Ferroconcrete-Inspired Construction of Self-Supporting Li$_2$S Cathode for
High-Performance Lithium-Sulfur Batteries

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Abstract

Lithium sulfide (Li$_2$S) could avoid the disadvantage of low melting point of elemental sulfur when applied as the starting active material of lithium-sulfur batteries (LSBs), thereby facilitating its encapsulation with host matrix via high-temperature treatment to simultaneously enhance the electronic conductivity of sulfur cathodes and ameliorate the notorious shuttle effect rooted from the diffusion of dissolved lithium polysulfides in ether-based electrolytes. However, Li$_2$S is highly sensitive to moisture in the atmospheric environment. In addition, its high cost would compromise the superiority of LSBs. Herein, interconnected carbon nanofibers (CNFs) and porous carbon (PC) supported Li$_2$S (Li$_2$S@PC@CNF) has been fabricated via a carbothermal reduction strategy by selecting a cost-effective and environmentally friendly precursor, i.e., bacterial cellulose (BC) hydrogel filled with glucose and Li$_2$SO$_4$. Li$_2$S@PC@CNF could be directly applied as the cathode, thereby detouring the routinely needed slurry-casting procedure which would cause contamination or oxidation of Li$_2$S. CNFs
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derived from BC serve as a network for electron transport and meanwhile a skeleton to support the free-standing Li$_2$S@PC@CNF electrode, while glucose derived PC seamlessly connects CNFs due to the initial hydrogen bonding between glucose and cellulose, providing physical confinement for lithium polysulfides and large interface area for electrochemical reaction. Thereby, due to its unique ferroconcrete-like architecture, Li$_2$S@PC@CNF based LSBs delivers a high initial specific capacity of 700 mA h g$^{-1}$ with 500 mA h g$^{-1}$ retained after 400 cycles, and presents promising rate capability of 450 mA h g$^{-1}$ at 2 C.

1. Introduction

Lithium-sulfur battery (LSB) is considered as a promising candidate for replacing currently used lithium ion battery (LIB) due to its high theoretical energy density (2600 W h Kg$^{-1}$) as well as the resource abundance and environmental friendliness of elemental sulfur$^1$. However, its practical application has been hindered by the chronic problematic issues including poor cyclic stability, undesirable low rate capability and low Coulombic efficiency due to the poor electronic conductivity of sulfur ($5 \times 10^{-30}$ S cm$^{-1}$), the rapid diffusion of dissolved lithium polysulfides and the shuttling effects, and the inhomogeneous deposition of lithium sulfide (Li$_2$S), together with the pulverization of sulfur cathodes resulting from the volume fluctuation during lithiation/delithiation. Thus, a holistically rational design of advanced sulfur cathodes to overcome these challenges has attracted significant interests in recent years.

Toward improvement of LSB electrochemical performance, three types of sulfur sources as the starting active material, including elemental sulfur$^{2-4}$, lithium polysulfides$^{5-7}$ and Li$_2$S$^8$-$^{10}$, have also been investigated. Among them Li$_2$S, as the fully lithiated sulfur phase, might mitigate the pulverization issue
of the electrode, and more importantly, it could pair with silicon, tin, or other high capacity metal-free anodes, thus avoiding lithium dendrite growth and the resulted challenging safety issue when a lithium metal anode. Furthermore, the much higher melting point of Li$_2$S ($\text{??value if known}$) than sulfur ($\text{??Value}$) widens the choices of electrode fabrication approach. widens the fabrication technology of its composition$^{11,12}$.

Even though, Li$_2$S-based electrode is still plagued by its poor electronic conductivity and the intractable shuttle effects, similar to the elemental sulfur-based. Great efforts have been devoted to attack these problems. For example, carbonaceous materials were introduced to form composites with Li$_2$S for simultaneously enhancing the electronic conductivity of Li$_2$S cathodes and mitigating shuttle of lithium polysulfides$^{13-18}$. The high price of Li$_2$S demands exploring a low-cost production protocol. Several approaches have been investigated to produce Li$_2$S or its composites, including burning lithium in carbon disulfide$^{19}$, reacting LiH with sulfur$^{20}$ and vapor-phase atomic layer deposition method$^{21}$, among which carbothermal reduction of Li$_2$SO$_4$ is considered to be cost-effective and environmentally friendly to fabricate Li$_2$S@carbon composite$^{22-24}$. However, in most work reporting synthesis of particulate Li$_2$S composites, a routine slurry-casting procedure is requisite to prepare Li$_2$S cathode, which would cause contamination or oxidation of Li$_2$S due to the chemical instability of Li$_2$S in the air atmosphere. Therefore, free-standing Li$_2$S composite sheets should be constructed to be directly applied as the LSB cathode$^{25-27}$.

