred to as plant-based materials derived from nature, are alternative low-cost candidates for the sustainable fabrication of 3D electrodes. Biomass structures with interconnected channels over multiple length scales can provide a natural 3D template for electrochemical energy storage systems.³⁹

As widely abundant biomass, natural wood has a unique hierarchical cellular structure.⁴⁰ Multiphase transport occurs continuously in trees, with water transporting ions from the roots to the upper trunk and photosynthetic products from the leaves being distributed throughout the tree.⁴¹ Inspired by such an efficient transport system with interconnected pathways, we developed a current-collector-free, SPAN-impregnated cathode from natural balsa wood. To facilitate the permeation of active material into the cellular structure, we first subjected the wood to a facile chemical treatment to remove lignin and hemicellulose. The delignified wood (DW) was then converted to an ultra-lightweight carbonized DW (CDW) scaffold using a low-temperature pyrolysis approach. Continuous electron transport through the CDW conductive network and ion transport along the highly porous cellular body facilitated intrinsic and effective charge transfer through the CDW scaffold. By pyrolyzing the DW at 600°C and impregnating it with an equivalent S content of $\sim 2 \text{ mg cm}^{-2}$, the SPAN@CDW600 cathode exhibited a high reversible specific capacity of $\sim 1350 \text{ mA h g}_s^{-1}$ after 500 cycles at 0.1 C ($1 \text{ C} = 1672 \text{ mA g}_s^{-1}$). The well-maintained porous structure combined with oxygen-containing surface groups allowed the production of electrodes with high SPAN loadings (up to $\sim 35 \text{ mg}_{\text{SPAN}} \text{ cm}^{-2}$), which delivered a high areal capacity of $\sim 15.1 \text{ mA h cm}^{-2}$ at 0.1 C . Previous reports in which wood-based materials were used in Li–S batteries mainly focused on (i) high-temperature pyrolysis ($>900^\circ\text{C}$) to directly convert woods into carbon, (ii) modification of carbon framework through activation, surface treatment, or coating, and (iii) infusion of elemental S.^{42–44} In the current study, we prepared CDWs via a low-temperature pyrolysis method that conserves energy during electrode preparation. Moreover, our CDWs, when directly infiltrated with SPAN slurry without any prior surface modifications, enabled the best Li–S battery performance to date. Our SPAN@CDW electrodes with an equivalent S loading of 12.3 mg cm^{-2} exhibited an areal capacity of $\sim 15.1 \text{ mA h cm}^{-2}$ (at 167 mA g_s^{-1}), bringing Li–S batteries a step closer to lithium-ion batteries. Such a high areal capacity could only be realized in S@carbon electrodes with a S mass loading of 21.3 mg cm^{-2} .⁴⁴ This study suggests that the green, environmentally friendly, and low-cost CDW-based electrodes could open doors for high-areal capacity Li–S batteries for practical energy storage applications.

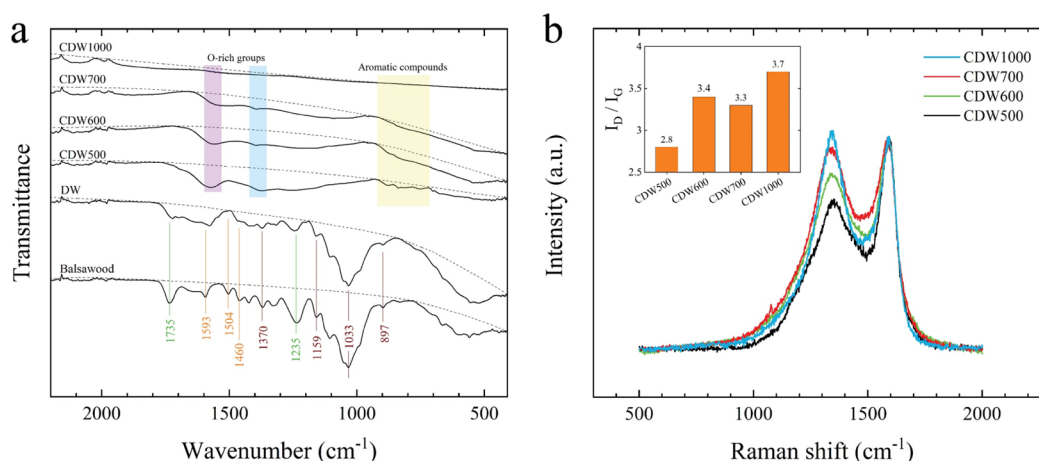


Figure 2. Evolution of chemical structure from wood to carbonaceous scaffold. (a) FTIR spectra of balsawood, DW, and various CDWs pyrolyzed at different temperatures. Peak assignments for lignin, hemicellulose, cellulose, aromatic compounds, and oxygen-containing groups are illustrated. (b) Raman spectra of all CDWs. The inset shows the area ratios of the D- and G-bands for CDWs.

RESULTS AND DISCUSSION

Three-Dimensional CDW. The process of preparation of the electrodes is shown in Figure 1a. First, a natural wood block was sliced into thin sheets (~1.5 mm thick) parallel to the tree growth direction (green arrows indicate this direction in Figure 1). To increase the porosity of the wood template and facilitate the permeation of active material into the wood cell structure, matrix substances such as lignin were fully or partially removed from wood slices using acidic sodium chlorite (NaClO₂) solution until they turned completely white. After freeze-drying, the delignified wood (DW) was pyrolyzed under an argon atmosphere to achieve CDW scaffolds. To conserve the energy consumed for the production of carbonaceous electrode components, we aimed to prepare CDW materials using a low-temperature pyrolysis approach and evaluate their suitability as 3D electrode frameworks. To this end, we pyrolyzed DWs at 500, 600, and 700 °C for 3 h. For comparison, a CDW material was prepared at a pyrolysis temperature of 1000 °C.

We performed a thorough microstructural study to reveal the effects of delignification and low-temperature pyrolysis on the CDW structure. The CDW scaffold was sectioned normal to the tree growth direction, and microstructural features of the transverse cross-section are presented in Figure 1b. Similar to the original balsawood,⁴⁵ the CDW's cellular structure (e.g., fibers, rays, and vessels) was largely retained. The fibers, known as tracheids, are long prismatic cells aligned axially along the tree's trunk. The cross-section of fibers is polygonal, and the average fiber diameter in the DW is ~25 μm (Figure S1). After pyrolysis, fibers maintain their original polygonal shape, and their average diameter decreases to ~20 μm. The average fiber size remains unchanged with pyrolysis temperature, possibly due to the physical constraints of adjacent cells. The rays, which are brick-like short cells, propagated radially from the central pith to the outer part of the trunk.⁴⁶ As shown in Figure 1b, rays propagate through the thickness of the CDW scaffold and could be potential structural features for conducting ions from the surface to the core. The cross-section of CDW also possesses several circular vessels with a large diameter (~120 μm on average). The vessels are embedded in the CDW frame parallel to the tree growth direction and, therefore, could facilitate the in-plane conduction of ions during electro-

chemical reactions. Numerous micron-sized open pits are present in the walls of fibers, rays, and vessels, which are marked with yellow arrows in Figure 1b. Balsawood contains numerous pits and pit membranes on the cell walls, connecting adjacent tracheids/rays/vessels for water absorption and transportation.⁴⁷ The delignification and pyrolysis treatments caused the pit membranes to open, thus providing additional paths for incorporating more active material into the scaffold. More importantly, Li⁺ ions could easily pass through these pits during the electrochemical cycling process, shortening their transmission path and significantly improving the electrochemical performance of CDW-based electrodes.

Fourier-transform infrared (FTIR) spectroscopy can reveal changes in the chemical structure during the evolution from natural wood to porous carbons. The FTIR spectra of balsawood, DW, and CDW scaffolds are shown in Figure 2. The IR spectra of balsawood and DW exhibit multiple characteristic peaks of cellulose, including peaks at 1370 cm⁻¹ for symmetric C–H deformation, 1159 cm⁻¹ for asymmetric C–O–C stretching, 1033 cm⁻¹ for C–O stretching, and 897 cm⁻¹ for glucose ring stretching. After delignification, the characteristic peaks of lignin (1593 and 1504 cm⁻¹ for aromatic skeletal vibrations and 1460 cm⁻¹ for asymmetric C–H deformation) diminish, confirming the lignin removal. The color change from light brown (for balsawood) to white (for DW) is another confirmation of lignin removal by the chemical treatment. Also, a significant intensity reduction in peaks at 1735 and 1235 cm⁻¹ for carbonyl stretching and C–O stretching in hemicellulose after delignification indicates partial removal of hemicellulose.^{48–52}

For carbonized scaffolds, a series of bands are detected over 900–700 cm⁻¹ due to the formation of aromatic carbon compounds. The intensity of bands decreases with pyrolysis temperature. The loss of spectral resolution with increasing pyrolysis temperature can be attributed to two causes. First, by increasing the pyrolysis temperature, the functional groups within aromatic compounds are lost as a result of dehydration or decarboxylation reactions.⁵³ Second, higher pyrolysis temperatures result in highly condensed aromatic structures, which lack normal mode vibrations.^{54,55} This loss of spectral resolution is particularly evident in the nearly flat-line spectrum obtained for the CDW1000 scaffold. The mass loss due to carbonization (Figure S2a) also shows a gradual increase with

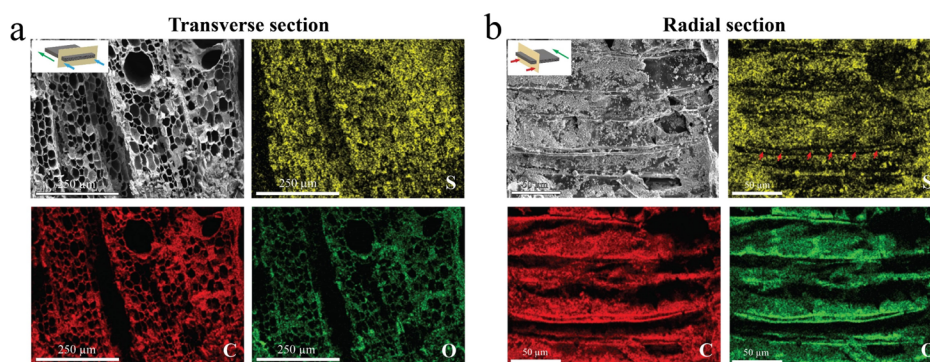


Figure 3. (a) Transverse and (b) radial images of a SPAN@CDW700 electrode with a S loading of 5.0 mg cm^{-2} , with corresponding EDS maps for S, C, and O. The effective infusion of SPAN into porous features of CDW700 and the excellent dispersion of SPAN along the fiber length are clear.

