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Aligned sulfur-coated carbon nanotubes with a polyethylene glycol barrier at one end for use as a high efficiency sulfur cathode

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ABSTRACT

High efficient sulfur cathode materials were constructed by the incorporation of aligned sulfur-coated carbon nanotubes (CNTs) and a polyethylene glycol (PEG) barrier at one end. During the charge and discharge of lithium sulfur batteries, high Li ion storage performance can be achieved on the composite electrode, which was benefited from both the aligned CNT structure and the polymer barrier. Aligned CNT framework afforded high conductivity for electron transportation and ordered pores for lithium ion transportation. Meanwhile, the PEG barrier layer greatly suppressed the shuttle of polysulfides. Therefore, this aligned sulfur-coated CNTs with a PEG barrier showed a high initial discharge capacity of 920 and 1128 mAh g^{-1} in lithium bis(trifluoromethanesulfonyl)imide/1,3-dioxolane/1,2-dimethoxyethane and electrolyte with $LiNO_3$ additives, respectively. The PEG coated cathode showed high cycle stability that a low degradation with 0.38% per cycle during the 100 cycles at 0.1 C was achieved in $LiNO_3$-free electrolytes. These Li storage performance was superior to the aligned sulfur-coated CNT electrode without PEG barrier.

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1. Introduction

Excellent arrangement of oriented nanostructures is an efficient and effective way to gain fundamental insights and improve the generation and transport of electrons, ions, and other molecular species for energy harvesting, conversion, and storage [1,2]. Ordered nanoarchitectures with controllable components and sites render high surface area, tunable order pore channels, and good alignment of building blocks to optimize the electron and ion transport. For instance, the use of aligned Si nanowires affords excellent ion/electron pathway and abundant space for Li storage [3], while aligned TiO_2 nanotubes [4] with high surface area are introduced to trap the dye molecules as well as to provide intrinsic electron pathway for charge transport, which significantly improved the performance of the dye sensitized solar cells. Recently, the use of aligned carbon nanotubes (CNTs) as an aligned current collector and/or the scaffold in the electrode for supercapacitor and Li battery with superb energy storage performance is widely reported [2,5,6]. These progresses provide the fundamental understanding of the transport of electrons, ions, and other molecular species in complex nanostructures for energy technologies such as photovoltaics, thermoelectrics, supercapacitors, and batteries.

Among the myriad of energy-storage technologies, lithium batteries play an increasingly critical role because of their

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high specific energy (energy per unit weight) and energy density (energy per unit volume) [7]. However, the highest energy storage that Li-ion batteries can deliver is too low to meet the demands of key markets, such as transport, in the long term. The development of novel lithium battery system and the related chemistry knowledge is an urgent research topic [7]. Owing to the multiple-electron-transfer electrochemistry of light element-sulfur, lithium sulfur batteries are considered one of the most promising candidates due to its very high theoretical energy density of 2600 Wh kg^{-1}, high natural abundance, and environment friendly nature as well [7]. However, several intrinsic obstacles have to be overcome, including the ultra-low conductivity of element sulfur and lithium sulfide, the shuttle behavior of lithium polysulfides [8,9]. The introduction of conductive polymer or nanocarbon is an attractive strategy to overcome these hindrances. For instance, the use of polyaniline [10], polyacrylonitrile [11], polypyrrole [12]. Multi-walled [13] and single-walled CNTs [14], nanofibers [5], graphene [15,16], CNT/graphene hybrid [17], graphene oxide [18], and mesoporous carbon [19], were efficient in improving the Li-ion storage performance of the sulfur cathodes. Nevertheless, these nanomaterials are always randomly distributed into the composite electrode, which heavily hinder the understanding of the mechanistic insight and demonstration of their potential for Li–S battery.

The use of vertically aligned CNTs was a promising way to load the active sulfur phase for Li–S battery [20,21]. Very recently, a binder free aligned CNT/sulfur composite electrode with a quite high discharge capacity higher than 800 mAh g^{-1} based on the mass of sulfur was available [22]. To prevent the rapid decay, $LiNO_3$ is used as electrolyte additive during the electrochemical tests [22–24]. In this work, polymer barrier was introduced to retard the shuttle of sulfur-containing compounds and improve cycling stability, as well as increase the discharging capacities.