Herein, we report a three-dimensional (3D) self-supporting cathode with a ferroconcrete-like architecture for better LSB performance. It is constructed from Li$_2$S particles-decorated porous carbon (PC) materials, which are embedded in an interconnected carbon nanofibers (CNFs) scaffold (Li$_2$S@PC@CNF). Bacterial cellulose (BC) hydrogel filled with glucose and Li$_2$SO$_4$, as an economic
and environmentally friendly precursor, was used to fabricate this structure. The as-obtained Li$_2$S@PC@CNF membrane could be directly applied as the cathode without other extra steps, which otherwise would cause contamination or oxidation of Li$_2$S. In this structure, intrinsically interconnected CNFs derived from BC serve as a skeleton of the free-standing electrode and an electronic conductivity network by connecting PC together. PC facilitates charge transfer between active materials and electrolyte and confines dissolved lithium polysulfides in the cathode. With such a unique ferroconcrete-like architecture, Li$_2$S@PC@CNF, when applied as the cathode of LSBs, delivers a high initial specific capacity of 700 mA h g$^{-1}$ with 500 mA h g$^{-1}$ retained after 400 cycles, and demonstrates promising rate capability of 450 mA h g$^{-1}$ at 2 C.

2. Results and discussion

The fabrication process of Li$_2$S@PC@CNF structure is schematically illustrated in Fig. 1 (a). First, a BC hydrogel slice with the A4 paper size is pressed to a thin slice and then cut into small rectangular pieces. Li$_2$SO$_4$@glucose@BC hydrogel pieces are achieved by soaking the small BC pieces in a mixed solution of glucose and Li$_2$SO$_4$ for 30 mins. After freeze-dry, they are punched into round discs. Finally, disk-shape Li$_2$S@PC@CNF electrodes used for coin-cell assembly are attained after pyrolyzing Li$_2$SO$_4$@glucose@BC.
Fig. 1. Schematic diagrams of (a) the fabrication process of Li$_2$S@PC@CNF electrode, (b) the formation of hydrogen bonding between BC nanofibers and glucose molecules, and (c) the ferroconcrete-like structure of Li$_2$S@PC@CNF.

The digital photos of the samples at each stage in fabrication are shown in Fig. S1. Thin BC slice recovers to its original thickness after soaked in mixed solution of Li$_2$SO$_4$ and glucose, which ensures a large amount of glucose and Li$_2$SO$_4$ be uniformly absorbed on BC nanofibers. Moreover, with their abundance of hydroxyl groups, hydrogen bonds will be formed between BC nanofibers and glucose molecules and between glucose molecules themselves, as shown in Fig. 1 (b). Thus, an intimately connected structure is formed. After carbonization, the porous carbon derived from glucose will integrates firmly with the carbon nanofibers (CNFs) scaffold derived from BC (Fig. 1 (c)), forming a ferroconcrete-like structure, which will facilitate electron transport within the carbon matrix and also reaction kinetics at the interface between PC and an electrolyte. Li$_2$S@PC@CNF retained the round disc morphology of freeze-dried Li$_2$SO$_4$@glucose@BC with a slightly reduced diameter due to the evaporation of ice water in Li$_2$SO$_4$ and glucose, the loss of hydrogen and oxygen during carbonization.
of glucose and BC, and the thermal reduction reaction between Li$_2$SO$_4$ and carbon. The obtained Li$_2$S@PC@CNF round discs were promptly transferred into an argon-filled glove box for assembling cells. With a self-supporting structure of Li$_2$S@PC@CNF, current collector, polymer binder and conductive additives are not needed, further enhancing the electronic conductivity and elevating the active materials content in the sulfur cathodes.