the pyrolysis temperature from 500 to 700 °C, and it then sharply increases when the DW is pyrolyzed at 1000 °C. The CDW scaffolds possess a low density of $50\text{--}85 \text{ mg cm}^{-3}$, compared with 155 mg cm^{-3} for the DW (Figure S2b). In the IR spectra of CDW500, CDW600, and CDW700, two new peaks in the $1580\text{--}1560 \text{ cm}^{-1}$ and $1400\text{--}1380 \text{ cm}^{-1}$ regions are detected, which correspond to asymmetric and symmetric stretching vibrations of the carboxylate (COO^-) group, respectively.⁵⁶ The appearance of these new peaks implies the existence of oxygen-containing groups (e.g., carboxylic acid salts) in CDWs caused by the delignification process. To verify this, we prepared CW700 (i.e., balsawood directly pyrolyzed at 700 °C without prior delignification) and evaluated its structural characteristics. As seen in Figure S3a, the IR spectrum of CW700 did not exhibit the two peaks related to the carboxylate group. In addition, energy-dispersive X-ray spectroscopy (EDS) elemental analysis revealed a higher oxygen content in CDW700 than in CW700 (Figure S3b). Furthermore, at the highest pyrolysis temperature of 1000 °C, the peaks corresponding to carboxylate disappear, suggesting the removal of functional groups from the surface of CDW1000. The thermogravimetric analysis (TGA) of CDWs also revealed the highest residue in CDW1000 (Figures S2c,d), confirming the IR observations related to removal of functional groups and the formation of highly condensed aromatic carbon structures in CDW1000. Therefore, our delignification/low-temperature pyrolysis approach can result in more oxygen-containing surface groups compared to direct or high-temperature pyrolysis of wood. It is reported that the oxygen-containing groups in carbonaceous electrodes can bond with sulfur species to improve the sulfur affinity/philicity of the electrode.⁵⁷ To check the affinity/philicity between SPAN (discussed below) and CDW, we prepared an aqueous slurry of SPAN without CMC binder and Super P additive and put both CDW600 and CDW1000 scaffolds under vacuum-assisted impregnation, followed by drying. Next, we washed the impregnated CDW600 and CDW1000 several times with DI water and dried them. We performed scanning electron microscopy (SEM)-EDS on both SPAN-impregnated CDW600 and CDW1000 scaffolds before and after washing, and the results are presented in Figure S4. After washing, we noticed that the relative amount of SPAN attached to the cell walls is greater for CDW600 than for CDW1000, implying stronger affinity between SPAN and the cell walls of CDW600. The lower amount of SPAN attached to the cell walls in CDW1000 is due to the combined effects of cell wall thinning (Figure S2f) and loss of O-rich functional groups (Figure 2a).

The carbonized scaffolds were also evaluated by Raman spectroscopy (Figure 2b). The two main bands typical of carbon are present: (1) the D-band (at $\sim 1350 \text{ cm}^{-1}$) corresponding to the disordered graphitic carbon and (2) the G-band (at $\sim 1575 \text{ cm}^{-1}$) corresponding to the in-plane stretching of the C–C bond and which is indicative of sp^2 -hybridized carbon. Highly conductive carbon species, such as defect-free carbon nanotubes and graphene, have indiscernible D-bands.^{58,59} The integrated intensity of the D- and G-bands (I_D/I_G) was calculated and is presented in Figure 2b (inset). The increase in the I_D/I_G ratio reflects the disordering of sp^2 -bonded graphitic domains.⁶⁰ Pyrolyzing at higher temperatures increases the I_D/I_G area ratio from 2.8 to 3.7, indicating an increase in the disordering of the graphite-like carbon lattice. According to microscopy studies, the average fiber diameter in all CDWs remained unchanged ($\sim 20 \text{ }\mu\text{m}$, as shown in Figure S1f), but the cellular morphology became more distorted after pyrolysis at high temperatures (Figure S1e). Besides, a significant cell wall thinning was observed by increasing the pyrolysis temperature from 500 to 1000 °C (Figures S2e,f). The thinning of cell walls and the distortion of the cellular structure due to higher pyrolysis temperatures indicate the existence of internal stresses in the CDW skeleton. Higher internal stress would directly affect the disordering of carbon lattice, leading to a higher I_D/I_G ratio.

SPAN@CDW Electrodes. SPAN active material was prepared by following our previous study.³⁶ In short, the elemental sulfur and polyacrylonitrile (PAN) were mixed in the ratio of 3:1 and annealed together to form the black SPAN powder with a sulfur content of 34.8 wt % (Figure S5a). The diameter of SPAN particles was in the range of 100–180 nm and displayed a normal distribution (Figure S5b,c). To fabricate freestanding CDW-based electrodes, CDWs with a thickness of 0.8–1.0 mm were cut into square pieces ($1.00 \pm 0.05 \text{ cm}^2$) and impregnated by the SPAN slurry under vacuum (Figure 1a). The vacuum facilitates the permeation of slurry into the CDW pores. The SPAN-impregnated CDWs were air-dried and then oven-dried to realize the final SPAN@CDW electrodes.

To investigate the infusion of SPAN into the CDW skeleton, a SPAN@CDW700 electrode with a S mass loading of 5 mg cm^{-2} was sliced in both transverse and radial directions. The elemental composition at each cross-section was analyzed by the EDS method, and elemental maps related to C, O, and S are illustrated in Figure 3. The infusion of S into fibers, rays, and vessels is clear (Figure 3a, transverse section). A uniform distribution of S along the fiber length is detected (Figure 3b,

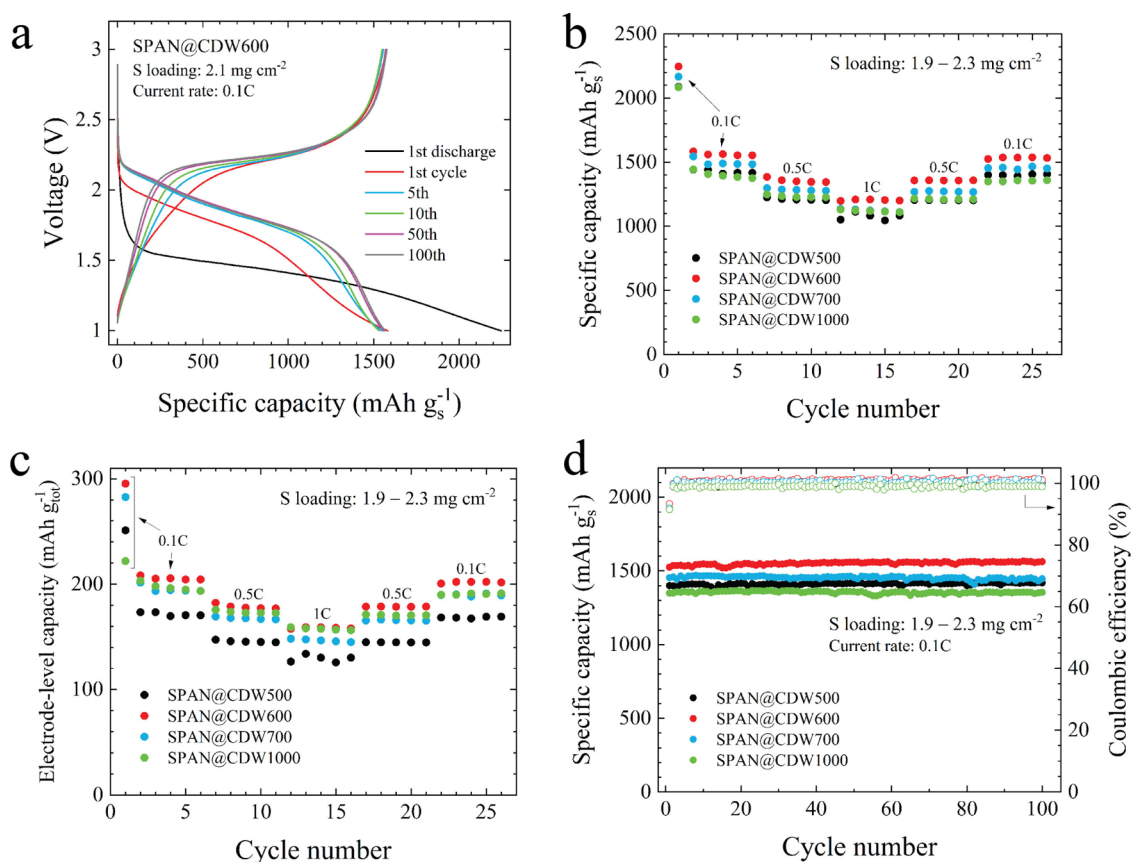


Figure 4. Electrochemical properties of SPAN@CDW cathodes, considering a similar S mass loading level. (a) Charge–discharge profiles of SPAN@CDW700 cathode up to 100 cycles at 0.1 C. (b) Sulfur-level and (c) electrode-level rate performances of SPAN@CDW electrodes at different current rates of 0.1 C, 0.5 C, and 1 C. (d) Cycling performance of SPAN@CDW cathodes at 0.1 C.

lateral section), indicating a good SPAN affinity of the CDW, as discussed previously. The SPAN slurry is infused into spaces between fibers (marked by red arrows in Figure 3b). We emphasize that the cellular structure of the SPAN@CDW electrode possesses some free (unfilled) openings, which provide sufficient room for the volume expansion of sulfur-based active material.

