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RAPID COMMUNICATION

Entrapment of sulfur in hierarchical porous graphene for lithium-sulfur batteries with high rate performance from −40 to 60 °C

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Abstract
The Li-S battery is with a much greater theoretical energy density than those of conventional lithium ion batteries. The key to achieve a high performance electrode for Li-S battery lies in the arrangement of the building blocks into a well-designed structure, in which the nanocarbon framework not only acts as an electronic conduit to the encapsulated active materials but also serves as a mini-electrochemical reaction chamber. Therefore, a nanocomposite with sulfur entrapped into hierarchical porous graphene was proposed and fabricated for Li-S batteries. The nanocomposite electrode exhibits high discharging capacitance of 1068 and 543 mA h g^{-1} at a current density of 0.5 and 10 C, respectively. The discharging capacity of 386 mA h g^{-1} can be presented at ultra-low temperature of −40 °C, which far exceeds the operating range of conventional lithium-ion batteries. The large scale produced hierarchal graphene was mainly decorated with epoxy and hydroxyl groups, which can enhance the binding of S to the C-C bonds due to the induced ripples by the functional groups. These results provided a promising electrode material for energy storage device with high capacitance, which is important for the increasing demands of power sources in cold environments, such as battery systems for electric vehicles in cold zone or for aeronautic applications.

Introduction

The exploration of advanced electrode materials for high energy density, high power density, and robust charging-discharging

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in a wide temperature range is one of most important research activities for a sustainable society [1-3]. Among various power sources, the lithium-sulfur (Li-S) battery is based on the electrochemical reaction between the metal lithium as anode and sulfur as cathode. In a typical discharge process, there are two discharge stages: the reduction of sulfur to polysulfide in the first stage and the further reduction of polysulfide into lithium sulfide in the second stage:

$$S_8 + Li^+ + e^- \rightarrow Li_2S_x (2.4-2.1\ V) \quad (1)$$

$$Li_2S_x + Li^+ + e^- \rightarrow Li_2S_2 \quad \text{and/or} \quad Li_2S (2.1-1.5\ V) \quad (2)$$

The sulfur cathode is with a theoretical capacity of 1672 mA h g^{-1}. This is much higher than those of conventional lithium ion batteries. In addition to its high capacity, the high natural abundance of sulfur makes it low cost raw materials, and sulfur is also an environmental-friendly material for cathode [1,2]. The research investigation of Li-S battery systems started more than 32 years ago [4]. However, due to the major hurdles of Li-S batteries such as the poor conductivity for sulfur and Li_2S_x (x=1 or 2), the dissolution of polysulfide anions (S_n^{2-}) in the electrolyte, the lack of applicable electrolytes, the low utilization of active material, and the fast capacity degradation, the enthusiasm in the development of these systems decayed fast. In recent years, with the rising demands of high energy density rechargeable batteries for electric vehicles and personal electronics devices, the interests on Li-S batteries were reanimated with recent progress on advanced sp^2 carbon materials.

