

# High-Performance Lithium—Sulfur Batteries with a Cost-Effective Carbon Paper Electrode and High Sulfur-Loading

Jianhua Yan,<sup>†,‡</sup> Xingbo Liu,<sup>‡</sup> He Qi,<sup>‡</sup> Wenyuan Li,<sup>‡</sup> Yue Zhou,<sup>‡</sup> Meng Yao,<sup>‡</sup> and Bingyun Li<sup>\*,†</sup>

<sup>†</sup>Biomaterials, Bioengineering & Nanotechnology Laboratory, Department of Orthopaedics, West Virginia University, Morgantown, West Virginia 26506, United States

<sup>‡</sup>Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia 26506, United States

Supporting Information

**ABSTRACT:** The lithium sulfur (Li–S) battery has attracted much attention due to its high energy density and the low cost of sulfur, but practical applications are still impeded by its short cycle life and low practical energy density due to polysulfide shuttle and low sulfur-loading. Here, we report a novel electrode design to achieve high energy density and long-cycling Li–S batteries, which rely on a cost-effective and well-performed carbon nanofiber-porous carbon paper (CNFPC) electrode. In this design, the CNF substrate with a high electrical conductivity (420 S cm<sup>-1</sup>) and an extremely low density (~0.2 g cm<sup>-3</sup>) is used as a current collector and as a host for high sulfur-loading (~6.7 mg cm<sup>-2</sup>), while the carbon black nanoparticles which are well-distributed within the CNF substrate function as electrical bridges for nonconductive sulfur and highly conductive CNF



framework. In addition, the densely packed (~6.6 g cm<sup>-3</sup>) porous carbon layer (~5  $\mu$ m) on the top of CNF acts as a protective layer to inhibit polysulfide shuttle between cathode and anode. As a result, this unique design enables the fabrication of Li–S batteries with a remarkably high reversible capacity exceeding 900 mAh g<sup>-1</sup> at 0.2 C, 800 mAh g<sup>-1</sup> at 0.5 C, and 700 mAh g<sup>-1</sup> at 1 C, while the average coulombic efficiency is greater than 99.5%. Moreover, at a high current rate of 1.5 C, capacity retention from 709 to 302 mAh g<sup>-1</sup>, corresponding to an areal capacity of >2 mAh cm<sup>-2</sup>, is obtained over 1000 cycles.

#### INTRODUCTION

While lithium-ion batteries (LIBs) have enjoyed a significant degree of success, there is evidence that their rise has started to plateau due to their high cost and low energy density, which limited their further applications in grid-level energy storage and the emerging electrical vehicle (EV) market.<sup>1-3</sup> On the other hand, sodium batteries are receiving a lot of attention due to the abundance of sodium materials on Earth; however, their limited specific energy densities (Na-ion battery) and high temperature requirements (Na-S battery) may limit their applications in large-scale energy storage systems.<sup>4,5</sup> Changing battery chemistry from the current lithium/sodium intercalation reactions to other promising reactions is a means to enhance the energy density and low cost of rechargeable batteries.<sup>6</sup> Li–S batteries that employ integrated chemistry are regarded as one of the prospective candidates for next-generation energy storage systems due to their high theoretical energy density (2567 Wh  $kg^{-1}$ ), which is 10-fold higher than that of traditional LIBs.<sup>7–11</sup> In addition, the Li-S battery has been regarded as an inexpensive alternative to current batteries, owing to the abundance of sulfur.<sup>9–11</sup>

