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3D-hybrid material design with electron/lithium-ion dualconductivity for high-performance Li-sulfur batteries



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HIGHLIGHTS

- A novel 3D-hybrid Sulfur based composite is proposed.
- EDA-functionalized GO/CNT hybrid (N-GO/CNT) works as 3D conductive frame network.
- Electrons/Li-ions-conductive (dual-functional) SPANI works as the coating layers.
- Remarkable electrochemical performances of S@N-GO/CNT@SPANI were obtained.
- The mechanism of high rate performances was studied.

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ABSTRACT

We report a novel 3D-hybrid cathode material with three-dimensional (3D) N-GO/CNT framework to load sulfur (77.6 wt %), and sulfonated polyaniline (SPANI) of coating layer. Used as a cathode material, it possesses a high capacity (1196 mAh g⁻¹@0.3 A g⁻¹@1.6 mg cm⁻²), excellent charging-discharging rate (680 mAh g⁻¹@7.5 A g⁻¹) and long-life performance (maintaining 71.1% capacity over 450 cycles), which is mainly attributed to the benefits of excellent electronic/Li-ionic dual-conductivity and confinement effect of the 3D-hybrid N-GO/CNT framework coated by self-doping conducting polymer SPANI. Thus, a 3D sulfur cathode modified with electronic/Li-ionic dual-conduction network can significantly enhance the electrochemical performance and stability, and this novel type of material is very promising for commercial applications that require high energy and power density, long life, and excellent abuse tolerance.

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1. Introduction

Secondary Li-ion batteries play a very important role in energy storage and conversion. However, the currently used cathode materials based on the lithiated transition-metal oxide and phosphate are not able to meet the increasing requirements of electric vehicles, hybrid electric vehicles and other portable electronics owing to limited theoretical specific capacity and energy density [1]. Thus, developing advanced materials as Li-ion cathodes is an urgent task. With substantial merits of extremely high theoretical specific capacity (1675 mAh g⁻¹), superior energy density (2600 Wh kg⁻¹),

widespread availability and environmental friendliness, sulfur has been considered as the most promising candidate as the cathode material for the next-generation rechargeable battery [2–4]. However, several obstacles associated with sulfur electrode materials have hampered their commercialization, including: (i) the insulating nature and insolubility in electrolytes of sulfur species (S, Li_2S and Li_2S_2) impede the full utilization of sulfur and limit specific capacity and rate capability; (ii) the dissolution of polysulfides in electrolytes and subsequent "shutting effect" during cycling cause fast capacity fading; (iii) large volume change in the chargedischarge processes induces the mechanical damage of electrode [5–9].

To address these issues, considerable efforts have been devoted to dealing sulfur with the conductive nanocarbons including carbon nanospheres [5,8], graphene oxide sheets [10-12], carbon nanotubes [6,13,14], and meso-/microporous carbons [15].



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Graphene, a typical two-dimensional carbonaceous material, has now been a good choice to prepare carbon/sulfur composites due to huge surface area and outstanding electronic conductivity. Through the controllable preparation of graphene structure, the composite provides a huge space conductive network that not only improves the electronic conductivity of the electrode but also accommodates volume expansion during cycling. What's more, several researchers found that the introduction of polar chemistry groups (such as $-NH_2$ [10], -F [16] and $-PhSO_3$ [17]) are able to trap polysulfides and mitigate the dissolution of polysulfides ianto electrolytes. Therefore, to fabricate a multi-dimension conductive network functionalized by polar chemistry groups may enhance the comprehensive electrochemical performance of sulfur carbon composites.

Another strategy to overcome the obstacles of sulfur cathode is to modify the surface properties of sulfur-carbon composites with conductive polymer such as polyaniline (PANI) [18], polypyrrole [19], polydopamine [20], Poly (3,4-ethylenedioxythiophene) [21], etc. The coating polymers can efficiently suppress polysulfide dissolution and improve the stability of sulfur cathode during electrochemical cycling because of the strong chemical interactions between polar functional groups and polysulfides. Although these conductive polymers can enhance the conductivity of cathode materials and inhibit diffuse of polysulfides, there still exist some issues such as the low Li⁺ conductivity and electronic conductivity depended on the doping condition, constraining the rate performance of cathode composites.