Our concept was demonstrated by the introduction of a polyethylene glycol (PEG) barrier layer on the top of the aligned sulfur-coated CNT electrode (Fig. 1). Such an oriented nanoarchitectures has the advantages of: (1) the CNTs in the composite cathode are a high efficient conductive network directly attached to the current collectors, (2) the pores in the aligned sulfur-coated CNT electrode serves as highly efficient pathway for ion transfer; (3) the PEG acts as a barrier to block the shuttle of the polysulfides and a reservoir for the intermediate polysulfide products, (4) the surface of the aligned sulfur-coated CNT cathode becomes highly hydrophilic, and a chemical barrier is constructed so that the polysulfides would preferentially be trapped. Such a composite electrode was fabricated, its Li storage performance was evaluated, and the shuttle effect was described by a mathematical model as well.

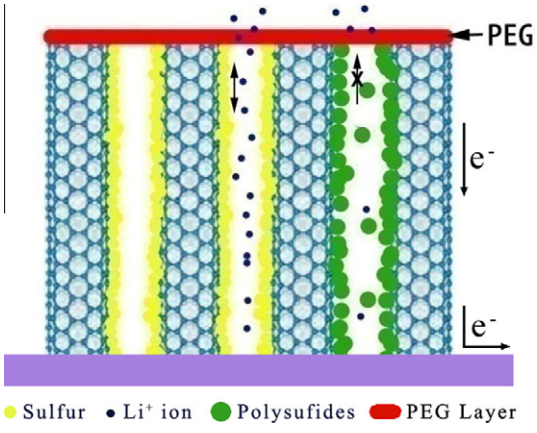

Fig. 1 – The schematic of aligned sulfur-coated CNT electrode with PEG barrier layer for high efficient sulfur cathodes.

2. Experimental

2.1. Synthesis of aligned CNTs

The aligned CNTs were synthesized on quartz plates through floating catalyst method by using ferrocene as the catalyst precursor and xylene as the carbon source as reported previously [25]. The concentration of the ferrocene in xylene was 10 g L^{-1}. The quartz plates were used as the growth substrates and were placed in the center of a horizontal quartz tube (inner diameter of 30 mm) set in a tubular furnace. The xylene solution was injected into the reactor with a feed rate of 6.0 mL h^{-1} using a motorized syringe pump after the react temperature reached 800 °C. The carrier gas was composed of 600 sccm Ar and 40 sccm H_2. After 30 min growth of CNT array, the feed of xylene solution were terminated, and the furnace was cooled down under the protection of Ar gas. The CNT arrays were peel off from quartz plate with a blaze, and were cut into a size of around 10 × 10 mm for the following process in making electrodes. The heights of the CNT arrays were around 500 μm.

2.2. Fabrication of aligned sulfur-coated CNT cathodes

The element sulfur was loaded into the CNT array framework by co-heating. Typically, sulfur powder with same mass to the CNT array framework were dispersed on the top of the CNT array, which were set in a bottle filled with inert N_2 gas and heated to 155 °C. With a 12-h heating, the sulfur immersed into the CNT framework and formed aligned sulfur-coated CNT electrode. The contents of S in the electrodes were then determined by thermogravimetric analysis (TGA). For aligned sulfur-coated CNT cathodes, the mass of cathode per area was around 5.0 mg cm^{-2}, in which the sulfur loading amount was approximate 2.5 mg cm^{-2}.

When fabricating aligned sulfur-coated CNT electrode with PEG barrier, the aligned sulfur-coated CNT electrode was fixed on a spinning coater. Then PEG-20000 solution were dropped onto the electrode and allowed to dry in an oven at 60 °C. The content of PEG in the sample was obtained by comparing the change in mass before and after the loading of PEG barrier layer. For PEG-coated cathodes, the PEG loading amount is *ca.* 1 mg cm^{-2}, namely 20 wt.% of the total cathode materials.

2.3. Characterizations

High-resolution scanning electron microscopy (SEM, JSM 7401F, at 5.0 kV) was used to characterize the morphology of

the CNT array electrodes. High-resolution transmission electron microscopy (TEM, JEM 2010, at 120.0 kV) was used to observe the detailed structure of sulfur-coated CNT structures for the electrodes. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed using a EDAX apparatus with the analytical software Genesis Apex EDS System, and the accelerating voltage applied was 20.0 kV. The sulfur content of aligned sulfur-coated CNT electrode was obtained by TGA heated at 20 °C min^{-1} using TGA/DSC1 STAR^e system with N_2 atmosphere. The IR spectra were collected using a Nicolet Nexus 670 spectrometer. The contact angles were measured by Dataphysics OCA20 with 2 μL pure water droplet to show the wettability of cathode material with and without PEG barrier layer.