Despite the promising attributes, inferior cycling performance and low practical energy density  $(350-700 \text{ Wh kg}^{-1})^{12}$  are challenging the real applications of Li–S batteries, mainly due to the intrinsic limitations of sulfur chemistry.<sup>13–24</sup> First, during

cycling, sulfur undergoes a multistep reaction ( $S_8 \leftrightarrow S_8^{2-} \leftrightarrow S_6^{2-}$  $\leftrightarrow$  S<sub>4</sub><sup>2-</sup>  $\leftrightarrow$  Li<sub>2</sub>S<sub>2</sub>  $\leftrightarrow$  Li<sub>2</sub>S) and produces soluble high-order lithium polysulfides  $(Li_2S_8/Li_2S_6/Li_2S_4)$ , which can diffuse to the dead corner of electrolyte, decreasing the overall quantity of sulfur and thus leading to capacity fading with cycle numbers.<sup>13,14</sup> In addition, these soluble species can further migrate to and react with the Li-anode, causing an unstable Li-anode and a low battery coulombic efficiency.<sup>15–19</sup> Second, because of the insulating nature of  $S_8$  and the final discharge products of  $Li_2S_2/Li_2S$ , Li-Sbatteries require a significant amount of conductive carbon agents, which neutralize the advantages of high energy density of Li–S batteries.<sup>20–22</sup> Aside from this, the sulfur utilization in Li–S batteries is still low due to the difficulty in maintaining sufficient contact between sulfur species and the conductive matrix. For one thing, the volume expansion ( $\sim$ 80% from S to Li<sub>2</sub>S) causes structural changes and leads to isolated active materials from the conductive matrix, deteriorating the reversibility of the battery.<sup>23</sup> For another, the detachment of highly polar polysulfides from nonpolar carbon conductive agents during discharge/charge is a major concern.<sup>24</sup>

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Great efforts on sulfur cathode designs have been made to improve the performance of Li-S batteries.<sup>25-39</sup> For example, the use of hybrid carbon structures, such as carbon nanotubes and carbon fibers, was more effective to enhance the conductivity of the active sulfur materials, to gain a much lower polarizations and to retard the polysulfide migrations in the cathode compared with the use of single conductive carbon agents.<sup>28-33</sup> However, most reported literature had a low areal sulfur-loading (<2 mg  $cm^{-2}$ ), resulting in a low energy density that is far below the standard for commercialization. In the reported Li-S batteries with high sulfur-loading, the researchers found that increasing the amount of sulfur-loading resulted in decreased transport efficiency for electrons and ions and thus inferior performance of Li–S batteries.<sup>34–38</sup> Recently, Zu et al.<sup>38</sup> fabricated a sulfur cathode with a high sulfur-loading of 5.5 mg  $cm^{-2}$  using soluble polysulfides as the active material in the cathode and a carbon nanofiber (CNF) film as the current collector. In their cells, high capacities, larger than 1000 mAh g<sup>-1</sup>, were obtained. However, these exceptional capacities were achieved only at very low current densities (i.e., 0.2 and 0.1 C). Further, their cells had inferior cycling performance (50 cycles) due to the anode corrosion caused by side reactions between the lithium metal and soluble polysulfides. Their configuration is also conducive to the formation of dendrites upon repeated charges and discharges, resulting in an unstable Li-anode. Therefore, a rational design for a sulfur cathode structure that can achieve high sulfur-loading capability<sup>37-39</sup> while making full use of these sulfur materials over long cycle lifetimes is warranted and presented in this study.

Here, a commercialized CNF-porous carbon paper (CNFPC,  $\sim 165 \ \mu m$ ) coupled with carbon black nanoparticles and soluble lithium polysulfides was used as a sulfur electrode and a current collector (Figure 1a,b). In this structure, the three-dimensional



**Figure 1.** (a) Schematic of the CNFPC electrode design, (b) large areal figure of the CNFPC electrode, and (c) carbon black/soluble  $Li_2S_6$  liquid catholyte.