Sulfonated polyaniline (SPANI), a novel self-doped water soluble conducting polymer [22–28], has been widely utilized in fabricating supercapacitor [25] and multilayer hetero-structure light emitting diode devices [29], while no example about SPANI used in rechargeable lithium ion batteries was found. Compared with PANI, which is easy to become insulating for $pH \ge 3$, SPANI is capable of self-doping without external protonic doping and maintain high activity over a wide range of pH values by introducing a -SO₃H group regarded as a strong acid on PANI chain [22]. Moreover, the solubility of SPANI and the good environmental stability is highly improved by the presence of the polar –SO₃H groups on the phenyl rings. Especially, previous studies have revealed that -SO₃H of SPANI can be translated into non-protonated sodium salt -SO₃Na [23], in which case $-SO_3$ is able to serve as the lithium ion transmission sites to own ion conductivity. Based on these, the selfdoped SPANI may have the potential use in secondary lithium ion batteries.

Differing from the previous reports about absorption of polysulfides [30,31] or high-rate S cathodes [32,33], this work reported a novel 3D-hybrid material with three-dimensional (3D) N-GO/CNT framework to load sulfur (77.6 wt %), and sulfonated polyaniline (SPANI) of coating layer. By using these novel composites as cathode materials for Li-sulfur batteries, the high caposities as called a materials for E bands barrens, e^{-2} , excellent charging-discharging rate (680 mAhg⁻¹@7.5 A g⁻¹) and long-life (maintaining 71.1% capacity over 450 cycles), were obtained. These results are mainly attributed to the 3D-hybrid N-GO/CNT framework coated by self-doping conducting polymer SPANI, which owns excellent electronic/Li-ionic dual-conductivity as well as effective confinement effect of polysulfide intermediates. Thus, such a 3D sulfur cathode modified with electronic/Li-ionic dual-conduction network can significantly enhance the electrochemical performance and stability, and this novel type of material is very promising for commercial applications that require high energy and power density, long life, and excellent abuse tolerance.

2. Experimental

Synthesis of GO and N-GO/CNT hybrid: GO was prepared from natural graphite flake (-325 mesh, Alfa Aesar) by a modified Hummars' method using NaNO₃, KMnO₄ and concentrated H₂SO₄. In a typical procedure, 50 mg Carboxylic MWCNTs were dispersed in 100 mL distilled water by ultrasonic treatment for 30 min. After that, 100 mg freshly prepared GO was added, and then sonicated for another 1 h. Subsequently, the mixture of the obtained dispersion solution and 200 µL ethylenediamine (EDA) was heated at 75 °C for 6 h in a sealed vessel to obtain the N-doped GO/CNT hybrid.

Synthesis of S@N-GO/CNT@SPANI hybrid: Firstly, for the synthesis of S@N-GO/CNT hybrid, Na₂S₂O₃·5H₂O (7.45 g, 30 mmol) was added into fresh N-GO/CNT suspension (the above resultant suspension was diluted to 150 mL) under vigorous stirring, followed by adding HCl (60 mL, 1 M) dropwisely in 1 h. After stirring for 3 h, the products were filtered and washed several times with distilled water until the effluent became neutral. Subsequently, to fabricate S@N-GO/CNT@SPANI hybrid, S@N-GO/CNT hybrid were dispersed in HCl (50 mL, 1 M). After stirring vigorously for 3 h, aniline (0.75 mmol) and metanilic acid (0.75 mmol) were dissolved into above suspension, followed by slowly adding 1.5 mmol of ammonium persulfate (APS) under N2 gas and stirring for 24 h. The obtained hybrids were filtered and rinsed several times with distilled water, and then dried at 50 °C for 24 h in vacuum oven. In contrast, S@N-GO/CNT@PANI hybrid was synthesized in the same method with 1.5 mmol aniline instead of aniline (0.75 mmol) and metanilic acid (0.75 mmol).

Material characterization: The sample structures were characterized with the scanning electron microscopy (ZEISS Supra 55, Oxford X-Max 20, 20 kV) and Transmission electron microscope (HRTEM, JEM-100F, 200 kV) as well as Powder X-ray diffraction (XRD, Bruker D8 Advance diffractometer using Cu K α). Thermogravimetric analysis (TGA) data was collected on a TGA/DSC system at a heating rate of 10 °C/min under nitrogen flow. Raman spectrum was recorded by iHR 320. The electrical conductivity was measured by a standard four-point probe resistivity measurement system.