The electrochemical performance of SPAN@CDW electrodes was first investigated by galvanostatic cycling of cathodes using a Li chip as the counter electrode. To make a rational comparison, electrodes with similar S loading levels, in the range of 1.9–2.3 mg cm⁻², were cycled at 0.1 C. The charge–discharge profiles of all electrodes exhibit a single discharge plateau within the range of 1.6–1.0 V in the first discharge process (Figures 4a and S6a–c). In the second cycle, the discharge plateau of all SPAN@CDW cathodes shifts to a higher potential and remains the same for the subsequent cycles, implying that the lithiation process requires lower energy for the second cycle and beyond.⁶¹ The initial discharge capacity of SPAN@CDW cathodes exceeds the theoretical capacity of sulfur (1672 mA h g⁻¹). To explore this excess capacity, we tested a CDW scaffold without SPAN impregnation at a 1–3 V window and a current rate of 0.1 C. The battery exhibited a very low capacity (Figure S7), implying that the contribution from CDW to the first discharge capacity is negligible. It has been reported that Li⁺ ions react with the conjugated π -system of the SPAN backbone, and the dissociation of Li⁺ ions from the backbone is almost irreversible.^{62,63} On the contrary, other studies show that the

interactions of Li⁺ ions with the π -system of SPAN are reversible.²⁶ Therefore, further research is required to identify the contributing mechanisms to the observed elevated capacity. During the second discharge, the SPAN@CDW cathodes with CDW500, CDW600, CDW700, and CDW1000 exhibited S utilizations (i.e., the ratio of the reversible capacity to 1672 mA h g⁻¹) of 86, 95, 92, and 86%, respectively.

Rate performance is a crucial parameter for energy storage devices, controlled by both electron and ion conduction of electrodes. The CDW-based electrodes demonstrated an excellent rate capability (Figure 4b), with high specific capacities of >1000 mA h g⁻¹ at 1 C. This is due to the effective ion conduction in porous 3D CDW scaffolds. At the electrode level, cathodes with CDW600, CDW700, and CDW1000 exhibited high capacities of 205, 197, and 195 mA h g_{tot}⁻¹ at 0.1 C, respectively. At the same time, the SPAN@CDW500 battery delivered the lowest electrode-level capacity at all C-rates (Figure 4c), which is mainly due to the higher density of CDW500 compared to other scaffolds (Figure S2b). Following the rate studies, we evaluated the cycling performance of electrodes at 0.1 C. All SPAN@CDW electrodes showed excellent cycle stability up to 100 cycles with no capacity loss and nearly 100% CE (Figure 4d), demonstrating stable electrochemical reactions over 100 cycles.

Electrochemical impedance spectroscopy (EIS) measurements of SPAN@CDW cathodes were performed at the end of the 1st, 5th, 10th, 25th, and 50th cycles (i.e., discharged to 1.0 V), and Nyquist plots are presented in Figure 5. All spectra were modeled using the Randles circuit shown in Figure S8 to

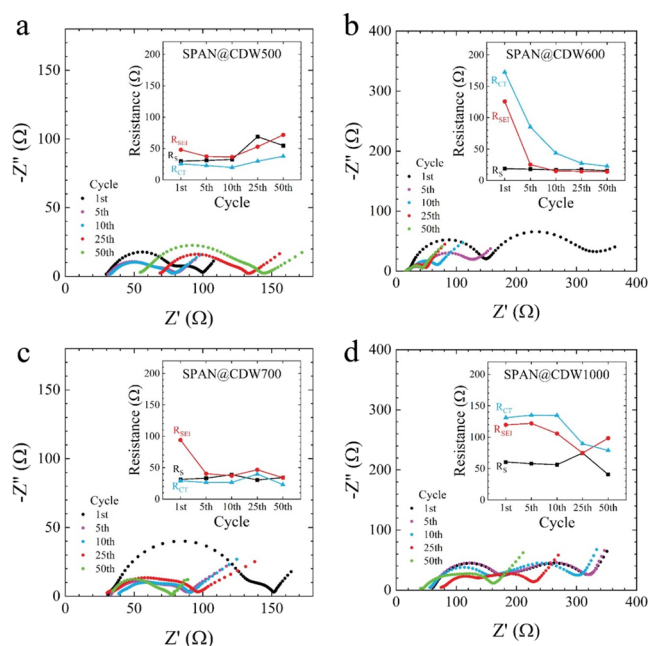


Figure 5. Nyquist plots of (a) SPAN@CDW500, (b) SPAN@CDW600, (c) SPAN@CDW700, and (d) SPAN@CDW1000 electrodes after cycles 1, 5, 10, 25, and 50. The series, SEI, and charge-transfer resistance values corresponding to each Nyquist plot were derived. The variations of these internal resistances over cycling are plotted in the insets.

derive the series resistance (R_s), the SEI resistance (R_{SEI}), and the charge-transfer resistance (R_{CT}). The variations of R_s , R_{SEI} , and R_{CT} over cycling are also presented in Figure 5 (inset). After the first cycle, the SPAN@CDW1000 cathode shows a higher R_s than the others. The total pore volume of CDWs increases with pyrolysis temperature (Figure S9). With the highest pore volume of $0.19 \text{ cm}^3 \text{ g}^{-1}$, the CDW1000 scaffold may contain unfilled pores at the SPAN mass loading level of $\sim 2 \text{ mg cm}^{-2}$, which leads to higher series resistance. R_s remains almost stable with the cycling of electrodes. R_{SEI} and R_{CT} of cathodes are initially higher and then decrease during the cycling process. The reduction of R_{SEI} and R_{CT} is more noticeable in the case of SPAN@CDW600 cathode. The high initial resistance after the first cycle could be attributed to the development of the SEI layer.^{64,65} Besides, the decreased R_{CT} of cycled cells implies that the reaction kinetics were accelerated through activating and stabilizing electrochemical active species.⁶³

Based on the rate capability, cycling stability, and EIS studies, the SPAN@CDW600 and SPAN@CDW700 cathodes showed the best performance. As such, we intentionally depict different electrochemical properties of either electrode to broadly demonstrate the potential of low-temperature pyrolysis. We chose SPAN@CDW700 for further evaluation using cyclic voltammetry (CV) to understand the electrochemical processes further. The CV curves exhibit a single reduction peak in the first cycle, typical for SPAN-based cathodes,²⁶ and the reduction peak shifts to higher voltages in the following cycles (Figure S10a). CV measurements were carried out at various scan rates from 0.1 to 1.0 mV s^{-1} to

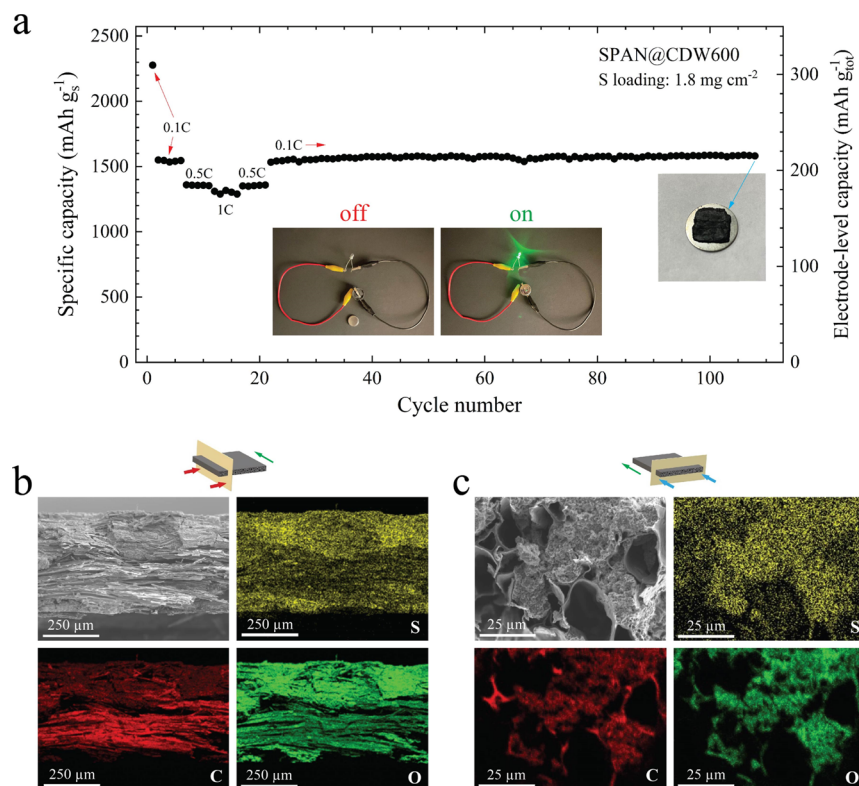


Figure 6. Structural integrity of CDW-based electrode over cycling. (a) Electrochemical properties of a SPAN@CDW600 cathode. The photograph of the opened electrode after nearly 120 cycles shows the robustness of SPAN@CDW cathodes. The illumination of an LED light using the SPAN@CDW600 coin cell is demonstrated. (b) Radial and (c) transverse views of the cycled electrode. SEM micrographs and corresponding EDS elemental maps also confirm the suitability of CDW as a robust scaffold for hosting SPAN.