(3D) CNF substrate provided multiple 3D interlinked electron pathways and sufficient space to accommodate a large amount of active sulfur materials. On top of the CNF substrate was a compact porous carbon film (~5  $\mu$ m) with a high tap density of 6.6 g cm<sup>-3</sup>, which was designed to keep the soluble high-order polysulfides within the cathode. A liquid polysulfide (Li<sub>2</sub>S<sub>6</sub>) catholyte (Figure 1c and Figure S1) was used as the active

material, simplifying the fabrication process and ensuring efficient contact with the conductive CNF matrix. The CNF acted as the long-range conductive framework, while the carbon black nanoparticles served as the short-range conductive agents, which bridged the gaps between sulfur materials and the CNF framework. As a result, reversible capacities over 900 mAh  $g_{sulfur}^{-1}$  at 0.2 C, 800 mAh  $g_{sulfur}^{-1}$  at 0.5 C, and 700 mAh  $g_{sulfur}^{-1}$  at 1 C over 200 cycles were obtained with a high sulfur-loading of 6.7 mg cm<sup>-2</sup>. Therefore, our simple and cost-effective sulfur cathode structure led to Li–S batteries with high performance.

#### RESULTS

Battery Performance. Using our developed CNFPC sulfur electrode, the Li-S battery delivered a reversible capacity of >700 mAh g<sup>-1</sup> over 200 cycles at 1670 mA g<sup>-1</sup> ( $\sim$ 1 C) as shown in Figure 2a; this improvement in capacity retention in such a high sulfur-loading electrode is remarkable. However, the initial discharge capacity was lower than 600 mAh g<sup>-1</sup> due to the loss of the high voltage plateau near 2.35 V, which was ascribed to the transition from  $S/Li_2S_8$  to  $Li_2S_6$ .<sup>13</sup> As the soluble lithium polysulfides  $(Li_2S_6)$  were directly used as the active materials, the discharge process started at the transition from Li<sub>2</sub>S<sub>6</sub> to Li<sub>2</sub>S<sub>4</sub>. In addition, a severe voltage hysteresis was observed in the initial discharge curve, which was possibly caused by severe battery polarization because of large amounts of active sulfur materials, as indicated by the large charge-transfer resistance in EIS images (Figure S2). These soluble active materials rearranged themselves to electrochemically favorable positions in the electrode after the first cycle,<sup>40,41</sup> and then the discharge profiles came back to normal, as shown in Figure 2a. This phenomenon was also verified by cyclic voltammogram (CV) testing (Figure 2b): the overpotential of the first cathodic peak disappeared after the first cycle, and then the CV curves presented a high reversibility of the electrode. Figure 2c presents the discharge/ charge voltage profiles (the second cycle) of the Li/CNFPC batteries at different current densities. Even at a current rate of 2500 mA g<sup>-1</sup> ( $\sim$ 1.5 C), the battery capacity exceeded 650 mAh  $g^{-1}$ , demonstrating exceptional rate performance. Of note, the voltage gap between discharge and charge was obviously reduced using CNFPC electrodes compared to that from the using traditional sulfur electrodes we previously reported.41,42 For example, the charging voltage plateau decreased to 2.2 V at 167 mA  $g^{-1}$  (~0.1 C). The smaller voltage plateau difference was probably attributed to the fast kinetics in the surface oxidation reaction, and thus a high redox electrochemical reversibility within this electrode. The porous and thick structure of the CNFPC cathode drove the soluble polysulfides to electrochemically favorable sites and stabilized them, which could be further reduced or oxidized with the help of long-range CNF conductive agents.

Figure 2d compares the cycling performance and coulombic efficiency of the Li/CNFPC batteries at 335 mA  $g^{-1}$  (~0.2 C), 840 mA  $g^{-1}$  (~0.5 C), and 1670 mA  $g^{-1}$  (~1 C). Reversible capacities of ~900 mAh  $g^{-1}$  (at 335 mA  $g^{-1}$ ), ~ 830 mAh  $g^{-1}$  (at 840 mA  $g^{-1}$ ), and 710 mAh  $g^{-1}$  (at 1670 mA  $g^{-1}$ ) over 200 cycles were obtained. The coulombic efficiency approached 100% for most cycles, indicating that polysulfide migration from cathode to anode was significantly reduced in this novel sulfur electrode structure. It is worth mentioning that long-term cycle stability of the high sulfur-loading batteries at 2500 mA  $g^{-1}$  was also observed (Figure 2e). The battery retained a capacity of 302 mAh  $g^{-1}$  after 1000 cycles, corresponding to only 0.057% capacity fade per cycle. Particularly, the coulombic efficiency of the Li–S