Thermal gravimetric analysis (TGA) was conducted to reveal the reactions during the heating process of freeze-dried Li$_2$SO$_4$@glucose@BC. As shown in Fig. S2, the weight loss at around 100 °C and 240 °C is attributed to the loss of crystallization water in Li$_2$SO$_4$ and glucose, and the carbonization of glucose and BC, respectively. The generation of Li$_2$S via the carbothermal reduction reaction of Li$_2$SO$_4$ and carbon (Li$_2$SO$_4$ + C→Li$_2$S + CO$_x$) is considered occurring at 740 °C, in accordance with other publications$^{22, 28}$. Of the precursors used to produce the Li$_2$S@PC@CNF electrode, BC could be produced on an industrial scale via an economical and environmentally-friendly microbial fermentation process. The price of Li$_2$SO$_4$ is only around one third that of Li$_2$S and glucose is an abundant and common industrial precursor. Hence the protocol adopted here to fabricate the composite of Li$_2$S and carbon is economically scalable. Besides, blending of glucose and Li$_2$SO$_4$ and facile carbonization of glucose would result in an ideal encapsulation of generated Li$_2$S in carbon, thereby effectively alleviating the shuttle effect.

The microscale morphology of CNFs, Li$_2$S@PC@CNF and PC@CNF was analyzed using electron microscopies. As shown in Fig. S3, carbonized BC is composed of branched and interconnected nanofibers with a diameter of around 30 nm, making it an ideal reinforcing skeleton for a self-supporting electrode, similar to the steel bar in ferroconcrete. Previous studies indicate that carbonized BC has a high conductivity of 20.6 S m$^{-1}$, which endows it an excellent network for electron conduction$^{29}$, thus
alleviating the low conductivity issue of Li$_2$S itself. As shown in Fig. 2 (a) and 2 (b), Li$_2$S@PC@CNF is composed of interconnected CNFs anchored with lumps of porous carbon which avails the loading and encapsulation of Li$_2$S. The composition of Li$_2$S@PC@CNF was identified by the elemental mapping as shown in Fig. S4. The EDS mapping shows the homogeneous distribution of carbon and sulfur in Li$_2$S@PC@CNF, indicating that Li$_2$S distributes uniformly in the sample and “dead” clusters of Li$_2$S has been effectively avoided. There is small amount of nitrogen element dispersed in the composite, which could be attributed to the nitrogen-containing compounds left by culture media and secretions from bacteria$^{30}$. The nitrogen dopants in carbon will not only elevate the electronic conductivity of CNFs but also enhance the chemical bonding between the carbon host and lithium polysulfides$^{31, 32}$, thereby effectively inhibiting the diffusion of soluble sulfur species. TEM and HRTEM measurements were conducted to further characterize the morphology and microstructure of Li$_2$S@PC@CNF. As shown in Fig. 2 (c), the composite has a dendrite-like structure which should be derived from the conformal transformation of BC nanofibers surrounded with glucose molecules. The hydrogen bonding between glucose and BC results in seamless connection between CNFs and PC as illustrated in Fig. 1 (c). The enlarged TEM image in Fig. 2 (d) presents more clearly the dendrite-like morphology of Li$_2$S@PC@CNF. The interplanar lattice spacing of around 0.32 nm, as shown in Fig. 2 (e), is assigned to the (111) plane spacing of Li$_2$S, revealing the generation of Li$_2$S after high-temperature treatment. The selected area electron diffraction (SAED) patterns of Li$_2$S@PC@CNF (the inset in Fig. 2 (e)) are assigned to lattice planes of Li$_2$S (111), Li$_2$S (200), LiOH (101), LiOH (110), Li$_2$S (220), Li$_2$S (311) and Li$_2$S (222). The presence of LiOH might be caused by reaction of Li$_2$S with environmental moisture before the sample was transferred to the TEM chamber. This also suggests the sensitivity of Li$_2$S and indicates the criticalness of fabricating self-supporting Li$_2$S cathode to avoid the
routine time-consuming slurry-casting procedure.

Fig. 2. (a) and (b) SEM images of Li$_2$S@PC@CNF, (c) and (d) TEM images of Li$_2$S@PC@CNF, (e) HRTEM image of Li$_2$S@PC@CNF (the inset showing SAED pattern of Li$_2$S@PC@CNF), (f) elemental mapping of C, N, O and S corresponding to Li$_2$S@PC@CNF, (g) SEM image of PC@CNF.

The EDS mapping (Fig. 2 (f)) acquired with TEM imaging further illustrates the homogeneous distribution of Li$_2$S. The oxygen should be attributed to the residual oxygen in carbon or the reaction
between Li$_2$S and moisture when the sample was transferred to TEM chamber, in accordance with SAED pattern. Li$_2$S@PC@CNF was ultrasonicated in a mixture of ethanol and distilled water to remove Li$_2$S and PC@CNF was further characterized. Fig. 2 (g) shows similar morphology of PC@CNF with Li$_2$S@PC@CNF, indicating that aggregation of Li$_2$S has been effectively avoided by means of this strategy in accordance with the EDS mapping of Li$_2$S@PC@CNF. The uniform distribution of Li$_2$S is considered to improve the redox reaction kinetics, thereby enhancing the electrochemical performance of LSBs. It is worth pointing out that even after sonication, CNFs still connect PC lumps firmly, indicating that CNFs effectively serve as a reinforcing agent in Li$_2$S@PC@CNF.