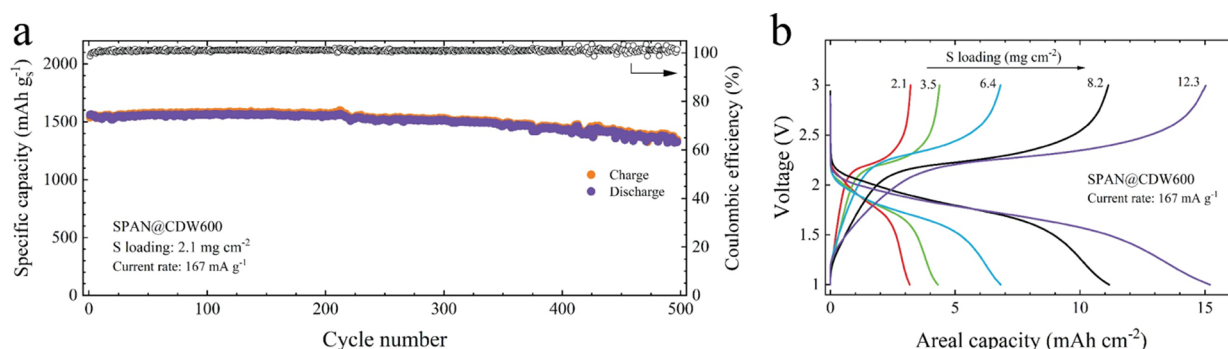


Figure 7. (a) Cycling performance of SPAN@CDW600 electrode with a S loading of 2.1 mg cm^{-2} at 0.1 C. (b) Charge–discharge profiles of SPAN@CDW600 electrodes with various S loadings from 2.1 to 12.3 mg cm^{-2} at the 25th cycle.

understand the electrochemical reactions' kinetics better. Generally, the CV curves display similar shapes at various rates, with a gradual broadening of the peaks at higher scan rates (Figure S10b). The measured current, i , obeys a power-law relationship with the scan rate, v , according to eq 1

$$i = av^b \quad (1)$$

where a and b are adjustable parameters. The b -value is calculated from the slope by plotting $\log i$ vs $\log v$. The b -value of 0.5 indicates a diffusion-controlled process, whereas the b -value of 1.0 represents a capacitive process.^{18,66} From our analysis (Figure S10c), b -values of 0.67 and 0.70 were calculated for anodic and cathodic peaks, respectively. This implies that both capacitive and diffusion-controlled processes contribute to the current at the peak potential and can be attributed to the porous structure of SPAN@CDW electrodes.

To explore the integrity of electrodes over cycling, we disassembled a SPAN@CDW600 battery after nearly 120 cycles, including rate and cycling tests (Figure 6), and analyzed the structural evolution and elemental composition. The electrode remained intact after cycling (inset, Figure 6a). SEM micrographs indicate the compression of the electrode from 800 to $470 \mu\text{m}$ (Figure 6b), which is due to crimping during coin cell assembly. However, the original cellular structure was maintained and supported the active material within porous cells (Figure 6c). Such structural stability originates from the specific 3D morphology of the wood (Figure 1b), which provides a continuous 3D electronic network. The EDS elemental maps of S (Figure 6b,c) also show an excellent active material dispersion, implying that oxygen-containing groups in the CDW scaffold are still bonded with the sulfur species even after 120 cycles.

The long-term cycling performance of the SPAN@CDW600 electrode with a sulfur loading of 2.1 mg cm^{-2} at 0.1 C was also evaluated. As Figure 7a illustrates, the battery delivered a stable discharge capacity of $\sim 1580 \text{ mA h g}^{-1}$ up to 220 cycles, which corresponds to a specific energy of 494 W h kg^{-1} with respect to the mass of cathode. The capacity gradually decreased to 1344 mA h g^{-1} (85% capacity retention) after 500 cycles. The delivered capacity of 1344 mA h g^{-1} by SPAN@CDW600 electrode after 500 cycles is still beyond the reported values from other SPAN-based electrodes (Table S1). This makes our wood-based electrode design a strong candidate for advancing high-energy Li–S batteries. We attempted to increase the S mass loading in SPAN@CDW600 electrodes to meet the areal capacity of 5 mA h cm^{-2} required to compete with the state-of-the-art LIBs.³⁰ A series of electrodes with S mass loadings up to 12.3 mg cm^{-2} (i.e., a SPAN mass loading of 35.3 mg cm^{-2})

were fabricated and tested at 0.1 C. With the highest S loading, an areal capacity of $15.13 \text{ mA h cm}^{-2}$ was achieved (Figure 7b), which is more than 3 times the practical Li–S battery requirements. In Table S2, we presented the sulfur-level and electrode-level energy densities of SPAN@CDW600 with a sulfur loading of 12.3 mg cm^{-2} and compared them with the reported energy density values from other SPAN-based electrodes. To better illustrate the potential of wood-derived CDWs in realizing high-performance Li–S batteries, we plotted the areal capacity of our SPAN@CDW electrodes vs sulfur loading in Figure S11. Compared to synthetic 3D scaffolds, the biobased CDW framework in this study worked as an effective support for high-areal capacity Li–S batteries.

CONCLUSIONS

In summary, a freestanding SPAN@CDW electrode was prepared by a low-cost approach combining delignification, low-temperature pyrolysis, and vacuum-assisted impregnation. The interconnected networks of CDW and numerous open pores on cellular walls provide short pathways for electron and ion transport, which collectively enabled SPAN@CDW electrodes to deliver a reversible specific capacity $>1000 \text{ mA h g}^{-1}$ at 1 C. We demonstrated that relatively thin CDW scaffolds could take up to $35 \text{ mg}_{\text{SPAN}} \text{ cm}^{-2}$, implying a good SPAN affinity of CDW due to this delignification/low-temperature pyrolysis approach. This work supports the use of CDW as a more sustainable source in high-areal capacity Li–S batteries for practical energy storage applications.

MATERIALS AND METHODS

Materials and Chemicals. Balsa wood (*Ochroma pyramidale*), imported from Ecuador, was purchased from Hobby Lobby Stores, USA. Sodium chlorite (NaClO_2 , CAS number 7758-19-2, $\geq 80\%$) was procured from BeanTown Chemical (Hudson, NH, USA). The sulfur powder (CAS number 7704-34-9, sublimed, 100 mesh, 99.5%) was purchased from Alfa Aesar (Haverhill, MA, USA). Carboxymethyl cellulose (CMC, CAS number 9004-32-4), carbon black (Super P, CAS number 1333-86-4), and Li chips were acquired from MTI Corporation (Richmond, CA, USA). Lithium bis(trifluoromethane)sulfonamide (LiTFSI, CAS Number 33454-82-9, 99.995%), polyacrylonitrile (PAN, CAS number 25014-41-9, $M_w = 150,000$), ethylene carbonate (EC), 1,2-dimethoxyethane (DME), 1,3-dioxolane (DOL), and acetic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Preparation of Wood-Based Scaffolds. A wood block was sliced into thin sheets parallel to the tree's growth direction. The longest dimension of thin sheets was in the longitudinal (tree growth) direction. To prepare DW, wood sheets were boiled with 2% sodium chlorite aqueous solution buffered with acetic acid at pH 4.6.⁶⁷ The

solution was changed every 6 h, and the reaction was continued until white DW was attained. The DW pieces were washed thoroughly with DI water and freeze-dried using a FreeZone freeze dry system (Labconco, MO, USA). To prepare CDW scaffolds, the DW sheets were pyrolyzed at 500, 600, 700, and 1000 °C for 3 h with a ramp rate of 5 °C min⁻¹ in a tube furnace under an argon flow of 300 sccm. Based on the pyrolysis temperature, the carbonized pieces were labeled as CDW500, CDW600, CDW700, and CDW1000. To explore the effects of the delignification process before pyrolysis, wood sheets were directly pyrolyzed at 700 °C, and the resulting material was marked as CW700. All scaffolds in this study were derived from a singular balsa wood block to avoid variations in the density and cellular geometry.

Fabrication of SPAN-Impregnated Electrodes. SPAN active material was synthesized according to our previous report.³⁶ Briefly, elemental S and PAN were mixed with a mass ratio of 3:1 and pyrolyzed in a tube furnace at 450 °C (with a heating rate of 5 °C min⁻¹) for 6 h under nitrogen flow. An aqueous slurry of SPAN, CMC, and carbon black with a mass ratio of 70:15:15 was prepared. To make cathodes, CDWs were cut into squares with an area of 1.00 ± 0.05 cm², dipped into a beaker of SPAN slurry, and kept under a vacuum. Then, SPAN-impregnated electrodes were removed, and the excess slurry was wiped off of the top and bottom surfaces. After air-drying overnight, SPAN@CDW cathodes were dried in an oven at 110 °C for 12 h. To increase the SPAN/S mass loading, we utilized thicker CDWs (up to 1.5 mm) in conjunction with a prolonged soaking duration under vacuum.

Electrochemical Measurements. Our previous study optimized the electrolyte composition to enable the simultaneous formation of bilateral SEI layers on SPAN-based cathodes and the Li metal.¹⁸ Based on the optimized composition, we prepared an electrolyte with 1 M LiTFSI in EC_{0.5}DME_{0.25}DOL_{0.25} mixture solution. The CR2032-type coin cells were assembled in an argon-filled glovebox (water and oxygen content <0.5 ppm) using Li chip (16 mm diameter), SPAN@CDW, and Celgard 2325 as a counter electrode, working electrode, and separator, respectively. We used an electrolyte/sulfur (E/S) ratio of 25 μL mg_S⁻¹ for electrodes with a S loading up to 2 mg cm⁻² and decreased the E/S ratio to 10 μL mg_S⁻¹ for electrodes with higher S loadings. The galvanostatic charge/discharge experiments were performed at various current rates using an Arbin battery analyzer (LBT Series) in the voltage range of 1.0–3.0 V (vs Li/Li⁺). The capacities were normalized by the mass of sulfur or the cathode mass (i.e., the sum of masses of SPAN, CMC, Super P, and CDW) to calculate the specific capacity or electrode-level capacity, respectively. CV measurements were performed at various scan rates (0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 mV s⁻¹) over the potential range of 1.0–3.0 V. The EIS measurements were conducted at room temperature in the frequency range of 100 kHz to 0.01 Hz. Cells were measured in the discharged state (i.e., 1.0 V) after the 1st, 5th, 10th, 25th, and 50th cycles to ensure identical conditions. All CV and EIS experiments were carried out using a Gamry Reference 3000 potentiostat.

Characterizations. FTIR spectroscopic analysis was conducted directly on solid samples with a ThermoFisher Nicolet iS50 spectrometer equipped with a diamond attenuated total reflection. Raman spectroscopy was performed on CDWs using a Renishaw inVia Raman microscope, with 532 nm laser excitation and 10× objective beam focusing. A minimum of five spectra were collected from different points on each sample with 30 s data accumulation per point and then averaged. The total pore volume of CDWs was measured using a Quantachrome Autosorb iQ gas sorption analyzer. TGA was performed using a Q5000 thermal analyzer (TA Instruments) under a nitrogen atmosphere (25 mL min⁻¹) from room temperature to 1000 °C at a heating rate of 20 °C min⁻¹. SEM examinations were carried out using a Hitachi SU6600 FE-SEM at 5 kV with EDS. Dimensional analysis of microstructural features in SEM images was made using ImageJ software.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c05886>.