**Figure 2.** Electrochemical performance of Li/CNFPC cells. (a) Cycling ability of the battery at a rate of 1670 mA  $g^{-1}$ . (b) Continuous CV curves of the battery (scanning rate was 0.1 mV  $s^{-1}$ ). (c) Voltage profiles of the battery at different rates. (d, e) Long-term cycling stability and coulombic efficiency of the battery at different current rates.



**Figure 3.** Microstructure characterization of CNFPC electrodes. SEM images of (a) porous carbon film layer before cycling, (b) native CNF substrate, and (c) CNF substrate after infiltration with soluble lithium polysulfides. (d) TEM images of lithium polysulfide wrapped carbon black. (e, f) SEM images of CNF surface after 100th discharge at different magnifications. (g, h) SEM images of CNF surface after 100th charge at different magnifications. (i) SEM image of porous carbon film surface after 100th cycles.

battery decreased from 104.3% to 99.6% over 1000 cycles. In addition, a rapid capacity fading in the initial 100 cycles was noted, which was probably caused by a severe polarization in the electrode at such a high current rate. After some cycles, the resistance of polarization and reaction dynamics in the cell

reached equilibrium, and thus, the battery had a stable capacity with cycle numbers.

**Material Characterization.** Structural variations of the cycled CNFPC paper electrodes were characterized by scanning electron microscopy (SEM) and transmission electron micros-



Figure 4. Characterizations of surface films on Li-anode. (a, b) SEM images of the Li-metal surface from the Li/CNFPC batteries at different magnifications. (c, d) SEM images of the Li-metal surface from the Li/CNF batteries at different magnifications. (e, f) EDS and EDX (inner figures) data of Li-metals surface from (e) Li/CNFPC batteries and (f) Li/CNF batteries, respectively.

copy (TEM). The porous carbon nanoparticles with an average size of  $\sim 100$  nm constructed a densely compact film layer ( $\sim 6.6$ g cm<sup>-3</sup>) (Figure 3a). The native CNF current collector had a robust structure with large spaces between individual fibers (Figure 3b), which could hold large amounts of carbon black/ soluble lithium polysulfides (Figure 3c). TEM images showed that these soluble lithium polysulfides were uniformly coated onto the surfaces of carbon nanoparticles, which connected together and formed a well-distributed framework across the 3D CNF skeleton (Figure 3d). However, after the 100th discharge, these active sulfur nanoparticles changed into thin films and covered the surfaces of the CNF skeleton (Figure 3e,f). The chemical compositions of these thin films were identified as crystalline Li2S and other polysulfides by X-ray diffraction (XRD), as shown in Figure S3a. The cycled sulfur electrodes were further investigated after the 100th charge (Figure 3g). A magnified image of these films indicated that there were numerous nanoparticles after charging (Figure 3h). Most of these nanoparticles were amorphous sulfur, as verified by XRD in Figure S3b. The end discharge product of lithium sulfide formed at the end of discharge was converted to amorphous sulfur at the end of the following charge. The original morphology of the porous carbon layer was well-preserved even after 100 cycles (Figure 3i), indicating its robust mechanical structure. Energy dispersive spectroscopy (EDS) studies found that the chemical composition on the surface of the cycled porous carbon layer had a very small amount of sulfur or polysulfide species (Figure S4a). Unlike the traditional sulfur electrode, the chemical composition of surface film on the electrode was more sophisticated, as polysulfides are always involved (Figure S4b).<sup>19</sup> The results indicated high effectiveness of the porous carbon layer on trapping polysulfide species within CNFPC electrodes.