Electrochemical measurement: The working electrodes were prepared by mixing a sulfur based-material, carbon black and PTFE in isopropanol with a weight ratio of 6:3:1 through grinding in a mortar. Then the mixtures were pressed into rounds and dried at 60 °C for 24 h in the vacuum oven. The 2032 coin-type cells were finally assembled in an Ar-filled glovebox, using pure lithium foil as anode, cell grand 2400 as separator, and 1 M LiTFSI containing 0.3 M LiNO₃ in DOL/DME as electrolyte. The galvanostatic discharge/charge tests were performed at diverse current densities within a cut-off voltage window of 1.5–3.0 V. The cyclic voltammetry (CV) results were conducted by a CHI 660 E electrochemical workstation between 1.5 and 3.0 V. The electrochemical impedance measurements were carried out over the frequency range from 0.1 to 10^5 Hz.

3. Results and discussion

The synthesis scheme of 3D S@N-GO/CNT@SPANI hybrid is shown in Fig. 1. Firstly, GO and carboxylic CNTs were mixed in the deionized water by ultrasonic treatment to obtain homogeneous suspension. The abundant oxygen groups in GO and CNTs react with ammonium in EDA to gain the 3D porous structure of N-GO/ CNT hybrid, which can be observed from SEM image (Fig. 1b) and pore structure analysis of N₂ absorption test (Fig. S1). TEM image of the hybrid (Fig. S2) further proves that the undesired GO nanosheets agglomeration can be physically avoided and a homogeneous and synergistic 3D carbon network is formed due to the supporting role of CNT between GO nanosheets. Secondly, nano-sulfur from disproportionated reaction of Na₂S₂O₃ in the acidic environment was uniformly deposited to the 3D pores of N-GO/CNT hybrid, which can be validated by SEM image of S@N-GO/ CNT and elemental sulfur mapping in Fig. 1c (element mapping of C. N and O are shown in Fig. S3). Finally, the 3D S@N-GO/CNT hybrid was uniformly coated by self-doped SPANI polymer from the in-situ copolymerization of aniline and metanilic acid. The SEM image of S@N-GO/CNT@SPANI in Fig. 1d displays smooth and light bright surface, suggesting the existence of polymer coating on the surface of 3D hybrid. Therefore, we can assure that nano-sulfur precipitated into this 3D matrix with good contact with the conductive framework can perform excellent electrochemical performance and 3D framework with polymer coating can restrain the shutting of nanosulfur to maintain long life cycle.

The high-resolution TEM and elemental mapping images of the as-prepared S@N-GO/CNT@SPANI are shown in Fig. 2a. It can be observed that the N-GO/CNT in the as-prepared hybrid maintains a 3D scaffold, and nano-sulfur is uniformly distributed onto the interspaces of the 3D scaffold. In addition, the SPANI polymer layer can be observed by the time-varying TEM image due to the instability of SPANI in high voltage. To further prove the existence of SPANI layer on S cathode, the novel hybrids S@GO/CNT@SPANI and S@GO/CNT (which means GO/CNTs hybrids was not functionalized by EDA) was synthesized and the energy-spectrum scanning of SEM was conducted (Fig. S4 and Fig. S5). It was quite clear that nitrogen element of S@GO/CNT@SPANI was uniformly distributed throughout the hybrid while no N element was observed in S@GO/ CNT, suggesting that the S@GO/CNT hybrid was covered by the polymer SPANI. X-ray diffractions (XRD) are shown in Fig. 2b. It can be observed that GO exhibits a strong peak at approximately 11°, corresponding to (002) crystal face of carbon. In GO/CNT hybrid, the peak shifts to 10° and broadens, indicating that CNTs are intercalated into the interlayers of GO to prevent the GO agglomeration again. Comparing with the former GO/CNT, the peak of N-GO/CNT further migrates and widens, which is attributed to the interlamellar spacing change along with the EDA insertion under the reaction of amino with oxygen groups. The XRD patterns of S@N-GO/CNT@SPANI show the pronounced peaks which match well with pure sulfur, assigning to the orthorhombic phase [10] of sulfur with high crystallinity (other sulfur-loaded samples including S@N-GO/CNT, S@N-GO/CNT@PANI are shown in Fig. S6). Furthermore, sulfur contents of hybrids were carried out using TG (Fig. 2c). After coating SPANI, the sulfur loading in S@N-GO/CNT@SPANI hybrid is up to 77.6 wt%, comparable to the most of the reported sulfur carbon compounds.