Structural characteristics of DW and CDWs; effects of the delignification process before pyrolysis; affinity between SPAN and CDW scaffolds; preparation and characteristics of the SPAN active material; charge–discharge profiles of SPAN@CDW electrodes; contribution of CDW scaffold to the capacity of SPAN@CDW electrodes; EIS analysis and fitting model; total pore volume of CDW scaffolds; CV of SPAN@CDW electrodes; and comparisons of cycling stability, energy density, and areal capacity (PDF)

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Author Contributions

S.M.S. and N.S. authors contributed equally to this work. S.P., A.M.R., and S.M.S. conceived the project. S.M.S., T.Z., and S.C. developed the concept. S.M.S. and N.S. conducted the experiments and data analysis. S.M.S. and N.S. drafted the

manuscript. S.P., A.M.R., and C.M.C. reviewed and edited the manuscript. All authors discussed and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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Supplementary Information

Sulfurized Polyacrylonitrile Impregnated Delignified Wood-Based 3D Carbon Framework for High-Performance Lithium-Sulfur Batteries

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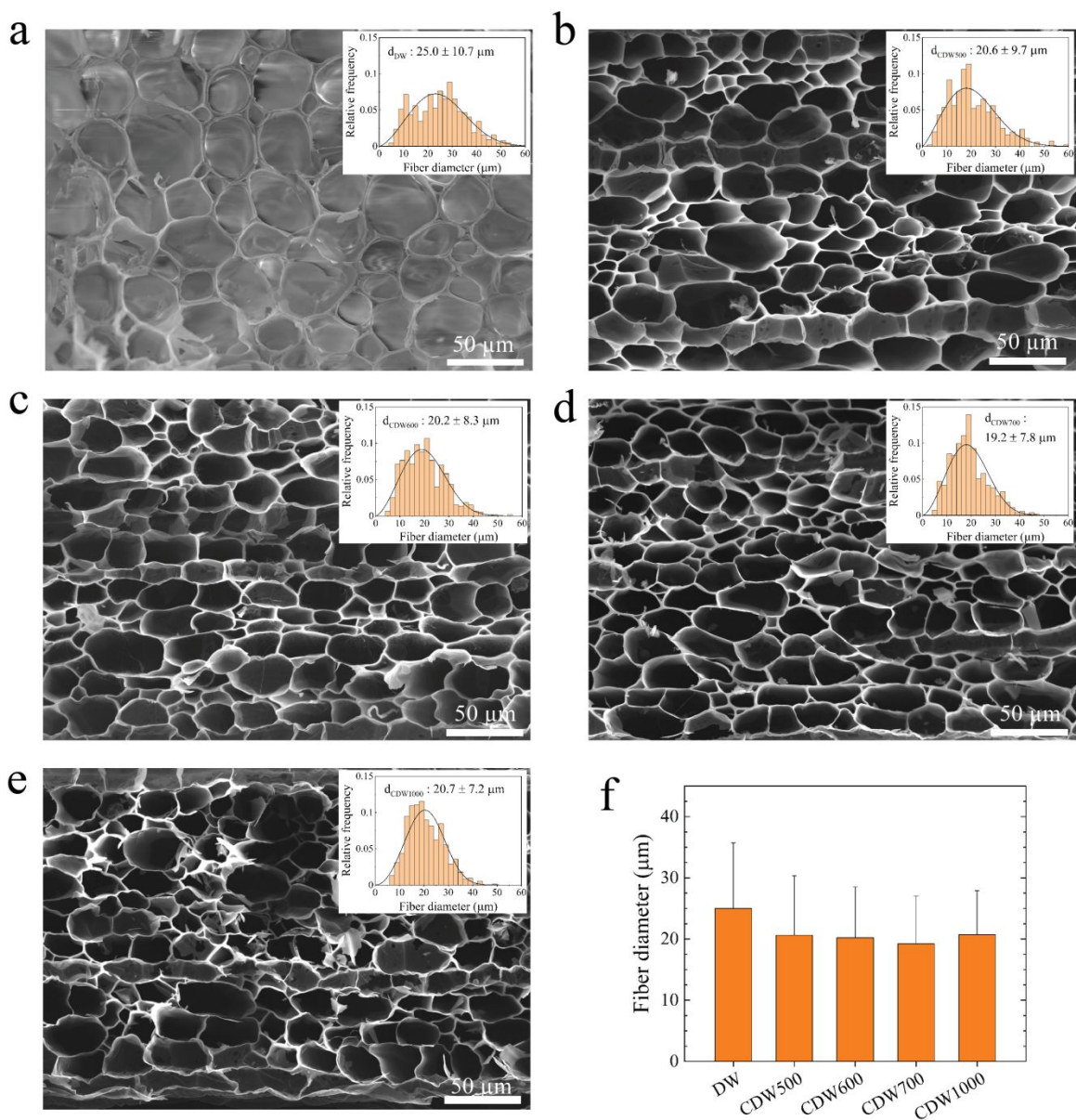


Figure S1: SEM micrographs of transverse cross-sections of (a) DW, (b) CDW500, (c) CDW600, (d) CDW700, and (e) CDW1000. The inset shows the distribution of fiber diameter. (f) Comparison of the fiber diameter between DW and CDW scaffolds.

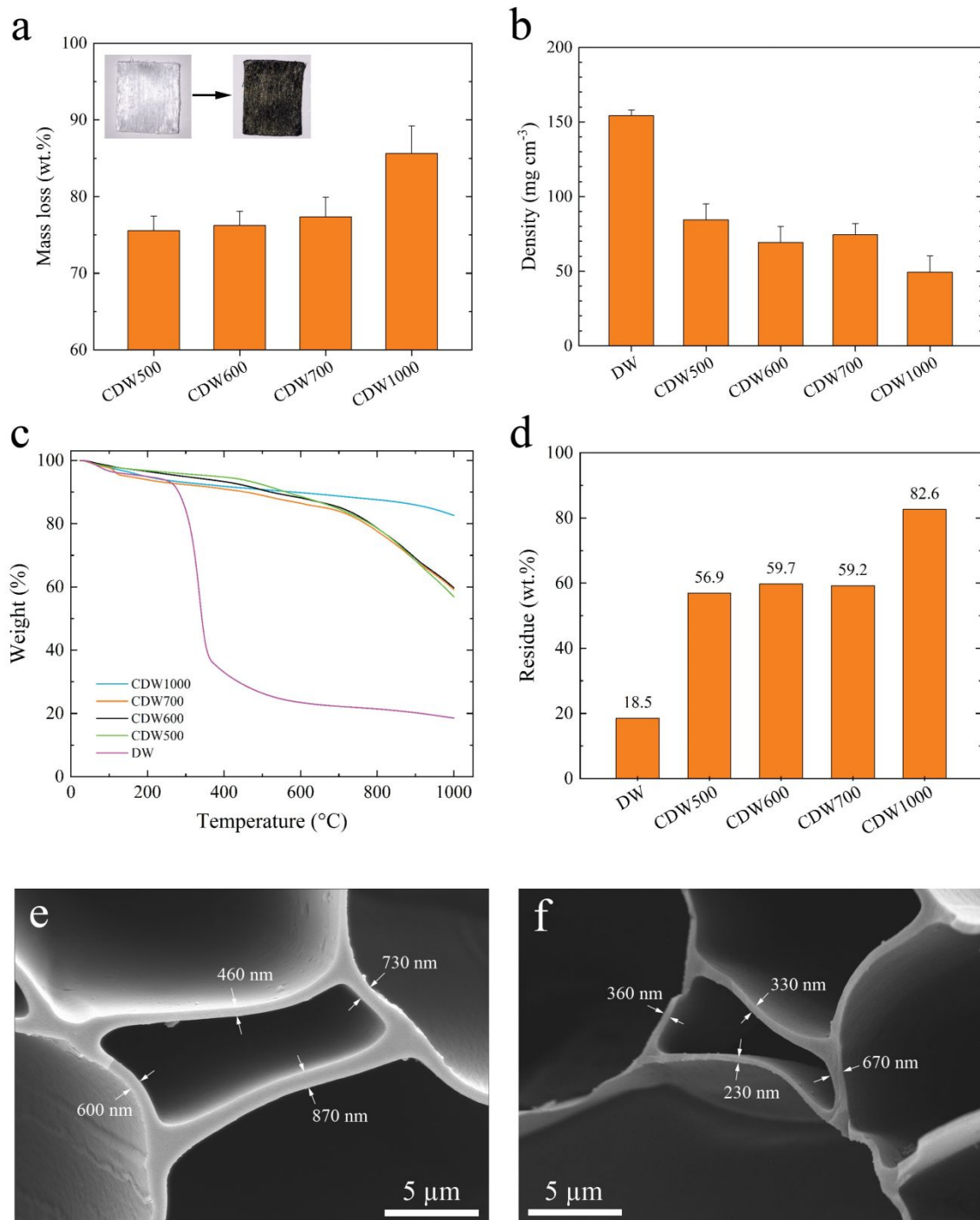


Figure S2: Structural characteristics of CDWs. (a) Mass loss due to conversion of DW into CDW. (b) The density of porous scaffolds. (c) TGA thermograms and (d) corresponding residue (after TGA) for all scaffolds. (e) SEM micrograph of the cell structure of CDW500. (f) SEM micrograph of wood fiber in CDW1000.