2.4. Li-ion storage performance

As aligned CNTs are free standing and with high conductivities, the aligned sulfur-coated CNT electrodes with and without PEG barrier were used directly as the electrodes for the evaluation of electrochemical performances. The electrodes were assembled into a two-electrode cells configuration using standard 2025 coin-type cells with Li metal foil as counter electrodes (1 mm thick). The applied electrolyte were 1 M lithium bis(trifluoromethanesulfonyl)imide in 1,3-dioxolane: 1,2-dimethoxyethane (v/v = 1/1) solvent. The amount of electrolyte used in assembling the cell was 100 μL. The separators were Celgard 2400 polypropylene membranes. The assembling of cells was conducted in an Ar-filled glove box equipped with a purification system, and the oxygen and water content were below 1 ppm. For comparison, electrolyte with 0.25 M $LiNO_3$ additive were also used to test the cathode materials.

After assembled, a 12-h standing for the cells was conducted to ensure the immersion of electrolyte into the electrodes. The coin cells were tested in galvanostatic mode at various currents at 25 °C within a voltage window of 1.5–3.0 V using Neware battery tester.

3. Results and discussion

In general, the aligned CNTs obtained by floating catalyst chemical vapor deposition [25] were with an average diameter of 40 nm, BET surface area of *ca.* 51.7 $m^2 g^{-1}$, and a Raman I_G/I_D intensity of 1.36 (Raman result in Fig. S1). As shown in Fig. 2a, the aligned CNTs are with the height of around 500 μm, which differed from piece to piece. The CNTs inside the array are with consistent packing direction (Fig. 2b), which provides electronic pathway throughout the whole aligned CNT cathode. After sulfur coating, the microstructure of sulfur-coated CNT were characterized by TEM. As shown in Fig. 2c, the sulfur phase was wrapped on CNTs. A coaxial cable structured electrode was available. The thickness of sulfur layer was *ca.* 40 nm. The composition was confirmed to be 47.2 wt.% carbon and 52.8 wt.% sulfur (Cu signal come from the TEM sample grids, Fig. 2d). The loading amount of sulfur can be significantly increased if small diameter CNTs were employed. An 80% sulfur loading was attached on 3 nm CNTs [22]. The sulfur showed high wettability on the surface of CNTs, which ensured well attachment of sulfur and firmly-bonded coaxial structure.

After the introduction of sulfur and PEG layer, the alignment of CNTs in the arrays and also the overall morphologies of the aligned CNTs were well preserved (Fig. 3a). It was also observed by SEM that with the coated PEG barrier was mostly distributed on the top of the array, in which the higher contrast in SEM micrograph derived from the low conductivity of PEG chains compared to that of CNTs. The existence of PEG was also confirmed by IR spectra as presented in Fig. 3b (IR spectra of raw CNTs, sulfur, S-coated CNT, and PEG in Fig. S2). A strong adsorption was observed at 1099 cm^{-1}, which corresponded to the ether groups in PEG. To further identify the location of PEG layers in the CNT cathode, EDS test in different areas were also conducted on the top and bottom of CNT cathodes. As shown in Fig. 3c and d, the content of oxygen is 16.4 wt.% on the top of aligned CNTs (PEG layer area) and 5.7 wt.% on the bottom of aligned CNTs (non-coating area). As the oxygen signals mostly corresponded to the ether groups in PEG, this result indicated the formation of PEG barrier mainly on one side. After the coating of PEG solution, a PEG barrier layer was formed in the top of CNT array, with the polymer chains attached to sulfur-coated CNTs.

The surface properties of CNT cathode were tuned with the coating of PEG. Pristine aligned CNTs and S-coated CNTs are hydrophobic. As indicated in Fig. 3e, the static contact angle was 125°. After the coating of PEG layer, the surface of CNT cathode turned into hydrophilic. Once the water droplet reach the CNT cathode with PEG barrier, it immersed into the CNT cathode within 3 s (Fig. 3f–h), indicating the hydrophilic nature of the sample.