#### DISCUSSION

The charge/discharge rates and sulfur-loading used in this study were found to be substantially higher than those used in conventional Li–S batteries.<sup>25–33</sup> More importantly, decent battery capacity retention over 1000 cycles was obtained at a large current rate of 1.5 C. A systematic investigation on the exact mechanisms controlling the CNFPC paper electrode for high rate capability and long-term stability were conducted. The function of a CNFPC paper as a sulfur host was quite different from a carbon or metal framework to conduct electrons and constrain polysulfide diffusion. Unlike the traditional slurrycoated electrodes with a compact conductive carbon framework that tended to fail after a few cycles if the sulfur-loading was high, the CNFPC paper electrode had a robust and effective conductive framework even after 1200 cycles (Figure S5). In this electrode structure, the current collector had multiple microscale spaces, which were built by interconnected CNFs with large diameters of  $6-10 \,\mu m$  (Figure S6). These spaces not only enabled a very high sulfur-loading of  $6.7 \text{ mg cm}^{-2}$ , but also favored the penetration of the electrolyte through the electrodes, and thus enhanced Li-ion conductivity in the electrode. In addition, the large CNFs served as the long-range conductive pathways, while the well-distributed carbon black nanoparticles (particle size of  $\sim$ 150 nm) in the interspaces acted as the shortrange conductive bridges. These two conductive systems facilitated effective electron conduction. As a result, the electrical conductivity,43 tested by the van der Pauw method, of the CNFPC paper electrode with high sulfur-loading reached 230 S  $\rm cm^{-1}$  , which was much larger than those formerly reported.  $^{44,45}$ For example, Zhang et al.<sup>44</sup> reported a carbon-nanotube paper electrode with a conductivity of 17.1 S cm<sup>-1</sup>, which was larger than the electrical conductivity of electrodes prepared by the slurry-coated method.

In addition, the direct use of soluble polysulfides resulted in good dispersion of active sulfur materials in the CNFPC electrodes. Both SEM images and EDS mapping showed that the active sulfur materials were uniformly integrated throughout the cathode without individual sulfur particles after 100 cycles (Figure S7), revealing the efficient electrical contact between active sulfur materials and the CNF conductive framework. Furthermore, the CNF paper current collector was still intact without damage, indicating the effectiveness of the electrode to accommodate volume changes of sulfur during the repeated cycles. The robust CNF structure with a large thickness (~160  $\mu$ m) favored the utilization of the active sulfur materials. Consequently, highly efficient electron/ion pathways and high sulfur-loading capability were obtained.

Now that the roles of the CNF current collector and carbon black have been investigated, the factors influencing long-term



**Figure 5.** Demonstration of the discharge/charge products in the high sulfur-loading CNFPC electrodes. High-resolution XPS S 2p spectra of the CNF current collector surface (a) before cycling, (b) after the initial discharge, and (c) after the initial charge. (d) The initial discharge/charge profiles at ~1 C rate. High-resolution XPS C 1s spectra of the CNF current collector surface (e) after the initial discharge and (f) before cycling.