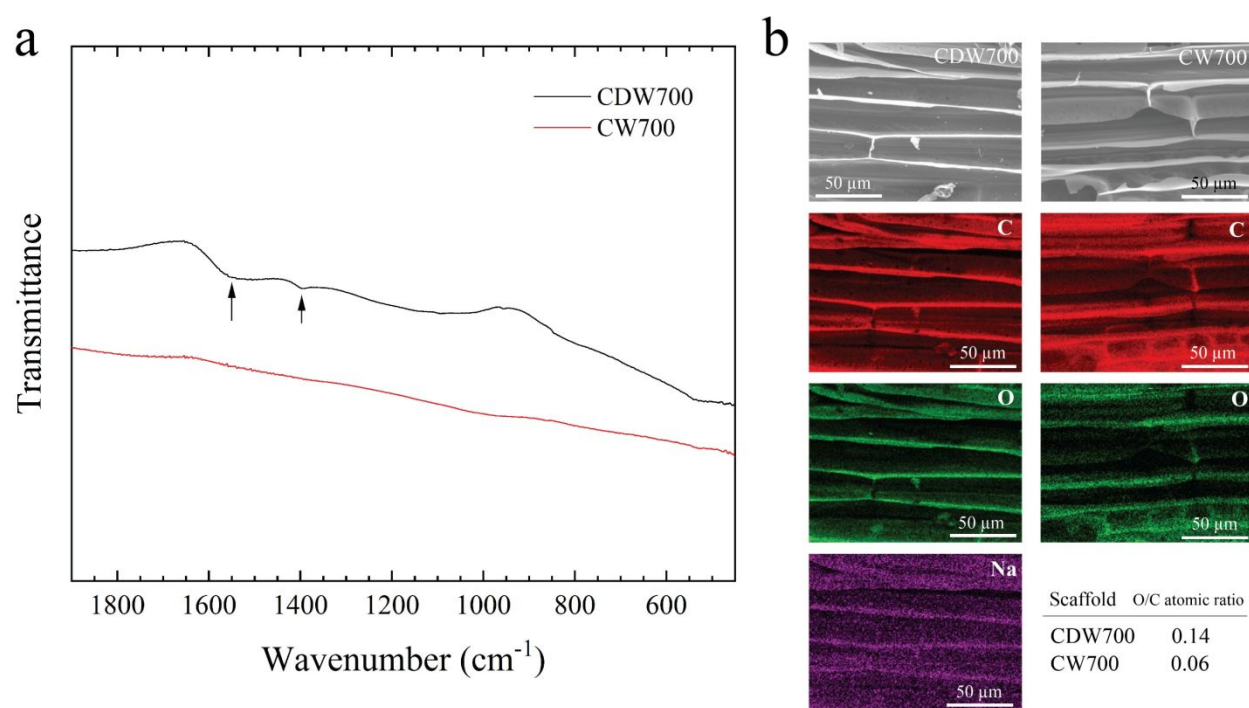


Figure S3: Effects of the delignification process before pyrolysis. (a) FTIR spectra and (b) EDS analysis of CDW700 and CW700 materials.

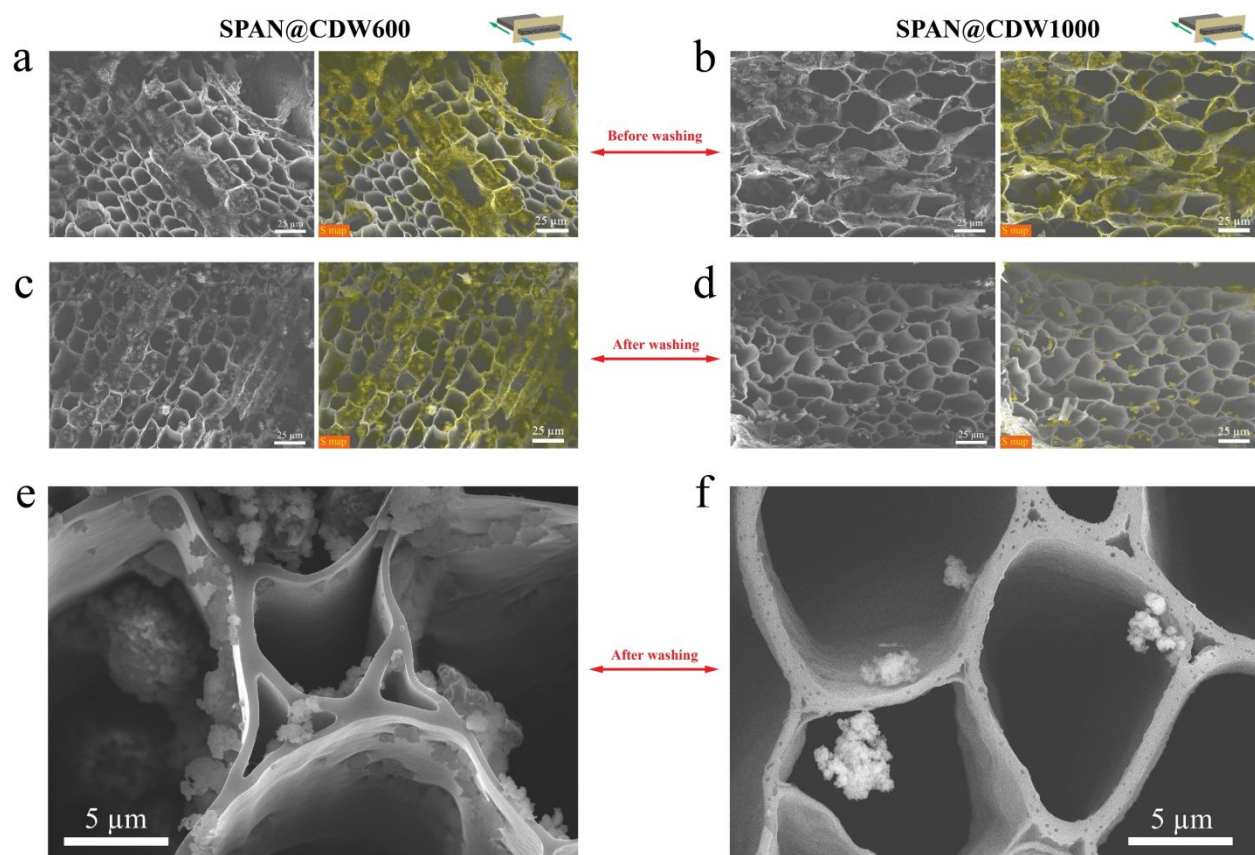


Figure S4: The affinity between SPAN and CDW scaffolds. SEM-EDS micrographs of (a) SPAN-impregnated CDW600, (b) SPAN-impregnated CDW1000, (c) SPAN-impregnated CDW600 after washing, (d) SPAN-impregnated CDW1000 after washing, (e) magnified view of washed SPAN@CDW600, and (f) magnified view of washed SPAN@CDW1000.

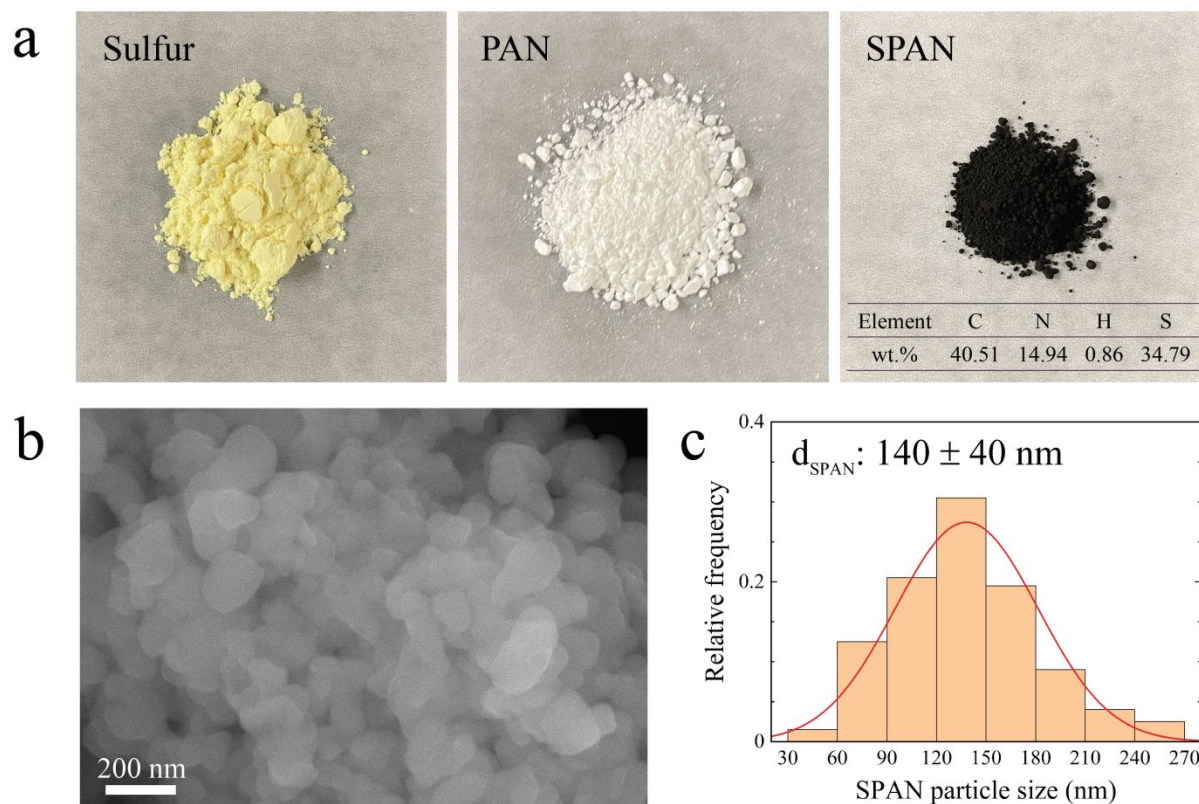


Figure S5: (a) Photographs of S powder, PAN powder, and SPAN product. The chemical composition of SPAN from CHNS analysis is presented. (b) SEM micrograph of SPAN particles. (c) Size distribution of SPAN particles, showing an average size of 140 nm.