To evaluate the Li storage performance of the composite electrode, the 2025 type cells were assembled with composite cathode and lithium foil directly. The PEG coating side were set towards the membrane to serve as a barrier for the diffusion of polysulfides. Compared with the pristine aligned sulfur-coated CNT electrode, the introduction of PEG barrier layer showed a significant improvement in the discharge capacity. The initial discharge capacities for aligned sulfur-coated CNT electrodes with and without PEG barrier layer were 945 and 831 mAh g^{-1}, respectively (Fig. 4a). After 100 cycles at a current rate of 0.1 C, the discharge capacities degrade to 589 and 381 mAh g^{-1}, which indicating a capacity loss per cycle of 0.38% and 0.54%, respectively. The decay rate was relatively low compared with the reported MWCNT/S cathode, as shown in Table 1. The introduction of PEG barrier layer showed advantages not only in the specific capacities, but also in the cycling stabilities.

The effect of PEG barrier layer is also evaluated at different charge/discharge currents (Fig. 4b). The discharge capacity for sulfur-coated CNT electrodes with and without PEG barrier were 863 and 693 mAh g^{-1} at 0.2 C, 438 and 452 mAh g^{-1} at 2 C, 94 and 405 mAh g^{-1} at 5 C, respectively. The cathode with PEG barrier layer presented higher capacities at low current densities, namely below 1 C. One possible reason for the high performance of PEG coated electrodes is that the polysulfides were limited by the PEG layer so that the diffusion distance towards the conducting surface is shortened, which favored the high utilization of polysulfides. However, cathodes with PEG barriers suffer from severe capacity degrading under high charge/discharge currents. The CNT cathode without PEG barrier showed much better performance at high current

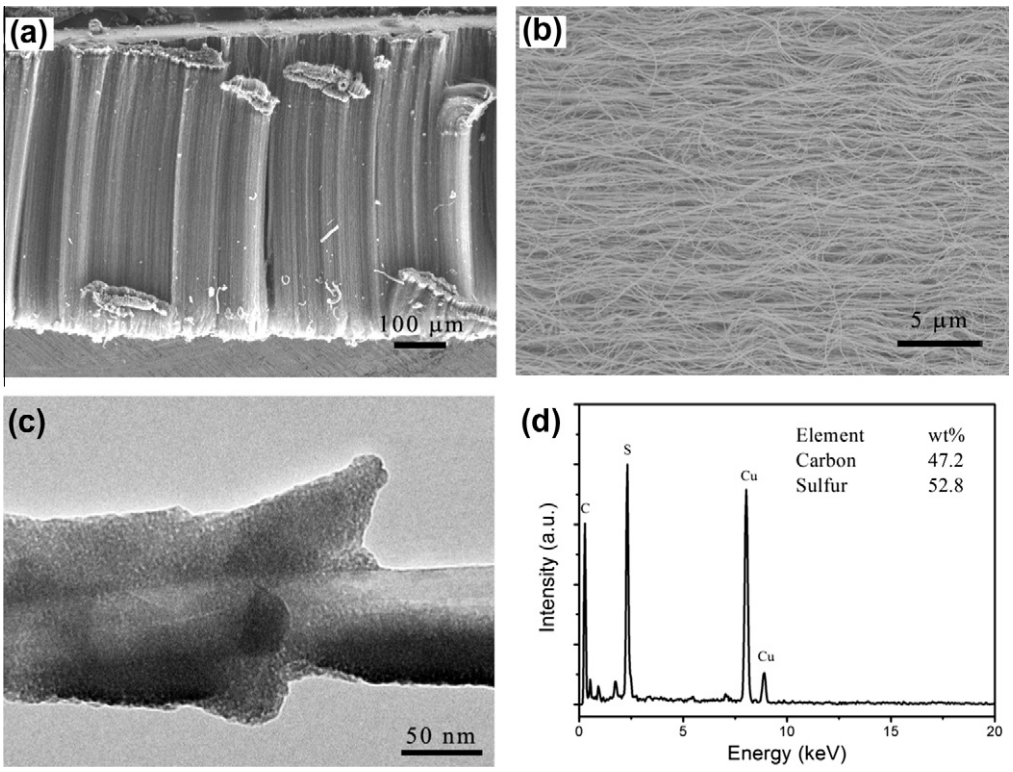

Fig. 2 – (a) SEM image of pristine CNT array; (b) SEM of the CNTs in the aligned CNTs; (c) TEM image of sulfur-coated CNT; (d) the EDS spectrum of sulfur-coated CNTs.