The phases, compositions and crystallographic structures of samples were investigated by XRD. As shown in Fig. 3 (a), Li$_2$S@PC@CNF and PC@CNF both demonstrate one broad XRD peak at 22.4° which should be assigned to the (002) plane of graphite, implying the partial graphitization of PC@CNF\textsuperscript{33}. Besides, Li$_2$S@PC@CNF presents several other peaks which could be indexed to LiOH (001), Li$_2$S (111), Li$_2$S (200), LiOH (101), LiOH (110), Li$_2$S (220), Li$_2$S (311) and Li$_2$S (222), in accordance with SAED pattern. The appearance of LiOH could be attributed to the reaction between Li$_2$S and moisture during the process of XRD measurement. As shown in Fig. S5, if Li$_2$S@PC@CNF was covered with transparent adhesive tape during the XRD measurement, peaks corresponding to LiOH were not found. Raman spectrum presents two broad peaks at around 1350 and 1580 cm$^{-1}$ which could be attributed to disorder induced D-band and graphitic G-band, respectively, as shown in Fig. 3 (b), implying successful carbonization of BC and glucose after high-temperature treatment. The presence of carbon and Li$_2$S in Li$_2$S@PC@CNF was further confirmed by the peaks at binding energy at 161.9 and 55.4 eV in XPS spectra, respectively, as shown in Fig. 3 (c), (d) and Fig. S6.
Nitrogen adsorption-desorption was conducted to measure the specific surface area and pore diameter distribution for Li$_2$S@PC@CNF and PC@CNF (Fig. 3 (e, f)). PC@CNF has a specific surface area of around 137 m$^2$ g$^{-1}$ and a pore volume density of 0.19 cm$^3$ g$^{-1}$, with majority of pore size less than 1 few nanometers, which is conducive for retarding lithium polysulfides diffusion. Li$_2$S@PC@CNF presented a much lower specific surface area ($\sim$ 19 m$^2$ g$^{-1}$) and a lower pore volume density (0.10 cm$^3$ g$^{-1}$) because most pores were now filled by Li$_2$S.

Fig. 3. (a) XRD pattern of Li$_2$S@PC and Li$_2$S@PC@CNF, (b) Raman spectrum of Li$_2$S@PC@CNF, (c) Li 1s and (d) S 2p XPS spectra of Li$_2$S@PC@CNF, (e) Nitrogen adsorption-desorption isotherms and (f) pore size distribution for PC@CNF and Li$_2$S@PC@CNF.

The freestanding Li$_2$S@PC@CNF or Li$_2$S@PC@CNF/CNF round disc was directly applied as the cathode and a lithium foil as the anode to assemble coin cells and their electrochemical performance was examined by electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and
galvanostatic charging/discharging (GCD) measurement. As shown in Fig. 4(a), the Nyquist plots of cells based on both samples are composed of a single depressed semicircle in the high-medium frequency range and an inclined line in the low-frequency region corresponding to the charge-transfer resistance ($R_{ct}$) and Warburg impedance, respectively. The cells based on Li$_2$S@PC@CNF/CNF presents a lower $R_{ct}$ than that based on Li$_2$S@PC@CNF, indicating faster charge transfer process for the former one. In addition, cells based on Li$_2$S@PC@CNF/CNF and Li$_2$S@PC@CNF demonstrate almost the same slope of the inclined line, indicating that the extra CNF layer does not retard lithium ion diffusion. The first cycle investigated by CV and GCD are shown in Fig. S7. The irreversible peak at 3.2 V in the CV curve is related to the initial activation of Li$_2$S, which could be ascribed to the poorly electronic and ionic conductivity of Li$_2$S. An initial charge barrier was observed at 3.3 V (Fig. S7 (b)), in accordance with the initial oxidation peak in CV curve. Thus, the cells were charged to 3.8 V in the first cycle to activate Li$_2$S, and they were then cycled between the voltage window of 1.7 ~2.8 V in the following cycles. Both the irreversible peak and the initial charge barrier are lower than many reported values [ref], implying the effectively reduced activation barrier for Li$_2$S in our structure. This improvement could be ascribed to the enhanced electronic conductivity of the cathodes and ideal encapsulation of Li$_2$S particles.
Fig. 4. (a) Nyquist plots of Li$_2$S@PC@CNF and Li$_2$S@PC@CNF/CNF electrodes, (b) CV profiles of Li$_2$S@PC@CNF electrode, charge-discharge profiles corresponding to (c) Li$_2$S@PC@CNF and (d) Li$_2$S@PC@CNF/CNF, (e) cycling stability and (f) rate capability of Li$_2$S@PC@CNF and Li$_2$S@PC@CNF/CNF electrodes.