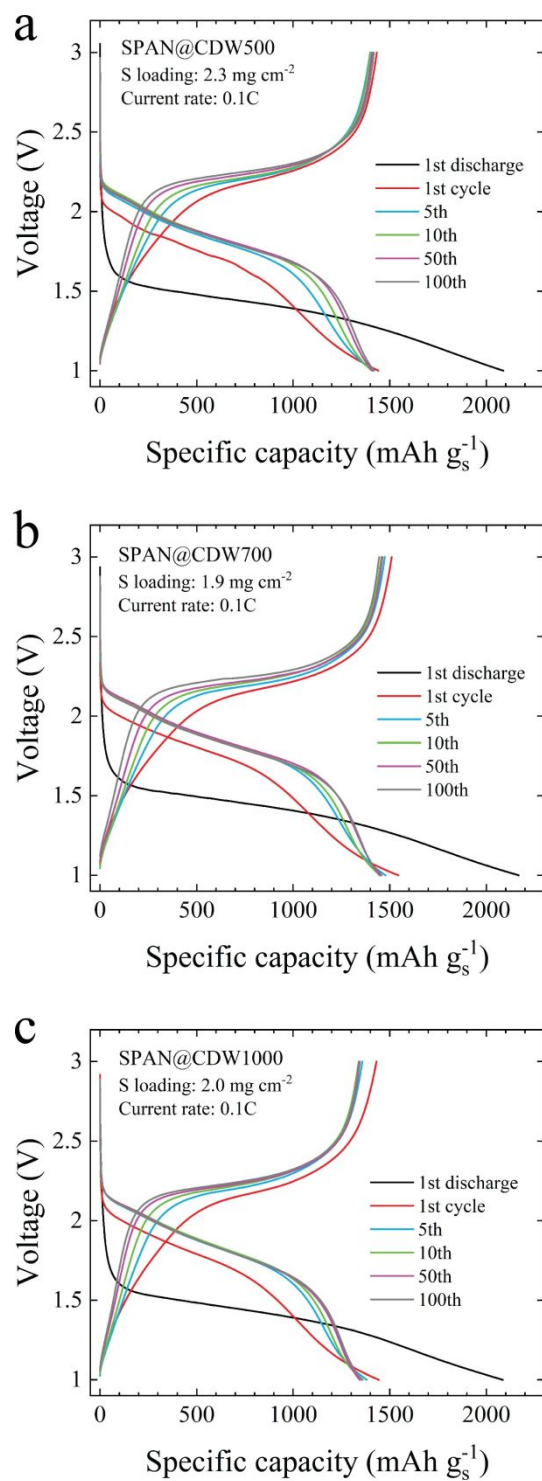


Figure S6: Charge-discharge profiles of (a) SPAN@CDW500, (b) SPAN@CDW600, and (c) SPAN@CDW1000 cathodes up to 100 cycles at 0.1C.

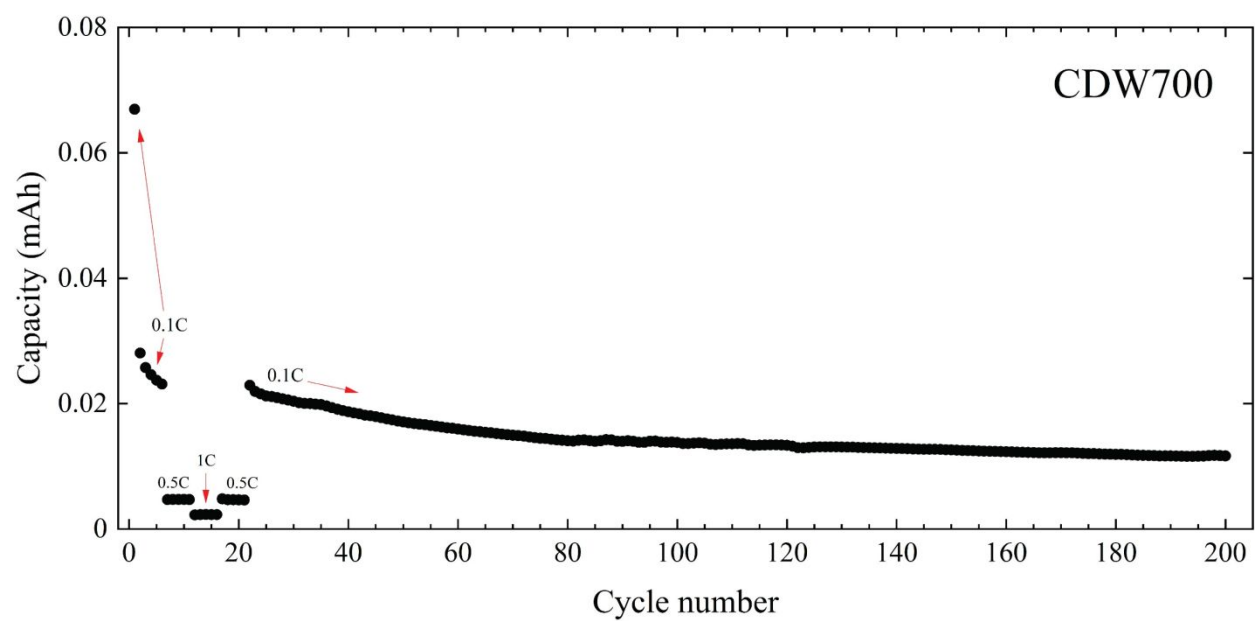


Figure S7: Capacity vs. cycle number for a CDW700 scaffold. The scaffold was subjected to rate performance (at 0.1C, 0.5C, and 1C) and cycling (at 0.1C) tests.

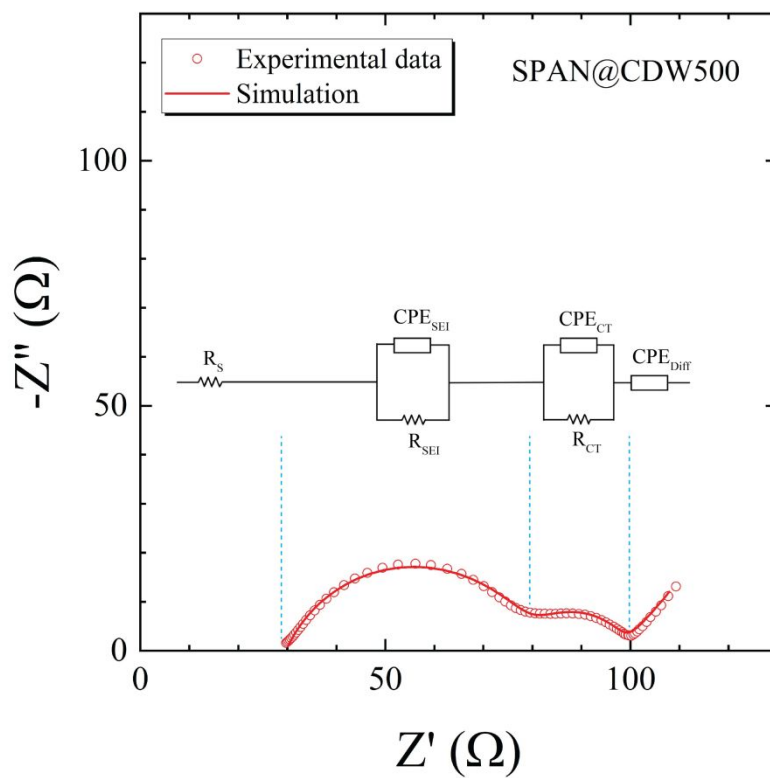


Figure S8: Experimental and simulative Nyquist plot of SPAN@CDW500 cathode. The equivalent Randles circuit used for modeling all EIS spectra is presented. The constant phase element (CPE), series resistance (R_s), SEI resistance (R_{SEI}), and charge-transfer resistance (R_{CT}) are also marked in the equivalent Randles circuit.

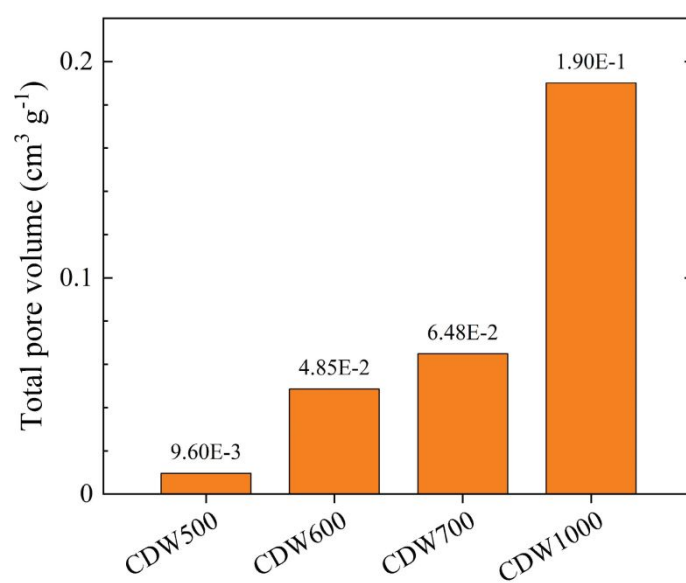


Figure S9: Total pore volume of CDWs derived from BET analysis.