The incorporation of nanocarbons and sulfur gives rise to advanced electrodes with improved capacity and cycling performance [5-13]. For instance, Nazar and coworkers [5] created highly ordered interwoven composites with mesoporous carbon CMK-3 constrained sulfur nanofiller growth within its channels for Li-S batteries with reversible capacities up to 1320 mA h g^{-1}. To overcome the problem of polysulfide shuttle effect, they employed the absorption of the intermediate polysulfide by a porous silica embedded within the carbon-sulfur composite that not only absorbs the polysulfide by means of weak binding, but also permits reversible desorption and release [12]. Very recently, a highly ordered mesoporous carbon with a bimodal pore structure was served as the scaffold for carbon/sulfur nanocomposites with an initial capacity of 995 mA h g^{-1} and a capacity of 550 mA h g^{-1} after 100 cycles at a high current rate of 1675 mA g^{-1} (1 C) [14]. Qiu and coworkers [6] found that the sulfur-coated multi-walled carbon nanotube (CNT) composite maintained a reversible capacity of 670 mA h g^{-1}. A mesoporous, hollow carbon capsule sulfur nanocomposite displays outstanding electrochemical features with a reversible capacity of 974 mA h g^{-1} at a rate of 0.5 C [8]. A sulfur-impregnated activated carbon fiber cloth was used directly as a binder-free cathode for rechargeable Li-S batteries with a capacity of 1000 mA h g^{-1} at a current of 150 mA g^{-1} [9]. Graphene, the one-atom-thick two dimensional nanomaterial with high surface area, unique conductivity, ultrathin thickness, superior structural flexibility, and good mechanical properties [15-18], has also been considered a novel nanocarbon component for the fabrication of advanced Li-S battery cathode electrodes. Compared with activated carbon, mesoporous carbon, and CNTs, graphene offers tunable porous structure and surface properties, which makes it a promising candidate as the building blocks for Li-S electrodes. Graphene has been employed as a conductive support for Li-S electrodes in the form of polymer wrapped sulfur particles [19], graphene enveloped sulfur [20], melt-infiltrated sulfur [21,22], interleaved expanded graphite-embedded sulfur [23], sacculelike structured sulfur@graphene [24], interstitial sulfur particles [25], and sulfur-reduced graphene oxide composite [26]. The graphene oxide was also used as supports to immobilize the sulfur and lithium polysulfides *via* reactive functional groups [27]. The as-obtained graphene/sulfur electrode exhibits extraordinary performance at a low discharging rate at room temperature. When polyacrylonitrile was introduced into the graphene/sulfur electrode, the graphene nanosheets act not only as electronic conductive matrix, but also as frameworks for Li-S battery with excellent electrochemical storage performance [28]. However, most of the graphene materials applied in previous reports were obtained by liquid phase reduction of graphene oxide, and thus shows a random agglomerating morphology with uncontrollable porous structure.

Meanwhile, the Li-S battery showed the advantage to be usable in a wide temperature range, especially at low temperature [29], which is important for the demands of power sources in cold environments, such as battery systems for electric vehicles at cold zone as well as some aeronautic applications. However, in these extreme situations, traditional Li-ion batteries cannot be operated. The potential for nanocarbon-incorporated sulfur electrodes for energy storage devices at low temperature still needs to be explored.

The key for a high performance nanocarbon/sulfur electrode lies in the arrangement of the building blocks into a well-designed structure, in which the carbon framework acts not only as an electronic conduit for the active mass encapsulated but also as a mini-electrochemical reaction chamber. Such entrapment ensures a more complete redox process and results in an enhanced utilization of the active sulfur material. To explore the potential use of graphene as conductive additives and also structure frameworks for advanced Li-S electrode materials, a nanocomposite with sulfur entrapped into hierarchical porous graphene was proposed as a proof of concept and applied as electrode materials for high rate Li-S batteries that can be operated over a wide range of operable temperature. With large surface area, high charge carrier density, hierarchical porous nanostructure, and extraordinary electronic conductivity, the graphene provides tunable 3D pore structures as reservoirs for electrolyte and sulfur, low-resistant pathways for the Li-ion transportation, and high conductive networks for electron transfer. As shown in Fig. 1, the sulfur and/or lithium polysulfide were assumed to be entrapped in the hierarchical porous graphene (HPG). In the discharging process, the Li ions will diffuse into the graphene, and incorporate with the initial sulfur particles to form soluble lithium polysulfide which is expected to be confined by the graphene. The insoluble lithium sulfide was likely to deposit on the conductive basal plane of graphene with further discharging. Such electrochemical process is reversible, which aims to enhance the performance of Li-S battery.

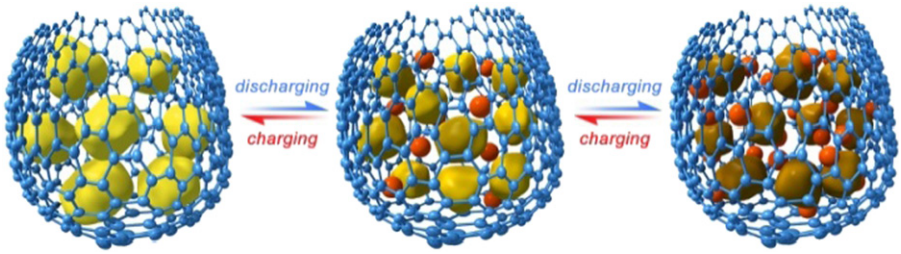

Fig. 1 Schematic illustration of entrapment of sulfur in graphene support for lithium–sulfur batteries during the charging–discharging process.