In order to investigate polymer coating on the surface of the 3D hybrid, Fourier transform-infrared spectroscopy (FTIR) was carried out, as shown in Fig. 2d. From FTIR spectra of S@N-GO/CNT@SPANI hybrid, the typical stretching vibrations are obtained. The peak at 1034 cm⁻¹ due to S=0 stretching confirms the presence of sulphonate in the SPANI [34]. In a typical FTIR spectrum, the bands at around 1299 cm^{-1} and 1137 cm^{-1} are assigned to the stretching vibration of C–N of aromatic amine and polaron CN^{+} in the proton-doping quinonoid structure, respectively.[25, 35] Two characteristic stretching corresponding to the stretching vibration of N = Q = N of quinonic rings and N-B-N of benzenic rings at 1574 cm⁻¹ and 1495 cm⁻¹, respectively, are also successfully observed [18,25,34]. These results are furtherly confirmed by the FTIR spectra of pure copolymer SPANI (Fig. S7), in which the existence of the peak at 1034 cm⁻¹ reveals the formation of the copolymer SPANI, although self-doped SPANI owns the similar absorption spectra with partly doped PAN (HCl). Therefore, all of the results suggest that SPANI rather than PANI is successfully formed on the surface of the S@N-GO/CNT hybrid.

The electrochemical performance of 3D S@N-GO/CNT@SPANI hybrid was firstly studied by cyclic voltammetry (CV) using coin cells. Fig. 3a shows the CV curves of the Li–S cell with S@N-GO/CNT@SPANI cathode at a scan rate of 0.2 mV s⁻¹. During the first cycle, two pronounced reduction peaks are clearly observed, which can be ascribed to the multistep reduction mechanism of elemental sulfur [4,9]. Specifically, the first peak centered around 2.26 V is generally attributed to the reduction of the S₈ ring and the formation of Li₂S₈, while the peak at 2.01 V is owing to the further reduction of the higher polysulfides (Li₂S_n, $4 \le n \le 8$) to the lower polysulfides (Li₂S_n, $n \le 3$). The anodic peak at 2.49 V is associated with the formation of Li polysulphides (Li₂S_x, $2 < x \le 6$) [9]. As cycling proceeds, the anodic and cathodic peak currents decrease slightly in intensity. The CV curves at subsequent cycles show good



Fig. 1. (a) Synthesis scheme of 3D S@N-GO/CNT@SPANI hybrid, (b-d) SEM images of N-GO/CNT, S@N-GO/CNT and S@N-GO/CNT@SPANI hybrids.



Fig. 2. Basic characteristics of 3D S@N-GO/CNT@SPANI hybrid: (a) TEM image, (b) XRD patterns, (c) TG curves, (d) FTIR spectra.

reproducibility with excellent overlapping of all the peaks, indicating relatively good capacity retention.

The charge/discharge profiles of the 3D S@N-GO/CNT@SPANI hybrid electrode at current density of 300 mA g⁻¹ are depicted in Fig. 3b. Two well-defined discharge plateaus and one charge plateau is consistent with the peaks in the CV plot. For comparison, the typical charge-discharge curve of S@N-GO/CNT@SPANI cathode with 1.0 and 1.6 mg cm^{-2} were studied. It can be observed that the specific capacity of cathode with 1.6 mg cm⁻² at 300 mA g⁻¹ is 1196 mAh g^{-1} , and the specific capacity of 1.0 mg cm⁻² is more close to the theoretical capacity of pure sulfur. The cycling performance and rate capability of 3D S@N-GO/CNT@SPANI hybrid were further investigated. Fig. 3c shows that the reversible specific capacities of 1377, 1040, 892, 744 and 527 mAh g^{-1} are obtained at current densities of 0.3, 0.75, 1.5, 3, 7.5 A g^{-1} , respectively. Although electrochemical polarization with the increase of charge/discharge current from 0.3 A g⁻¹ to 7.5 A g⁻¹ increase slightly, two typical discharge plateau can be clearly observed (Fig. S8). Especially, through multiple rate cycle, the capacity of 3D S@N-GO/ CNT@SPANI hybrid can be able to return back to 826 mAh g⁻¹ at 1.5 A g⁻¹. Compared to S@N-GO/CNT@PANI, S@N-GO/CNT and pure Sulfur, such 3D S@N-GO/CNT@SPANI hybrid possesses higher reversible capacity and more excellent high-rate performance.