densities. The capacity retention at 5 C reached 58% for that at 0.2 C, which can be attributed to the ordered porous structure of the CNT cathode and the high efficient electronic pathway constructed by aligned CNTs. In contrast, a sharp degrading of capacity was observed at high currents for PEG coated cathodes, and the capacity retention at 5 C is only 11% for the capacity at 0.2 C. The main reason may be attributed to the low ionic conductivity induced by the incorporation of poor-conductive PEG coating. However, the capacity of electrodes with PEG barriers retained 691 mAh g^{-1} when the current return form 5 to 0.2 C, indicating good cycling stability. It was also noticed that with the coating of PEG barrier, the coulombic efficiency was improved in all current densities, which is also in consistent with our assumption that the formation of PEG barrier can reduce the diffusion of polysulfides.

Fig. 4c and d present the voltage curves at different currents for sulfur-coated CNT cathodes with and without PEG barrier. The cathodes with PEG barrier showed more complete plateaus at 2.3 and 2.0 V at low current densities, corresponding to the two-step discharging electrochemical reactions. However, in case of high current densities, much severe polarization were observed for PEG coated cathode and no charge/discharge plateau can be observed at 5 C, which may also be attributed to the above mentioned low conductivity of PEG coating.

The electrochemical impedance spectroscopy was also adopted to analyze the resistance in the battery system. As indicated in Fig. 4e, the equivalent series resistances increased from 1.8 to 2.3 ohm when the PEG coating layer was introduced. The charge transfer resistance for PEG coated cathode (18.4 ohm) is higher than pristine cathode (7.6 ohm). The large resistances for PEG coated cathode explained the relatively poor performance at high current densities. As another common route to inhibit the shuttle effect and increase the cycling stability, $LiNO_3$ additives were also applied with CNT cathodes with and without PEG barrier. As indicated in Fig. 4f, when electrolytes with $LiNO_3$ additives was employed, both the coulombic efficiency and the capacity for CNT cathodes increased, no matter PEG barrier is applied or not. An initial discharging capacity of 1128 mAh g^{-1} was achieved at 0.2 C on PEG-coated CNT electrodes. The electrochemical performances of cathodes with and without PEG barrier were similar to that in $LiNO_3$ free electrolytes. Even with $LiNO_3$ additives, the PEG barrier layer showed advantages in improving the capacities at charge/discharge currents below 2 C.

The performance degradation of Li–S batteries is one of the main obstacles for the practical application of it. The shuttle effect, however, is responsible for the fast decay of Li–S batteries. The shuttle mechanism means the diffuse of high order polysulfides to the anode where they react directly with lithium metal, form lower-order polysulfides and diffuse back to cathode side. As suggested by Mikhaylik and Akridge [31], the shuttle effect is considered as the competition between the reactions caused by the charge/discharge current and by the diffusion of polysulfides between cathode and anode. Therefore, a shuttle factor was defined to reflect the extent of shuttle effect. By considering a complete electrochemical charge/discharge, the shuttle factor can be expressed as:

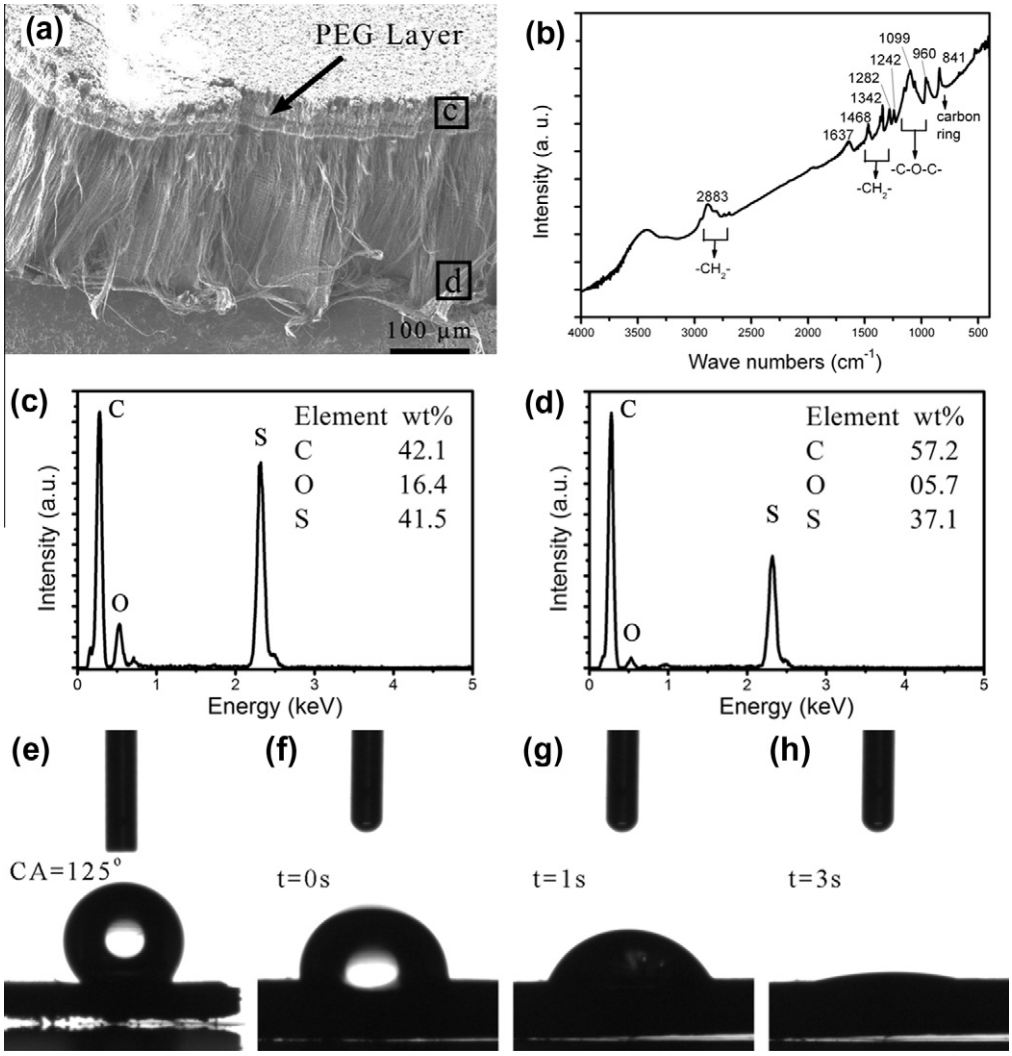

Fig. 3 – (a) SEM image of the sulfur-coated CNT cathode with PEG barrier; (b) the IR spectrum of S-coated CNT cathode with PEG barrier; (c and d) the EDS spectra on the PEG-coated side and non-PEG coated side as indicated in (a); (e) water droplet on S-coated CNT cathode; (f–h) the snapshots of water droplet on the S-coated CNT cathode with PEG barrier layer.

$$f = k_s \cdot q_H \cdot [S_{total}]/I \quad (1)$$

where k_s is the heterogeneous reaction constant related with polysulfide diffusion and reaction, q_H is the theoretical specific charge/discharge capacities of the high plateau, and I is the charge/discharge current.For a charge process, the amount change of high order polysulfide amount $[S_H]$ can be express with formula (2) and its solution formula (3):

$$\frac{d[S_H]}{dt} = \frac{I}{q_H} - k_s[S_H] \quad (2)$$

$$[S_H] = \frac{I}{k_s q_H}(1 - e^{-k_s t}) \quad (3)$$

Given the $[S_H] = [S_{total}]$ (full conversion of sulfur), the charge capacity for high plateau should be:

$$Q_{CH} = I \cdot t = -\frac{I}{k_s} \ln\left(1 - \frac{q_H k_s [S_{total}]}{I}\right) = -\frac{I}{k_s} \ln(1 - f) \quad (4)$$

The shuttle effect mainly affects electrochemical reactions for the high plateau, which prolong the charging and reduce the discharging capacity. With the assumptions that per sulfur atom accept/donate 0.5 and 1 electron for high and low plateau [31], the discharge capacity for the low plateau can be expressed as:

$$Q_{CL} = 2 \cdot q_H \cdot [S_{total}] = \frac{2I \cdot f}{k_s} \quad (5)$$

During the discharge process, the capacity in the high and low plateau can be expressed in similar form (with the assumption that the charge and discharge processes are of consistent shuttle factors):

$$Q_{DH} = \frac{I}{k_s} \ln(1 + f); \quad Q_{DL} = \frac{2I \cdot f}{k_s} \quad (6)$$