Results and discussion

Structure of graphene/sulfur electrodes

Our concept involves porous graphene to entrap the active sulfur cathode materials for Li–S battery application. In a typical process, the HPG-1000 was produced by a vacuum-assisted thermal expansion of graphene oxide at 1000 °C [30,31]. The as-prepared HPG-1000 was mixed with ultrafine sulfur and further treated at 155 °C for 3.0 h, and the as-obtained graphene/sulfur nanocomposites are denoted as PGS-1000. The representative scanning electron microscopy (SEM) images of the HPG-1000 are shown in Fig. 2a. The graphene sheets are loosely stacked or folded with each other to construct interconnected 3D macropores, with a specific BET area of 434 $m^2\ g^{-1}$. Several large pores with a size ranging from 30 to 200 nm are clearly presented. This unique nanoarchitecture is believed to be generated during the high-temperature vacuum-assisted exfoliation, where moderate interlayer expansions for graphene oxide were induced by negative pressure during annealing process. These pores were filled with sulfur nanoparticles during melt diffusion process (Fig. 2b). The PGS-1000 became densely packed, and the graphene nanosheets were coated by sulfur (Fig. 2c). As revealed by the N_2 sorption isotherm and pore size distribution shown in Fig. 2d, the volume of mesopores in HPG-1000 decreased obviously, indicating the sulfur particles were entrapped in the graphene mesoporous network of PGS-1000. As revealed by the XRD patterns shown in Fig. 2e, the sulfur phase in the PGS-1000 were with good crystallinity. The content of sulfur in the composite was determined to be 66 wt% in PGS-1000 by thermogravimetric analysis in Ar atmosphere (Fig. 2f). Compared with the evaporation of pure sulfur samples, the weight loss peak of sulfur in PGS-1000 shifted to high temperature range of 260–300 °C (Fig. 2f), indicating the confinement effect of sulfur in the graphene.

Electrochemical performance of graphene/sulfur nanocomposite electrodes

The electrochemical behaviour of the PGS-1000 cathode for Li–S battery was investigated by cyclic voltammogram (CV) and galvanostatic charge–discharge measurement. The CV measurement was conducted with a scan rate of 0.1 mV s^{-1} in the voltage range from 1.5 to 3.0 V vs. Li/Li^+. As shown in Fig. 3a, two main reduction peaks at around 2.4 and 1.95 V was clearly presented during the first cathodic scan. The first step is ascribed to the transformation from sulfur to lithium polysulfide (Li_2S_n, $4 \leq n \leq 8$), while the second step can be attributed to the reduction of higher order lithium polysulfide into lithium sulfide (Li_2S_2, Li_2S) at a lower potential of about 2.0 V [22,23,32]. In the subsequent anodic scan, two oxidation peaks at around 2.4 and 2.5 V were observed. The first one is associated to the conversion from lithium sulfide to lithium polysulfide, and the second peaks corresponded to the reduction of the polysulfide into element sulfur. Both the reduction and oxidation peaks were slightly shifted with the increase of cycle number, indicating a strong polarization of the electrode materials in the first cycle and the improvement of reversibility of the cell by cycling. Both the positions and currents of the CV peaks underwent very small changes after the second cycle, indicating satisfying capacity retention. This suggests that the graphene may efficiently prevent the sulfur from diffusing into the electrolyte due to its large surface area decorated with functional groups and lattice defects, and also the proper pore structures.

Fig. 3b displays the charge–discharge curves of the PGS-1000 cathode at −40, −20, 25, and 60 °C. When the temperature was at 25 °C, two typical plateaus at 2.3 and 2.1 V, respectively, were observed in the discharge process, which can be assigned to the two-step reaction of sulfur with lithium in the discharge process. There exhibited two plateaus in the charge process at about 2.37 and 2.47 V, respectively. The positions of the plateaus were in accordance with the typical peaks of the PGS-1000 electrode in the CV profiles. Similar charge–discharge curves were presented when the PGS-1000 electrodes were operated at 60 °C. When the temperature decreased to −20 °C, the plateau at 2.3 V was well preserved, while the peak around 2.1 V disappeared, indicating that the transformation of sulfur to lithium polysulfide (Li_2S_n, $4 \leq n \leq 8$) still occurred, while the reduction of higher order lithium polysulfide to lithium sulfide was inhibited. However, the transformation of sulfur to lithium polysulfide is highly reversible even at a low temperature of −40 °C, and the PGS-1000 still affords an initial discharging capacity of 164 mA h g^{-1} at a charge–discharge current density of 1 C.