Fig. 3d shows the cycling performances of the hybrids at current density of 1.5 A g⁻¹. It shows that after 200 cycles the S@N-GO-CNT@SPANI hybrid exhibits higher capacity (718.2 mAh g⁻¹) than other hybrids, indicating a better cycling stability of S@N-GO-CNT@SPANI at a medium current density. The long-term cycling performances at an ultrahigh current density of 7.5 A g⁻¹ are shown in Fig. 3e. It can be seen that the initial capacity of S@N-GO/CNT@SPANI cathode is 680 mAh g⁻¹, which is higher than that of other cathodes. Instead of fast initial capacity fade, there is a slow increase in capacity during the initial ~50 cycles, suggesting the

process of stabilization and activation, which is ascribed to the electrolyte infiltration and the re-distribution of the active materials on the interlayer surface [30,36]. More importantly, even after 450 cycles, its capacity and retention are 483 mAh g⁻¹ and 71.1% respectively, indicating a more excellent cycling stability than that of other hybrids and the previous S@GO/CNT composites (losing 20% after 100 cycles compared with an initial capacity) [32]. The excellent high-rate stability of the S@N-GO/CNT@SPANI hybrid is attributing to the confinement effect of the 3D conductive mechanical structure and the dual-functional coating layer SPANI.

To further clarify mechanisms behind the excellent electrochemical performances, the galvanostatic curves of the hybrids during the initial charge/discharge cycle at 0.3 A g^{-1} are performed in Fig. 4a. It can be observed that 3D S@N-GO/CNT@SPANI hybrid exhibits the minimum electrochemical polarization, suggesting the better kinetic process, whose result is consistent with that of the EIS spectra. In Fig. 4b, the EIS spectra of both pure Sulfur and S@N-GO/CNT cathodes show one semicircle in the high-frequency region corresponding to charge transfer resistance (R_{ct}) at the sulfur/ electrolyte interface. Obviously, the S@N-GO/CNT cathode has less R_{ct} than that of pure Sulfur cathode, which is attributed to the enhanced conductivity through the close contact of sulfur and N-GO/CNT framework. Different from the formers, the EIS spectra of hybrids with polymer coating show two semicircles, which is assigned to the charge transfer resistance at the sulfur/polymer coating (R_{ct1}) and polymer coating/electrolyte (R_{ct2}) interfaces. It can be observed that the $R_{ct} \left(R_{ct} = R_{ct1} + R_{ct2} \right)$ of the hybrid with SPANI coating reaches the minimum, indicating S@N-GO/ CNT@SPANI hybrid provides the best electrical conductivity. Furthermore, the calculated Li-ionic diffusion coefficient of S@N-GO/CNT@SPANI hybrid is 1.22×10^{-12} cm² s⁻¹ higher than $1.11 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ of S@N-GO/CNT@PANI, suggesting S@N-O/ CNT@SPANI hybrid possesses faster Li⁺ transfer rate (Seeing



Fig. 3. Electrochemical performances of the 3D sulfur hybrids: (a) CV curves of 3D S@N-GO/CNT@SPANI hybrid at 0.2 mv s⁻¹, (b) the typical charging-discharging profiles of 3D S@N-GO/CNT@SPANI hybrid with ~1.0 and ~1.6 mg cm⁻², (c) rate performances of four kinds of 3D sulfur hybrids, (d, e) cyclic performances of different 3D sulfur hybrids at 1.5 and 7.5 A g⁻¹.