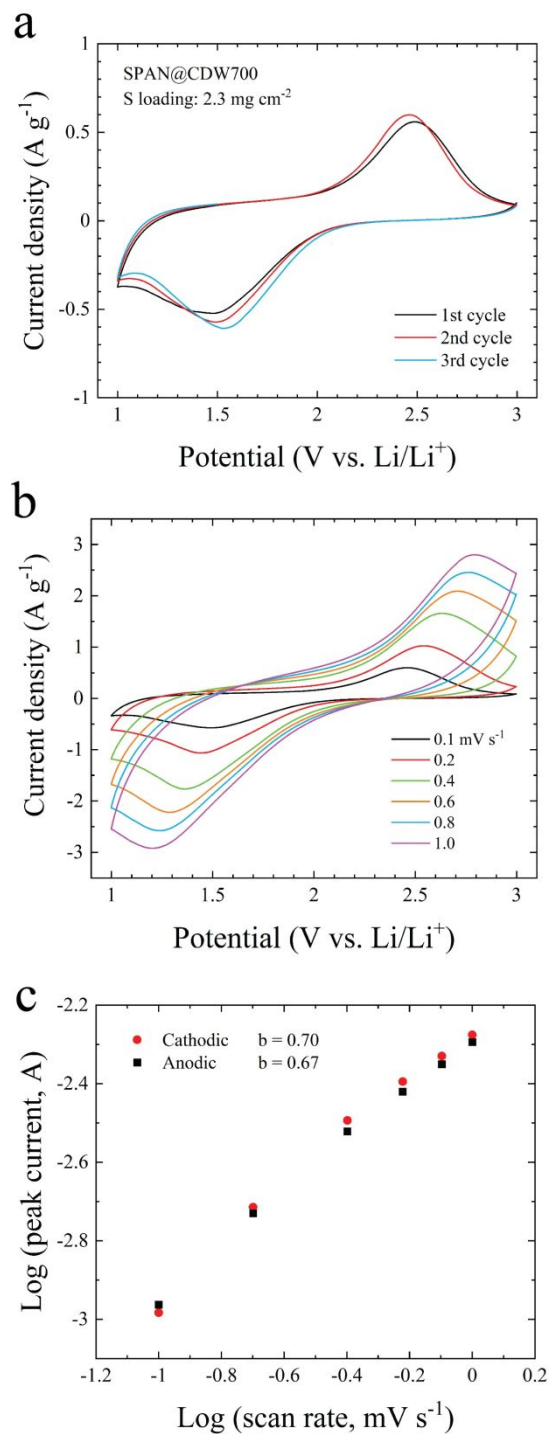


Figure S10: (a) Cyclic voltammetry curves of SPAN@CDW700 cathode at a scan rate of 0.1 mV s⁻¹ and a potential window of 1.0 – 3.0 V. (b) Cyclic voltammetry curves of SPAN@CDW700 cathode at various scan rates from 0.1 to 1.0 mV s⁻¹. (c) Kinetics analysis of SPAN@CDW700 battery.

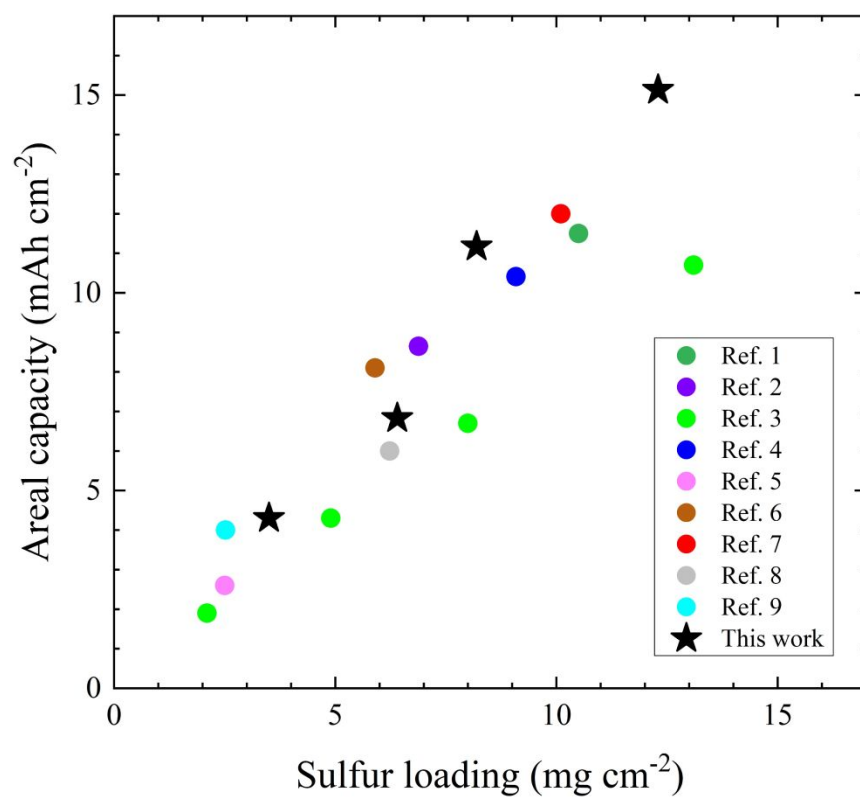


Figure S11: Areal capacity vs. sulfur loading comparison of the SPAN@CDW electrode with the reported SPAN-based electrodes.¹⁻⁹

Table S1: Comparison of the cycling stability of the SPAN@CDW cathode with those reported for SPAN-based Li-S batteries.

Ref.	SPAN	Sulfur content in SPAN (wt.%)	Slurry composition/ Electrode preparation	Current collector	S loading (mg/cm ²)	Electrochemical performance
10	Fibrous SPAN	40	SPAN, Carbon Black, PVDF (70:15:15 wt.%) in NMP	Al foil	-	990 mAh g ⁻¹ after 600 cycles at 0.5C
11	SPAN	42	SPAN, Carbon Black, CMC (70:15:15 wt.%) in water	Al foil	0.76	1218 mAh g ⁻¹ after 500 cycles at 1.5C
12	SPAN	45.6	SPAN, Carbon Black, PVDF (70:15:15 wt.%) in NMP	C-coated Al foil	0.38	1000 mAh g ⁻¹ after 1000 cycles at 0.4C
13	SPAN/CNT nanofibers	37.57	Binder-free SPAN/CNT	Freestanding	-	1280 mAh g ⁻¹ after 200 cycles at 0.24C
14	SPAN/CNT nanofiber film	42.8	Binder-free SPAN/CNT	Freestanding	2	1180 mAh g ⁻¹ after 1000 cycles at 0.48C
15	SPAN-CNT	39.3 – 42.5	Binder-free SPAN-CNT	Freestanding	0.9 – 1.1	1400 mAh g ⁻¹ after 200 cycles at 0.2C
16	SPAN	45.4	SPAN, Acetylene Black, and PVDF (80:10:10 wt.%) in NMP	Al foil	1.5	1089 mAh g ⁻¹ after 100 cycles at 0.1C
17	SPAN-CNT nanofiber films	38	Binder-free SPAN/ CNT	Freestanding	-	1080 mAh g ⁻¹ after 200 cycles at 0.48C
18	SPAN	39.10 – 48.14	SPAN, SuperP, CMC (80:10:10 wt.%) in water	Al foil	~0.86	1200 mAh g ⁻¹ after 250 cycles at 0.5C
19	Porous SPAN/VGCF	48.89	Binder-free SPAN/VGCF	Freestanding	2.4	600 mAh g ⁻¹ after 300 cycles at 2C
6	CoS ₂ -SPAN- CNT film	43.2	Binder-free CoS ₂ -SPAN-CNT	Freestanding	2.4	1240 mAh g ⁻¹ after 100 cycles at 0.2C

20	SPAN/RGO composite	44 – 46.2	Infusion of active material, Katjen Black, PVDF (80:10:10 wt.%) in NMP	Nickel foam	~2.64 – 3.52	1000 mAh g ⁻¹ after 200 cycles at 0.1C
21	Se _{0.6} SPAN composites	35.8 – 40.9	Se _x SPAN, Super P, NaCMC, SBR (80:10:5:5 wt.%) in water	Al foil	~0.41 – 1.2	1130 mAh g ⁻¹ after 500 cycles at 0.12C
22	H-SPAN	41.19	Active material, Acetylene Black, PVDF (80:10:10 wt.%) in NMP	Al foil	0.91	1250 mAh g ⁻¹ after 300 cycles at 0.1C
9	SPAN	42	SPAN, Acetylene Black, CMC (70:20:10 wt.%) in water	Al foil	2.52 – 2.94	670 mAh g ⁻¹ after 300 cycles at 0.2C
23	S/rSP@SPAN	54.5	S/rSP@SPAN, SuperP, CMC (85:5:10 wt.%) in water	Al foil	0.81	1251 mAh g ⁻¹ after 100 cycles at 0.1C
24	MSPAN	45.87	Active material, SuperP, PVDF (80:10:10 wt.%) in NMP	Al foil	1.12	610 mAh g ⁻¹ after 900 cycles at 2C
25	NiS ₂ -SPAN	46	Active material, Acetylene Black, LA132 as binder (80:10:10 wt.%)	Al foil	1.15	1533 mAh g ⁻¹ after 100 cycles at 0.12C
26	SPAN	43	SPAN, Acetylene Black, PAN binder (80:10:10 wt.%)	Al foil	-	930 mAh g ⁻¹ after 100 cycles at 2C
4	3DHG/PS	40.2	Binder-free 3DHG/PS	Freestanding	3.94	954 mAh g ⁻¹ after 800 cycles at 0.5C
3	SPAN/GF	34.79	Vacuum filtration of a slurry of SPAN, SuperP, CMC (70:15:15 wt.%) in water	Freestanding	2.1	700 mAh g ⁻¹ after 500 cycles at 1C
This work	SPAN@CDW	34.79	Vacuum-assisted impregnation of CDW by a slurry of SPAN, SuperP, CMC (70:15:15 wt.%) in water	Freestanding	2.1	1350 mAh g ⁻¹ after 500 cycles at 0.1C

Note: 1C = 1672 mA g⁻¹

Table S2: Comparison of the gravimetric and volumetric energy density of the SPAN@CDW cathode with those reported for SPAN-based Li-S batteries.

Ref.	Electrode structure	E/S ratio ($\mu\text{L}/\text{mg}$)	Sulfur loading (mg/cm^2)	Energy density
¹⁴	SPAN/CNT nanofibers	30	2.0	1016 Wh/kg _{cathode}
⁴	3D holey graphene / SPAN	18	6.11	2357.8 Wh/kg _{sulfur} 1548.1 Wh/L _{sulfur}
²⁷	Carbonized melamine foam/SPAN	53	1.0	157 Wh/kg _{cathode}
²⁷	Carbonized melamine foam@CNT/SPAN	53	1.0	273 Wh/kg _{cathode}
²⁸	FeS@SPAN nanofibers	-	~1.1	900 Wh/kg _{cathode}
This work	SPAN@CDW	10	12.3	2460 Wh/kg _{sulfur} 530 Wh/kg _{cathode} 505 Wh/L _{cathode}

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