The cycling performances of PGS-1000 are shown in Fig. 3c. A discharging capacity of 140 mA h g^{-1} after 80 cycles was achieved when the working temperature was −40 °C. When the temperature increased to −20 °C, an initial discharging capacity of 215 mA h g^{-1} was illustrated. The PGS-1000 undergoes a more obvious capacity degradation at this temperature, a capacity of 174 mA h g^{-1} were achieved after 80 cycles. When the temperature was 25 °C, the discharging capacity

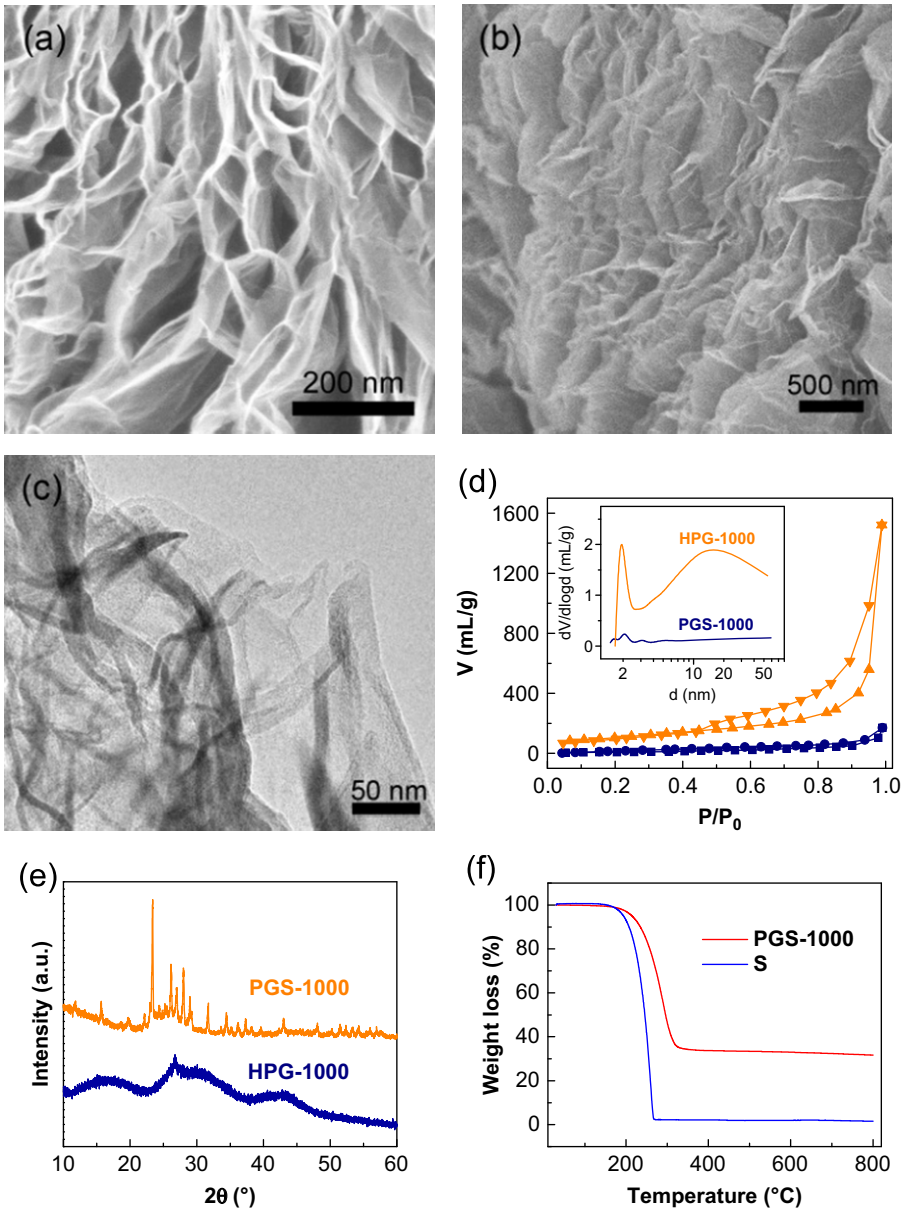

Fig. 2 SEM images of (a) HPG-1000 and (b) PGS-1000, (c) TEM image of entrap of sulfur in graphene support, (d) N_2 sorption isotherm, inset pore size distribution, and (e) XRD patterns of HPG-1000 and PGS-1000, and (f) TGA profiles of PGS-1000 and sulfur in Ar atmosphere.