Fig. S9). More importantly, after activating for 20 cycles, the charge transfer resistance and Warburg impedance of the S@N-GO/CNT@SPANI decrease significantly and just slight increase is observed within subsequent 50 cycles (Fig. S10), suggesting that the 3D conducting frameworks coated by the SPANI can provide optimized electron and ion transfer pathways for inside sulfur molecules.

Based on the above mention, remarkable electrochemical performances can be ascribed to the synergistic structure of the hierarchical 3D conductive networks and the dual-functional membranes in S@N-GO/CNT@SPANI hybrid. Fig. 4c depicts the scheme of charge transfer process of S@N-GO/CNT@SPANI hybrid. Firstly, N-GO/CNT constructs a 3D highly conducive nanocarbon network, and elemental sulfur is homogeneously distributed in the multidimensional structure. Unlike the reported porous carbonconfine sulfur hybrid, the N-GO/CNT structure not only provides high electronic conductivity, but also exhibits a more open 3D structure which is contributed to promoting electrolytes infiltration and facilitate diffusion of lithium ion for sulfur as reported [37]. Furthermore, besides improved charge transport, the 3D hierarchical nanocarbon network show good physical confinement of soluble polysulfide intermediates, that contributes to good battery performances. The self-doped SPANI as the coating layer consists of synergistic structure with the inner 3D hierarchical nanocarbon



Fig. 4. (a) First charging-discharging curves of four kinds of 3D sulfur hybrids, (b) EIS curves, (c) schematic diagram for electron and ion transferring mechanism, and (d) the typical charging-discharging curves of S@N-GO/CNT@SPANI cathodes with high sulfur loading compared with the sulfur cathode.

network, which plays a role of conductive polymer to provide increased conductive areas and also enhance the physical confinement significantly. What's more, SPANI plays a role of conductive bridges among different conductive nanocarbons and sulfur, and exhibits improved electrical conductivity because of increased electrical contact sites. Simultaneously, deriving from the introduction of -SO₃H on the polymer, the S@N-GO/CNT@SPANI hybrid shows faster ion transport mainly because -SO3 can behave as the lithium ion transmission sites [38-41]. To validate the enormous advantages of the self-doped SPANI, the electronic conductivity and ion conductivity are investigated as shown in Fig. S11. It is clearly observed that the electronic conductivity and ion conductivity of SPANI, corresponding to 0.16 S cm^{-1} and 1.2×10^{-4} S cm⁻¹ respectively at Li-ion situation, are higher than those of partly H⁺-doped PANI. Different from PANI (whose conductivity can be affected by the H⁺-doping level), electric conductivity of SPANI is almost independent of PH of the external medium in a pH range (pH < 7.5 [23]) due to $-SO_3H$ on the polymer chains serve as an intramolecular dopant to contribute the stability. Furthermore, the existence of -SO₃- can improve the compatibility

between the hybrid and the polar electrolytes and promote lithium ion transport as the lithium ion transmission sites. Fig. S12 presents the cycling performances of SPANI. At 0.06 mA g^{-1} , the capacity of SPANI is ~4 mAh g^{-1} from 1.5 to 3.0 V. The 1st, 100th, 200th, 500th, 1000th curves of SPANI is shown in the inset of Fig. S12, revealing the good stability of SPANI.

As is known to all, the active material loading is a crucial factor not only for the academic investigation but also the industrialization of Li–S batteries in the future. The S@N-GO/CNT@SPANI cathode with high loading (~3.3 mg cm⁻²) operated in the Li–S batteries at 75 mA g⁻¹ (seen in Fig. 4d). Compared with the charging-discharging curve of sulfur cathode at the same loading weight, the typical charging-discharging curves from the 1st cycle to the 3rd cycle shows the much lower over-potential and higher reversible capacity (824.1 mAh g⁻¹). When the cathode is thicker, the advantages of S@N-GO/CNT@SPANI become more outstanding, due to the excellent electronic and Li-ionic conductivity of 3Dframeworks with N-GO/CNT coated by SPANI from inside out. Thus this novel design will play a significant role in the development of cathode with high sulfur loading.