Therefore, the relationship between the coulombic efficiency and the shuttle factor can be expressed as formula (7):

$$C_{eff} = \frac{Q_{DH} + Q_{DL}}{Q_{CH} + Q_{CL}} = \frac{2f + \ln(1 + f)}{2f - \ln(1 - f)} \quad (7)$$

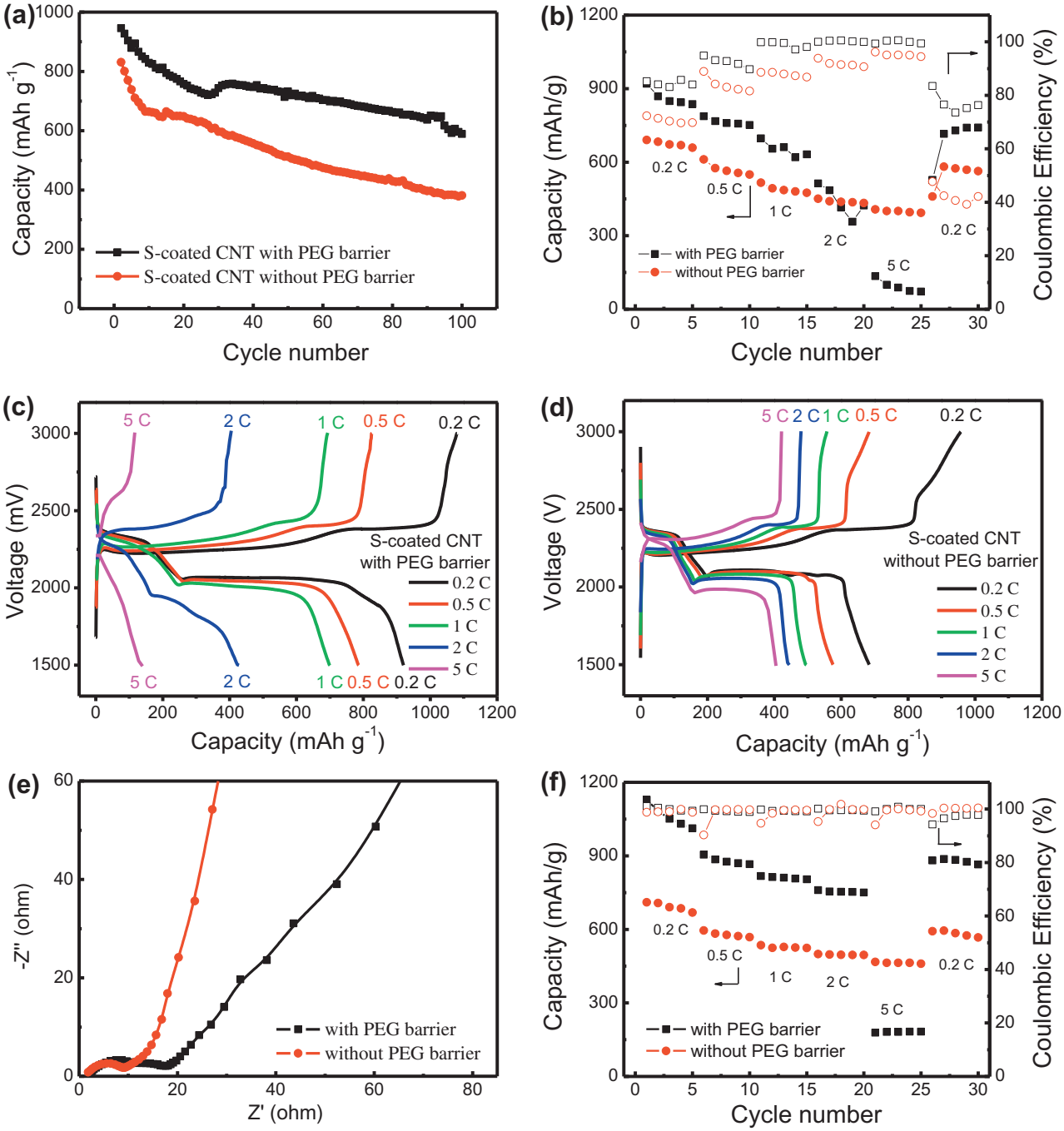

Fig. 4 – (a) The discharge capacity of sulfur-coated CNT cathodes with and without PEG barrier *vs.* cycle number with a current density of 0.1 C; (b) the discharge capacity with different current densities; Galvanostatic charge–discharge curves of sulfur-coated CNT cathodes (c) with PEG barrier (d) without PEG barrier; (e) the electrochemical impedance spectroscopy for cathodes with and without PEG barrier layer; (f) the performance of cathodes with $LiNO_3$ additives in electrolytes.

Based on the coulombic efficiency of cells at different currents, the shuttle factor can be calculated. As indicated in Fig. 4b, the coulombic efficiencies of the electrodes with PEG barrier layer were 85.1%, 94.9%, and 99.8% at 0.2, 0.5 and 1.0 C, respectively, which approaching 100% at higher currents. Therefore, the corresponding shuttle factors were 0.44, 0.16 and 0.004 at 0.2, 0.5 and 1.0 C, respectively. For comparison, the coulombic efficiencies at 0.2, 0.5, and 1.0 C were 71.2%, 84.3%, and 88.5% without PEG barrier layer, corresponding to shuttle factors of 0.75, 0.46, and 0.35, respectively (Fig. 5). The change of shuttle factors with current densities is reasonable, as higher currents suppressed the effect of shuttle based on diffusions according to formula (1).

The PEG barrier layer on the top of aligned composite cathode can greatly reduce the shuttle of polysulfides at different currents, which also prevents the degradation of sulfur

Table 1 – Summary of the decay rates of MWCNT/S cathodes for lithium sulfur batteries.

Decay rate (% per cycle)	Sulfur content (wt.%)	Ref.