was as high as 824 mA h g^{-1}. However, the decay was more obvious for the reason that the shuttle transport of lithium polysulfide (Li_2S_n, $4 \leq n \leq 8$). As indicated by the SEM images of the electrode morphology before and after the charge-discharge cycling, no obvious change of the nanostructure was observed, indicating a good structural stability of the electrode materials (Fig. S1). At even higher temperature of 60 °C, the Li-S battery can still be operated but with a much lower initial capacity of 551 mA h g^{-1}. The shuttle effect became more severe during the charge-discharge process at high temperature, and a more powerful strategy to entrap the lithium polysulfide at high temperature should be further explored.

Moreover, an excellent rate capability and lower over-discharged phenomena are also achieved at various working temperatures, as indicated in Fig. 3d. The PGS-1000 affords a very high discharging capacity of 1068 mA h g^{-1} at a current density of 0.5 C at 25 °C. This is larger than most discharging capacities of nanocarbon/sulfur electrode (such as polymer wrapped sulfur particles (about 580 mA h g^{-1}) [19], graphene enveloped sulfur (about 550 mA h g^{-1} at 0.2 C) [20], interstitial sulfur particles (around 840 mA h g^{-1}) [25], CMK-3 mesoporous carbon/sulfur cathode (930 mA h g^{-1} at 0.1 C) [5], sulfur-impregnated activated carbon fiber (ca. 1000 mA h g^{-1} at 150 mA g^{-1}) [9], and sulfur coated CNTs (650-850 mA h g^{-1} at 100 mA g^{-1}) [6]. Similar to other sulfur nanocomposite electrode, the capacity decreases slowly and the over-discharged phenomenon dramatically dwindles with the increase in the charge-discharge current density. However, the high current rate charge-discharge behavior of the reported

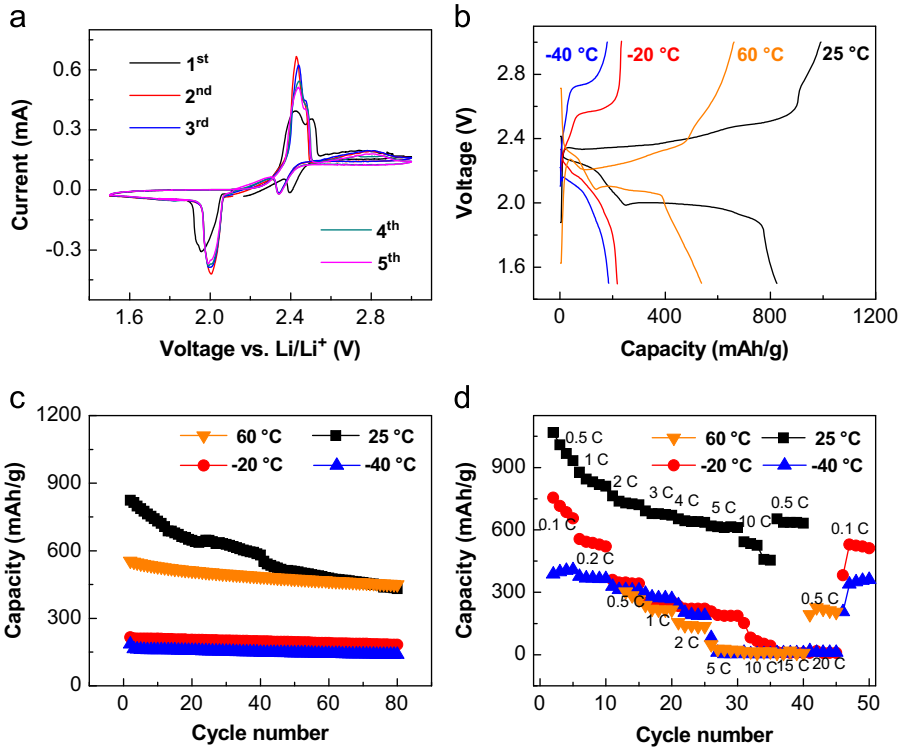

Fig. 3 (a) CV profiles of PGS-1000 with a scanning rate of 0.1 mV s^{-1}; (b) Galvanostatic charge-discharge curves of the first charge-discharge process, (c) Cycling performance at a current density of 1672 mA g^{-1} and (d) rate performance of PGS-1000 at −40, −20, 25, 60 °C.