cycling stability need to be discussed. One possible explanation for the excellent cycling stability was that the compact porous carbon layer with a high tap density on the surface of the CNF current collector may have functioned as a physical barrier that decreased the transport of polysulfides from cathode to anode. This layer was reasonably vital to retain the active mass and electrical contact of the CNFPC paper electrode, and thus enhanced the coulombic efficiency of Li-S batteries. Control cells adopting the CNF electrode without a porous carbon layer were assembled (Figure S8a). Capacities of these control cells decreased all the time at all rates studied (Figure S8b), and capacities of these batteries were low (Figure S8c), indicating that the porous carbon layer probably acted as a physical barrier that reduced polysulfide shuttle and thus protected capacity retention. On the other hand, the Li-anode dissembled from the Li/CNFPC battery after 100 cycles had a much more dense structure (Figure 4a,b). In contrast, there were obviously cracks and numerous lithium dendrites on the surface of the Li-anode in the control cells (Figure 4c,d). Magnified images showed these lithium dendrites had heights of several hundreds of nanometers (Figure S9). In addition, the chemical composition of surface film on the Li-anode in the control cells was more sophisticated and contained much more sulfur substance (Figure 4e,f). The results indicated that the side reactions between soluble polysulfides and Li-anode might be an important reason for the growth of lithium dendrites in Li-S batteries. These side reactions were largely alleviated in the Li/CNFPC batteries, further supporting the effectiveness of a porous carbon film layer on trapping polysulfides within CNFPC electrodes.

Furthermore, it is worth noting that the porous carbon layer in CNFPC electrodes reduced the charge-transfer resistance (activation polarizations), as characterized by the smaller semicircle at the high-frequency region in the electrochemical impedance spectroscopy spectra (Figure S10) compared to those

of the control batteries. However, the thickness of the porous carbon layer had a great influence on the performance of Li–S batteries. When the thickness is increased from 5 to 15  $\mu$ m, negative effects on electrochemical performance were observed (Figure S11). A high overpotential in the CV curves (Figure S11a) and a relatively fast capacity fading were noted (Figure S11b,c). One possible explanation is that the thick and densely tapped porous carbon film decreased the efficiency of Li-ion diffusion, which was governed by random jumps of Li-ions, leading to position exchange with their neighbors.<sup>46</sup> As shown in Figure S11b, the coulombic efficiency of the two batteries at different current rates was always larger than 100%, and the higher the current rate, the lower the coulombic efficiency. This result infers that it is more difficult for lithium ions to diffuse out of the cathode than to insert into the cathode.

From the above discussion, the combination of highly conductive CNFPC paper and carbon black nanoparticles with soluble lithium polysulfides resulted in a high sulfur-loading composite electrode that can take advantage of each part. However, the specific capacities at all of the rates studied were not high. To get insight into the chemistry of the Li/CNFPC battery, X-ray photoelectron spectroscopy (XPS) (Figure 5) was performed to confirm the surface compositions of the cathode after initial charge/discharge. The high-resolution S 2p region spectra of CNF current collector are shown in Figure 5a-c, corresponding to the three points A-C in Figure 5d, respectively. Initially, before cycling, the electrode contained high-order polysulfides (mainly as  $Li_2S_6$ ), as verified by the characteristic S 2p3/2 peak at 161.9 eV (Figure 5a).47,48 After being fully discharged to 1.8 V, the electrode contained Li<sub>2</sub>S (158.1 eV), Li<sub>2</sub>S<sub>2</sub> (159.4 eV), and high-order lithium polysulfides (centered at 160.9 eV) (Figure 5b). After being fully charged to 2.5 V, the electrode contained Li<sub>2</sub>S, Li<sub>2</sub>S<sub>2</sub>, high-order lithium polysulfides, and elemental sulfur (163.2 eV) (Figure 5c). The results showed an incomplete conversion in both discharge/ charge processes, resulting in a relatively low capacity, as shown in Figure 2d,e. In this study, the electrolyte-to-sulfur ratio was around 7.4 mL/g, which was a little smaller than the ratio reported,<sup>49</sup> and thus generated a relatively lower capacity. Since the reduction of sulfur and oxidation of Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S can only take place on the surface of carbon,<sup>15</sup> some of the active sulfur materials in the dead corner of the CNFPC structure that lost the direct contact with the conductive matrix did not contribute capacity. It was suggested that most of the polysulfides were transformed into intermediates with the most facile reduction and oxidation kinetics (via charge transfer), as the kinetic dynamics from high order polysulfides to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S or elemental sulfur were very slow. For example, after the initial cycle, most of the active materials in the electrode were soluble high-order polysulfides in the higher valence state (i.e.,  $S_8^{2-}$ ). Unlike the nonconductive sulfur or Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S, these incompletely transformed high-order polysulfides dissolved into the electrolyte might have enhanced the transports of Li-ions and electrons, which is why, at a large current rate of 1.5 C, a decent cell capacity was retained over 1000 cycles. In addition, the C 1s region spectra of the CNFPC electrodes were also performed. In a comparison to the electrode before cycling, which presented a main peak at 284.1 eV corresponding to sp<sup>2</sup> carbon (C-H) (Figure 5f), the one after the 100th discharge showed a new peak at 287.3 eV (Figure 5e), which was assigned to a combination of C—O and C=O bonds, implying the chemical stability of the electrodes.