0.38	40	This work
0.32	23	[13]
0.63	68	[26]
0.67	40	[27]
0.76	50	[28]
1.1	48	[29]
1.2	56	[30]

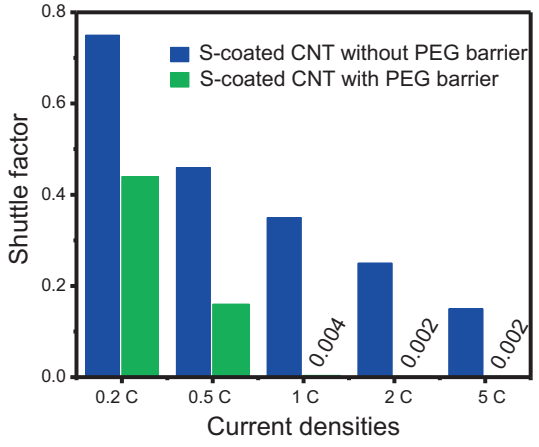

Fig. 5 – The shuttle factors at different charge/discharge current densities.

electrodes during the cycling. Such an improvement derived by adding a PEG layer built a chemical barrier by ether groups, and surface of sulfur-coated CNT electrode became highly hydrophilic. Such a barrier layer rich in ether groups suppressed the shuttle of polysulfides outwards the CNT electrode [19,32]. By the confinement of polysulfides and preservation of the channel for the transport of lithium ions and pathway for electrons, PEG barrier layer enhanced the cycling stability of aligned sulfur-coated CNT electrode materials.

4. Summary

The aligned sulfur-coated CNT cathodes were directly employed as electrodes for lithium sulfur batteries. By introducing the PEG barrier layer into aligned sulfur-coated CNT cathode, the shuttle of polysulfides was suppressed and the electrochemical performances were greatly improved. For the cycling test at 0.1 C, the electrode with PEG barrier showed an initial discharge capacity of 945 mAh g^{-1}, with the degradation of 0.38% per cycle during the 100 cycles, which was superior to the pristine cathodes without PEG layer. Attributed to the inhibition of shuttle phenomenon by PEG, the sulfur-coated CNT cathode with PEG barrier showed obvious improvements in both the capacities and the coulombic efficiencies at different charge/discharge currents. This provides not only fundamental new insight into the transport of electrons and ions in complex nanostructures, but also the strategy to improve the Li storage performance for energy technologies.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.02.037.

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