After the initial charging/discharging cycle, the CV curves and charging/discharging profiles resemble those of LSBs with elemental sulfur as the starting active material. Fig. 4 (b) shows the CV curves corresponding to the 2$^{nd}$, 3$^{rd}$, and 4$^{th}$ cycle. Two anodic peaks and two cathodic peaks could be observed. The two cathodic peaks at 2.3 and 2.1 V represent the conversion from S$_8$ to lithium polysulfides and then to Li$_2$S, while the anodic peaks show the reverse process. The curves overlapped each other well from the 3$^{rd}$ cycle, implying excellent reversible character. The charge-discharge profiles in the subsequent cycles are shown in Fig. 4 (c, d). All the discharging profiles contained a high plateau (2.3 V) and a low plateau (2.1 V). The cells based on Li$_2$S@PC@CNF shows an over-potential of 230 mV, while that based on Li$_2$S@PC@CNF/CNF shows an over-potential of only 215 mV, implying that
CNF could effectively enhance the electronic conductivity of the cathode and ameliorate the shuttle effect of lithium polysulfides.

Fig. 4 (e) shows the cycling performance of two samples at 0.2 C. Cells based on Li₂S@PC@CNF and Li₂S@PC@CNF/CNF deliver an initial specific capacity of 550 and 700 mA h g⁻¹, respectively. They present a high cycling stability with a specific capacity of 400 and 500 mA h g⁻¹ retained after 400 cycles. Besides, they hold a high Coulombic efficiency of around 99 % during the charging/discharging process, which could be ascribed to the excellent electronic conductivity of the electrodes and the effective inhibition of lithium polysulfides diffusion from PC and CNF. Fig. S8 shows the charging/discharging performance of PC@CNF within the voltage widow of 1.7~2.8 V. It delivers a small specific capacity of only several mA h g⁻¹, implying a negligible capacity from lithiation/delithiation of PC@CNF, because lithiation/delithiation within carbon mainly occurs at the potential of below 1.0 V.

The rate capability of cells based on Li₂S@PC@CNF/CNF is shown in Fig. 4 (f). It delivers a specific capacity of 700, 640, 550 and 450 mA h g⁻¹ at 0.2 C, 0.5 C, 1 C and 2 C, respectively. Especially when the charging/discharging rate is switched to 0.2 C again, the capacity recovers without loss, implying a good rate capability, which could be attributed to the unique architecture of Li₂S@PC@CNF. Fig. S9 shows the charge-discharge profiles under various rates. The polarization voltage increases with the charging/discharging rate increasing.

Although Li₂S@PC@CNF demonstrates excellent electrochemical performance, better Li₂S cathode could be constructed via the strategy we provide herein. An organic precursor with abundant nitrogen, phosphorus or boron element could be applied to substitute glucose to generate heteroatom-doped carbon so that stronger chemical bonding could be established between sulfur species and carbon.
host, thereby further elevating the usage rate of sulfur species. Besides, larger specific surface area and higher pore density are expected to generate in the polymer-derived carbon, thereby physically confining sulfur species. Synergistically physical and chemical immobilization of sulfur species are expected to be established via selecting other polymer precursors in our future work.

3. Conclusions

By pyrolysis of freeze-dried Li$_2$SO$_4$@glucose@BC, we have prepared porous carbon encapsulated Li$_2$S embedded in interconnected carbon nanofibers. When directly applied as a sulfur cathode, Li$_2$S@PC@CNF demonstrated excellent cycling stability and rate capability, which could be ascribed to its unique architecture. The CNF served not only as reinforcing agent for the electrode but also as a network for electron conductivity. And PC firmly attached on CNF provided an ideal interface for fast reaction kinetics. PC and CNF jointly ameliorate the shuttle of lithium polysulfides via physical confinement. Therefore, considering its excellent performance, together with their low cost and simple fabrication process, Li$_2$S@PC@CNF is a promising material for sulfur electrodes toward the development of practical LSBs.