On the basis of these discussions, the integrated CNF and carbon black system provided an effective conductive framework, which facilitated fast discharging/charging, while the porous carbon layer greatly reduced polysulfide migration, leading to excellent capacity retention. The primary results indicated that polysulfide dissolution was the reason for low capacity, and polysulfide migration was responsible for fast capacity decay. The areal capacity of Li/CNFPC battery was high. For example, at 0.5 C, the areal capacity reached 5.56 mAh cm<sup>-2</sup> over 200 cycles, which was pretty high and promising for commercial applications.

# CONCLUSIONS

We demonstrated herein an effective, low-cost method to achieve high sulfur-loading Li-S batteries with a great rate capability and an excellent long-cycle stability. The CNFPC electrode with an ultrahigh sulfur-loading of 6.7 mg cm<sup>-2</sup> and a high electrical conductivity was obtained using a simple method. The functions of each part in this unique CNFPC design were verified. The CNF current collector served as the long-range conductive framework and as a host for the soluble polysulfides while the incorporation of carbon black nanoparticles, which acted as the short-range conductive framework, further enhanced electron transport. In addition, the CNF framework had superior integrity and an improved ability to accommodate the volume changes of the active sulfur materials due to the large interspaces in this framework, which also facilitated electrolyte infiltration and thus enhanced Li-ion transport. We also found that the top layer of porous carbon film on the CNF current collector not only reduced polysulfide migration from cathode to anode, but also enhanced the integrity of the whole cathode structure. As a result, at a high current rate of 1.5 C, reversible capacities of 302 mAh g<sup>-1</sup> over 1000 cycles were achieved in such high sulfur-loading Li-S batteries. At the same time, the coulombic efficiency was always larger than 99.5%, indicating the highly reversible

capability of Li–S batteries employing CNFPC electrodes. We believe that these CNFPC electrodes fabricated using a simple method at low cost, producing Li–S batteries with high rate capability and long-cycling performance, move a step closer to Li–S battery commercialization.

#### EXPERIMENTAL SECTION

**1. Preparation of CNFPC Electrodes.** The CNF substrate used in this experiment had a thickness of ~160  $\mu$ m, an electrical conductivity of 420 S cm<sup>-1</sup>, and a density of ~0.2 g cm<sup>-3</sup>. The porous carbon layer had a thickness of ~5  $\mu$ m, and a density of ~6.6 g cm<sup>-3</sup>. According to these data, the areal loading of CNF was 3.2 mg cm<sup>-2</sup>, and the areal loading of porous carbon was 3.3 mg cm<sup>-2</sup>.