graphene/sulfur electrode was seldom mentioned in the literatures [5-11,19-25,27]. Herein, it can be seen that even at the highest current density of 10 C (16.7 A g^{-1}), the measured discharge capacity is still as high as 543 mA h g^{-1} at 25 °C, which indicated that the composite is a promising candidate for high-power electrode materials for Li-S batteries. When the current density returns to initial value (0.5 C) after 35 cycles, the capacity of PGS-1000 electrode recovered to 653 mA h g^{-1}.

When the PGS-1000 electrode was evaluated at −20 °C, discharging capacities of 755, 360, 234, 190, and 152 mA h g^{-1} were achieved at a current density of 0.1, 0.5, 2, 5, and 10 C, respectively. Meanwhile, as the temperature was brought down to a ultralow point of −40 °C, the value of 386, 327, 202, 11, and 4 mA h g^{-1} at a current density of 0.1, 0.5, 2, 5, and 10 C can be preserved, respectively. The loss of discharging capacity became more seriously at higher current rates, which can be attributed to the slow ion transfer rate at ultralow temperature. However, when the charge-discharging current returned from 20 to 0.1 C, the electrode retained its capacity of over 340 mA h g^{-1}, demonstrating a high stability in this condition.

Advantages of nanostructure and functionalization on electrochemical performance

The sp^2 conjugated network of graphene nanosheets provide low resistant pathways for electron transportation, while the hierarchical porous structure of HPG offers the necessary buffering space for volume change of sulfur and efficient diffusion channel for lithium ions during the charge-discharge process as well. Herein, chemical reduced graphene (CRG, presents disorderly packed morphology of agglomeration without hierarchical honeycomb structure), exfoliated graphite (EG, shows porous structure but multi-layered graphitic nanosheets building blocks (usually more than 10 layers of graphene)), and HPG-250 (shows similar porous nanostructure, while shows different degree of functionalization) were employed as control samples to demonstrate the design principles for advanced graphene/sulfur composite electrodes.

With hierarchical porous nanostructures, the HPG structure provides expansion space for sulfur active materials and confined space for polysulfide. To validate the importance of HPG structure on its electrochemical properties, both CRG and EG were used as control samples. The CRG shows a high BET surface area of 666 m^2 g^{-1}, which is higher than that of HPG-1000. The CRG/S electrode was named as CGS. However, the CRS only offers a discharging capacity of 110 mA h g^{-1} at a charge-discharge current of 1 C, indicating the low efficiency of sulfur in the CGS electrode (Fig. 4a). The rate performance of the CGS showed similar trends to that of PGS, while the capacitance of the CGS was quite low (Fig. 4b). As shown in Fig. S2, very few macropores and mesopores can be observed in the CRG, and therefore no porous structure is available to support element sulfur and form such entrapped structure. When EG was used as support for sulfur particles (composite denoted as EGS), the EGS provided a low capacity of 16 mA h g^{-1} at a current of 1 C (Fig. 4a), and the rate performance of EGS is poor. Although EG offers macroporous

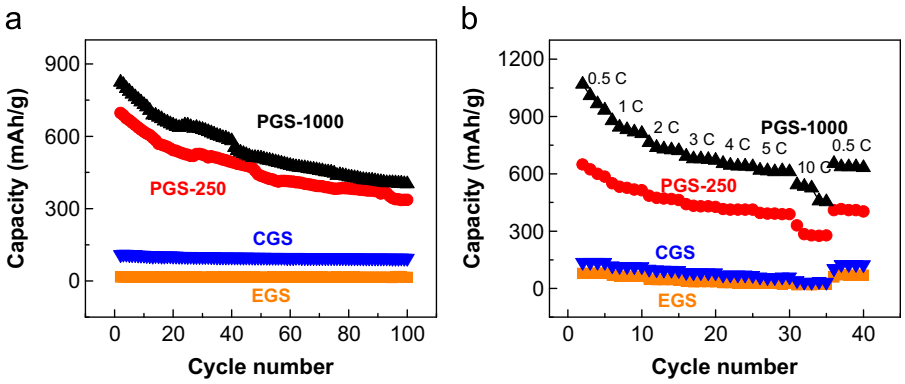

Fig. 4 (a) Cycling performance at a current density of 1672 mA g^{-1} and (b) rate performance of PGS-1000, PGS-250, CGS, and EGS at 25 °C.