4. Experimental methods

4.1 Fabrication of Li$_2$S@PC@CNF. A bacterial cellulose (BC) hydrogel slice with A4 paper size was first soaked in distilled water for three days to remove the acid solution, which was then pressed to a very thin slice and cut into rectangular pieces with an area of around 9 cm$^2$. The rectangular pieces were soaked in 180 mL solution containing 3 g glucose and 1 g Li$_2$SO$_4$. After they recovered to their original thickness, the pieces were freeze-dried to attain Li$_2$SO$_4$@glucose@BC, which were punched into round discs. They were then pyrolyzed at 800 °C for 2 hours in a furnace with a heating rate of 2 °C
min\(^{-1}\) under argon atmosphere to obtain Li\(_2\)S@PC@CNF. The PC@CNF sample was attained by first soaking Li\(_2\)S@HC@CNF in a mixture of distilled water and ethanol (1:2 ration V/V) and then drying in vacuum oven at 60 °C. Li\(_2\)S@PC@CNF/CNF was achieved by pyrolysis of freeze-dried Li\(_2\)SO\(_4\)@glucose@BC disc cling with a thin BC film.

4.2 Characterization. A field emission scanning electron microscope (FEI Inspect F50) and a transmission electron microscope (ZEISS Libra 200 FE) were used to characterize the morphology and structure of the Li\(_2\)S@PC@CNF and PC@CNF. X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5000 Versa Probe X-ray photoelectron spectrometer with an excitation source of Al K\(_{\alpha}\) radiation (1486.6 eV). X-ray powder diffraction (XRD) was carried out on a Bruker D2 PHASER X-ray diffractometer. Raman scattering spectra were recorded with an Andor SR-500i Raman microscope spectrometer with an excitation laser beam wavelength of 532 nm. N\(_2\) sorption analysis was carried out at AutoChem 2920. The content of Li\(_2\)S in Li\(_2\)S@PC@CNF was calculated by mass difference between Li\(_2\)S@PC@CNF and its corresponding PC@CNF. TGA was conducted on xxx. During the TGA measurement for Li\(_2\)S@PC@CNF, the sample was heated from room temperature to 300 °C under N\(_2\) flow and then switched to air from 300 to 900 °C with a heating rate of 5 °C min\(^{-1}\). For the TGA measurement of the freeze-dried Li\(_2\)SO\(_4\)@glucose@BC, the sample was heated from room temperature to 1000 °C under argon flow with a heating rate of 5 °C min\(^{-1}\).

4.3 Electrochemical measurements. CR2032 coin cells were assembled to evaluate the electrochemical performance of Li\(_2\)S@PC@CNF and Li\(_2\)S@PC@CNF/CNF. A round disc of Li\(_2\)S@PC@CNF or Li\(_2\)S@PC@CNF/CNF was applied as the cathode, and a lithium foil was applied as the anode. A Celgard separator was placed between the cathode and anode, on which 30 μL electrolyte containing lithium bis(tri-fluoromethanesulfonyl)imide (1 M) and LiNO\(_3\) (1 wt%) in 1, 2-
dimethoxyethane (DME) and 1, 3-dioxolane (DOL) (1:1 by volume) was dipped. To test the lithiation/delithiation capacity of PC@CNF, it was used as the cathode and the other procedure was the same. The assembling was carried out in an argon-filled glove box with O₂ and H₂O less than 0.1 ppm.

The cyclic voltammetry (CV) profiles and the electrochemical impedance spectra (EIS) of the assembled cells were obtained using an electrochemical workstation. The initial CV profile was recorded with a scan rate of 0.01 mV s⁻¹ from open circuit voltage to 3.8 V versus Li⁺/Li. Then CV measurements were conducted with a scan rate of 0.02 mV s⁻¹ between 1.7~2.8 V versus Li⁺/Li. Galvanostatic charging/discharging tests were performed using a LAND CT-2001A instrument. The cathode was first charged to 3.8 V versus Li⁺/Li at 0.1 C to activate Li₂S and then discharged/charged between 1.7~2.8 V to test its cycling and rate performance. The EIS was taken on a CHI660E electrochemical workstation in the frequency range of 1 MHz to 0.1 Hz with AC voltage amplitude of 5 mV versus the open-circuit voltage. Specific capacity values were calculated based on the mass of sulfur in the cathode unless otherwise specified.

Acknowledgements

The authors would like to appreciate Zhejiang Provincial Natural Science Foundation of China for providing financial support (Grant No. LY19E020011).

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