4. Conclusions

In summary, we demonstrated the superiority of the novel 3Dhybrid cathode material with three-dimensional N-GO/CNT framework and SPANI as coating layer. The N-GO/CNT structure not only provides enough space to accommodate sulfur but also exhibits smooth electron and ion transport high electronic conductivity. Meanwhile, the conductive polymer SPANI as the coating layer consists of synergistic structure with the inner 3D hierarchical nanocarbon network. On the one hand, SPANI further improves electron and ion transport of S@N-GO/CNT@SPANI hybrid because of itself electronic/Li-ionic dual-conductivity. On the other hand, it leads to improved physical confinement of polysulfide intermediates with the N-GO/CNT framework. Compared with S@N-GO/CNT@PANI hybrid and S@N-GO/CNT hybrid, the novel hybrid S@N-GO/CNT@SPANI hybrid (~1.0 mg/cm²) shows the superior high-rate electrochemical performance. Even at an ultrahigh current density of 7.5 A/g, the discharge capacity of 438.3 mAh g^{-1} is still retained after 450 cycles. Thus, such a 3D sulfur cathode modified with electronic/Li-ionic dual-conduction network can significantly enhance the electrochemical performance and stability, and this novel type of material is very promising for commercial applications that require high energy and power density, long life, and excellent abuse tolerance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jpowsour.2016.11.067.

References

- [1] R.G. Cao, W. Xu, D.P. Lv, J. Xiao, J.G. Zhang, Adv. Energy. Mater 5 (2015) 1402273-1402295.
- [2] X.A. Chen, Z.B. Xiao, X.T. Ning, Z. Liu, Z. Yang, C. Zou, S. Wang, X.H. Chen,
- Y. Chen, S.M. Huang, Adv. Energy. Mater 4 (2014) 1301988–1301995.
- [3] N. Moreno, M. Agostini, A. Caballero, J. Morales, J. Hassoun, Chem. Commun.

51 (2015) 14540-14542.