The controlled CNF paper electrode without the porous carbon layer had the same parameters of CNF, carbon black, and active sulfur materials. The soluble polysulfide catholyte was formed by chemically reacting 0.025 mol of sublimed sulfur (99.5%, Sigma-Aldrich) and 0.005 mol of lithium sulfide (Li2S, 99.98%, Sigma-Aldrich) in 10 mL of dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v). The chemical reaction was the following:  $5S + Li_2S = Li_2S_6$ . Next, 28 mg of carbon black (~150 nm, US Research Nanomaterials, Inc.) was added into the above solution and stirred for 2 h. Then, 300  $\mu$ L of polysulfide catholyte was added into a 2 cm × 2 cm CNFPC/CNF paper current collector (SGL group, the carbon company), corresponding to a carbonblack-loading of 0.23 mg cm<sup>-2</sup>, and a high sulfur-loading of 6.7 mg cm<sup>-2</sup>. Lastly, after the evaporation of DME and DOL, the prepared electrode was used for battery assembly. On the basis of the above calculation, the sulfur ratio in the whole electrode (including current collector) was 50 wt %. All of the experiments were conducted in a glovebox.

2. Material Characterization. Morphology of the CNFPC current collectors was examined by SEM, TEM, and EDX (EDS). Crystal structure characterization was conducted with a PANalytical XRD with Cu K $\alpha$  radiation between 10° and 80° at a scan rate of 0.1° s<sup>-1</sup>. Kratos Axis Ultra XPS (Kratos Analytical) with a monochromatized Al Ka X-ray source was used to analyze the surface chemistry of CNFPC electrodes. Deconvolution of the XPS spectra was performed with a Casa XPS program with Gaussian-Lorentzian functions after subtraction of a Shirley background. The pretreatments for the samples after cycling included the following several steps. First, the disassembled cathode and anode were washed with DOL solution 5 times to remove the soluble polysulfides on the surfaces and bottoms of the cathode and anode. Next, the cathode and anode were left in the glovebox for 1 day to evaporate the solution that remained. Then, the cathode and anode samples were anchored onto the SEM specimen mount holders, and placed into two separated vacuum jars for testing. Last, the samples were quickly transferred to the SEM chamber. For the XPS test, the electron gun was used to remove several nanometers of the oxidized surfaces of the samples.

3. Electrochemical Measurements. CR2032-type coin cells were used as the testing cells. Lithium foils were used as the anodes, Cellgard 2400 microporous membranes as separators, and 1.0 mol  $L^{-1}$ bis(trifluoromethane sulfonyl) imide (LiTFSI) and 0.1 mol  $L^{-1}$ LiNO<sub>3</sub> dissolved in dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v) as electrolytes. The ring lithium foil with a thickness of 20  $\mu$ m and diameter of 2.8 cm was used as the anode. LiNO<sub>3</sub> was used to form a protective film on the surface of Li-anode.<sup>50</sup> The cells were assembled in an argon-filled glovebox. The size of the electrode material was 0.9 cm  $\times$  0.9 cm, and the amount of electrolyte for each cell was about 0.04 mL. Electrochemical measurements were performed galvanostatically between 1.8 and 3.0 V at various current densities. Capacity was calculated on the basis of the weight of sulfur on the electrodes. CV experiments were conducted using a NOVA potentiostat at a scan rate of 0.1 mV s<sup>-1</sup>. EIS measurements were carried out using a NOVA electrochemical workstation in a frequency range between 100 kHz and 100 mHz at a potentiostatic signal amplitude of 5 mV. All of the CV, EIS, cycling, and rate performance were collected on Li-S batteries with an areal sulfur-loading of 6.7 mg cm<sup>-2</sup>. All experiments were conducted at room temperature.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.5b02533.

Figures showing colors of lithium polysulfides, EIS data, XRD data, EDS data, SEM images, and electrochemical performance (PDF)

# AUTHOR INFORMATION

# Corresponding Author

\*E-mail: bili@hsc.wvu.edu.

# Author Contributions

J.Y. and X.L. conceived and designed the experiments. J.Y. conducted the cathode fabrication and carried out characterization analysis for the cathodes and Li—S cells. Y.Z. helped with the TEM tests. X.L. and B.L. supervised the work. J.Y. wrote the manuscript. Technical editing was provided by B.L. H.Q., M.Y., and W. L. were involved in the discussions. All authors reviewed and approved the final manuscript.

# Notes

The authors declare no competing financial interest.

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