structures, the large pores with multi-layer graphene as building blocks limited the conductive contact area for sulfur active materials. Therefore, the well combination of the hierarchical graphene building blocks with sulfur in PGS structure is quite important for the advanced performances.

Besides, the functionalization in the carbon support is also considered an important factor to affect the performance of resulting electrode materials. This was also confirmed by the PGS-250 electrode, in which the graphene were formed by thermal reduction at 250 °C. The PGS-250 rendered a discharging capacity of 697 mA h g^{-1} with a current of 1 C, which was quite higher than that of CGS and EGS. However, it is still less than that of PGS-1000 (Fig. S3-S5). HPG-250 presents similar structures with HPG-100, while showing different degree of functionalization. HPG-250 contains functional groups of 1.41 at% quinone, 1.52 at% C(O)O, 1.40 at% C=O, 3.09 at% C-O, and 2.28 at% O-H. In contrast, the amounts of quinine, C(O)O, C-O, C-O, and O-H were 0.11, 0.27, 0.90, 1,09, 1.13 at% for HPG-1000, respectively [31]. The BET surface area of HPG-250 is 308.8 m^2 g^{-1}, which is slightly smaller than that of HPG-1000 (434 m^2 g^{-1}). Ji [27] reported that the functional groups, especially the epoxy and hydroxyl groups, show strong adsorbing ability to anchor sulfur atoms to the C-C bounds due to the induced ripples when GO was used as support with 1 mol kg^{-1} LiTFSI in PYR14TFSI/PEGDME as electrolyte. Herein, the 1,3-dioxolane (DOL):1,2-dimethoxyethane (DME) (v/v=1/1) with 1 mol L^{-1} LiTFSI were used as electrolyte, and the HPG-1000 was mainly with epoxy and hydroxyl groups, which can enhance the binding of S to the C-C bonds due to the induced ripples by the functional groups [27]. Combined with large surface area and uniform pore, the PGS-1000 was an excellent filler for Li-S battery. The full potential of HPG as support for sulfur electrode may be further improved by the design of graphene support with tunable surface area and proper functionalization.

Conclusions

A nanocomposite electrode with sulfur entrapped in porous graphene was fabricated for Li-S batteries. The sulfur particles confined by the porous graphene were of high activity for Li-S battery, e.g., the PGS-1000 provides a quite high discharging capacitance of 1068 mA h g^{-1} at a current density of 0.5 C. When the temperature decreased to −20 °C, discharging capacities of 755, 360, 152 mA h g^{-1} can still be achieved at a current density of 0.1, 0.5, 10 C, respectively. The discharging capacity preserved 386 mA h g^{-1} at a current density of 0.1 C when the PGS-1000 electrode was used at ultralow temperature of −40 °C. The HPG-1000 was mainly with epoxy and hydroxyl groups, which can enhance the binding of S to the C-C bonds due to the induced ripples by the functional groups. Combined with large surface area and uniform pore, the PGS-1000 was an excellent filler for Li-S battery. The current contribution provides a general way to entrap of active phase in porous graphene platform for further applications in the area of heterogeneous catalysis, cell culture, drug delivery, electrochemical energy storage, and so on.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2012.10.003.

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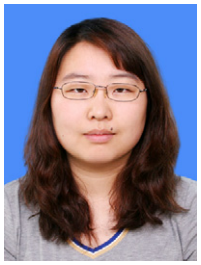

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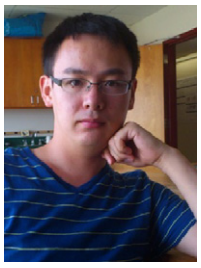
Meng-Qiang Zhao is currently a Ph.D. candidate at the Department of Chemical Engineering, Tsinghua University, China. He had been a one year visiting scholar at University of Virginia, USA. His research interests are synthesis chemistry, mass production, assembly of CNTs and lamellar particles.



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