- [4] H. Kim, J. Lee, H. Ahn, O. Kim, M.J. Park, Nat. Commun. 6 (2015) 7278.
- [5] W.D. Zhou, Y.C. Yu, H. Chen, F.J. DiSalvo, H.D. Abruna, J. Am. Chem. Soc. 135 (2013) 16736–16743.
- [6] Q. Fan, W. Liu, Z. Weng, Y.M. Sun, H.L. Wang, J. Am. Chem. Soc. 137 (2015) 12946–12953.
- [7] J.L. Wang, Y.S. He, J. Yang, Adv. Mater 27 (2015) 569–575.
- [8] H. Hu, H.Y. Cheng, Z.F. Liu, G.J. Li, Q.C. Zhu, Y. Yu, Nano. Lett. 15 (2015) 5116–5123.
- [9] L.F. Xiao, Y.L. Cao, J. Xiao, B. Schwenzer, M.H. Engelhard, L.V. Saraf, Z. Nie, G.J. Exarhos, J. Liu, Adv. Mater 24 (2012) 1176–1181.
- [10] Z.Y. Wang, Y.F. Dong, H.J. Li, Z.B. Zhao, H.B. Wu, C. Hao, S.H. Liu, J.S. Qiu, X.W. Lou, Nat. Commun. 5 (2014) 5002.
- [11] N.W. Li, Y.X. Yin, Y.G. Guo, RSC Adv. 6 (2016) 617-622.
- [12] N.W. Li, M.B. Zheng, H.L. Lu, Z.B. Hu, C.F. Shen, X.F. Chang, G.B. Ji, J.M. Cao, Y. Shi, Chem. Commun. 48 (2012) 4106–4108.
- [13] S. Xin, L. Gu, N.H. Zhao, Y.X. Yin, LJ. Zhou, Y.G. Guo, LJ. Wan, J. Am. Chem. Soc. 134 (2012) 18510–18513.
- [14] J.H. Kim, K. Fu, J. Choi, S. Sun, J. Kim, LB. Hu, U. Paik, Chem. Commun. 51 (2015) 13682–13685.
- [15] B. Zhang, X. Qin, G.R. Li, X.P. Gao, Energy Environ. Sci. 3 (2010) 1531–1537.
- [16] A. Vizintin, M. Lozinsek, R.K. Chellappan, Chem. Mater 27 (2015) 7070–7081.
- [17] L. Zhou, X.J. Lin, T. Huang, A.S. Y, J. Mater. Chem. A 2 (2014) 5117-5123.
- [18] G.C. Li, G.R. Li, S.H. Ye, X.P. Gao, Adv. Energy. Mater 2 (2012) 1238-1245.
- [19] J.E. Hyun, P.C. Lee, I. Tatsumi, Electrochim Acta 176 (2015) 887–892.
- [20] W.D. Zhou, X.C. Xiao, M. Cai, L. Yang, Nano Lett. 14 (2014) 5250-5256.
- [21] S.Q. Chen, B. Sun, X.Q. Xie, A.K. Mondal, X.D. Huang, G.X. Wang, Nano Energy 16 (2015) 268–280.
 [22] Y.L. Wei, Y.Z. Wang, S.M. Long, C. Bohargko, A.L. Fastoin, L.Am. Chem. Soc. 118.
- [22] X.L. Wei, Y.Z. Wang, S.M. Long, C. Bobeczko, A.J. Epstein, J. Am. Chem. Soc. 118 (1996) 2545–2555.
- [23] J. Yue, Z.H. Wang, K.R. Cromack, A.J. Epstein, A.G. MacDiarmid, J. Am. Chem. Soc. 113 (1991), 2665–2571.
- [24] Y.T. Xu, L.Z. Dai, J.F. Chen, J.Y. Gal, H.H. Wu, Eur. Polym. J. 43 (2007) 2072–2079.
- [25] L.J. Bian, F. Luan, S.S. Liu, X.X. Liu, Electrochim Acta 64 (2012) 17-22.
- [26] H. Varela, S.L. de Albuquerque Maranhao, R.M.Q. Mello, E.A. Ticianelli, R.M. Torresi, Synth. Met. 122 (2001) 321–327.
- [27] A.J. Dominis, G.M. Spinks, L.A.P. Kane-Maguire, G.G. Wallace, Synth. Mettals 129 (2002) 165–172.
- [28] A. Kitani, K. Satoguchi, K. Iwai, S. Ito, Synth. Met. 102 (1999) 1171-1172.
- [29] M. Onoda, K. Yoshino, J. Appl. Phys. 78 (1995) 4456-4462.
- [30] X.X. Gu, C.J. Tong, C. Lai, J.X. Qiu, X.X. Huang, W.L. Yang, B. Wen, L.M. Liu, Y.L. Hou, S.Q. Zhang, J. Mater. Chem. A 3 (2015) 16670–16678.
- [31] X.X. Gu, C.J. Tong, B. Wen, L.M. Liu, C. Lai, S.Q. Zhang, Electrochimica Acta 196 (2016) 369–376.
- [32] M.Q. Zhao, X.F. Liu, Q. Zhang, G.L. Tian, J.Q. Huang, W.C. Zhu, F. Wei, ACS nano 6 (2012) 10759–10769.
- [33] S.T. Lu, Y.W. Cheng, X.H. Wu, J. Liu, Nano Lett. 13 (2013) 2485-2489.
- [34] J.Y. Lee, C.Q. Cui, J. Electroanal. Chem. 143 (1996) 109–116.
- [35] X.W. Wang, Z. Zhang, X.L. Yan, Y.H. Qu, Y.Q. Lai, J. Li, Electrochim Acta 155 (2015) 54–60.
- [36] S.Z. Niu, W. Lv, C. Zhang, Y.T. Shi, J.F. Zhao, B.H. Li, Q.H. Yang, F.Y. Kang, J. Power Sources 295 (2015) 182–189.
- [37] W.C. Du, Y.X. Yin, X.X. Zeng, J.L. Shi, S.F. Zhang, LJ. Wan, Y.G. Guo, ACS Appl. Mater. Interfaces 8 (2016) 3584–3590.
- [38] C.H. Park, Y.K. Sun, D.W. Kim, Electrochim Acta 50 (2004) 375-378.
- [39] X.G. Sun, J. Hou, J.B. Kerr, Electrochim Acta 50 (2005) 1139–1147.
- [40] W. Xu, K.S. Siow, Z.Q. Gao, S.Y. Lee, Chem. Mater 10 (1998) 1951–1957.
- [41] Y. Nakai, K. Ito, H. Ohno, Solid State Ion. 113-115 (1998) 199-204.