

Fabrication and Electrochemical Performance of Sulfur/Carbon Composite Synthesized from Self-Assembled Phenol Resin

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Sulfur is a promising cathode material for secondary Li-S batteries for its high theoretic capacity although it is confronted with serious issues of high dissolution in electrolyte and low conductivity. High dispersion of sulfur is demonstrated a feasible way to improve the conductivity of sulfur and simultaneously alleviate the mass loss for the dissolution of intermediate Li_2S_x ($x < 4$) compounds during cycling. In this paper, sulfur/carbon composite composed of sulfur and microporous carbon was prepared by facile heat diffusion method, in which sulfur was impregnated in the micropores of carbon matrix. The electrochemical performance of this composite as cathode material in Li-S batteries was investigated. The specific capacity of sulfur involved in the composite was close to 1467 mAhg^{-1} based on the weight fraction of sulfur, ignoring the possible lithium insertion into carbon matrix. The utilization efficiency of sulfur is higher than most reports related to sulfur cathode, achieving 90% of its theoretic capacity. The cyclability of the sulfur/carbon composite is very excellent and the retained capacity after 100 cycles is 91% of its first discharging capacity.

Keywords: sulfur; composite; microporous carbon; phenol resin; Li-S batteries

1. INTRODUCTION

Lithium-sulfur batteries have been paid intense attention recently for their high power and energy density. However, there are many issues to be addressed while sulfur is employed as cathode material although it possesses the highest specific capacity of all-known cathode materials [1-2]. When sulfur reacts electrochemically with lithium ions, the intermediate products, lithium polysulfide phases (Li_2S_x , $x < 8$), which are soluble in the organic electrolyte, are formed based on the multi-electron-transfer cathode reaction ($\text{S}_8 + 16\text{Li}^+ + 16\text{e}^- = 8\text{Li}_2\text{S}$), resulting in the irreversible consumption of lithium ion and sulfur. Moreover, the low conductivity of both sulfur and the intermediate products deposited on the electrode surface would cause electronic contact problem, which would lower the application efficiency of active materials [3-19].

The application of all-solid or sol-gel electrolyte has been demonstrated a feasible way to decrease the solubility of polysulfide [7, 8]. However, the increased electrolyte viscosity limits the further application of sulfur cathode especially in the field of requiring high-rate and high power sources. Therefore, the modification of sulfur material is indispensable. Sulfur cathode material has been modified in several ways including the formation of sulfur composites [10-15, 17], sulfur-containing organic compound [3-9, 16], inorganic sulfide [20, 21], of which the formation of sulfur composite embedded in high conductive matrix is the most favorite way. Porous carbon [12, 18], including microporous, mesoporous and macroporous carbon, is a favorite matrix candidate for sulfur composite, not only for its high conductivity, but also its porous microstructure, which could accommodate sulfur in relatively compacted space to mitigate the direct dissolution of intermediate products in organic electrolyte, and therefore decrease the mass loss of the active center. To embed sulfur particles into the pores of carbon matrix not only makes sulfur active center highly dispersed, but also creates a barrier structure to resist against the dissolution of Li-sulfur intermediate products. The dispersion of sulfur cluster is a key factor related to the utilization efficiency of sulfur active center, therefore the structure and volume capacity for individual pores in carbon matrix is fundamentally the key factor related to the performance of sulfur composite. Mesoporous carbon is considered as the promising matrix to get high performance sulfur composite for its highly ordered and repetitive structure with high specific surface and applicable volume capacity, which already has been proved feasible and high effective as carrier for catalyst [19].

Phenomenon that can not be ignored is that seldom reports focused on microporous carbon as the matrix of sulfur composite. It is speculated that smaller pore size of matrix and highly dispersion of active center is beneficial for the utilization of active sulfur, considering the insulation and the solvent-dissolution of the sulfur active center. The pore size of the carbon matrix practically provided an impact space for sulfur dispersing. In this paper, we explored the possibility of carbon matrix with microporous structure to act as the host material for sulfur-containing composite. The sulfur/carbon composite was prepared by a facile heat-diffusion way, by which the melted sulfur could be imbibed into the microporous carbon matrix by capillary force. The massive load of the sulfur was controlled at 32 wt% unless stated otherwise. The electrochemical reversibility of the sulfur/carbon composite as cathode material for secondary lithium-sulfur batteries was investigated.

2. EXPERIMENTAL SECTION

2.1. The preparation of carbon matrix

The preparation of carbon matrix with micropores was made by the means of hydrothermal method with low concentration of phenol resin precursors, referred to reference 19. 0.8g phenol and 2.8ml formaldehyde solution (37%) and 20ml NaOH solution (0.1M) was mixed together and stirred constantly at 70 ° C in water bath for about 2 hours, followed by the addition of 50ml water and 1.28g PF-127. PF-127 acted as the soft template for fabricating micropores in phenol resin. The mixture was stirred constantly at 66° C until the color of the mixture became to crimson. Subsequently, 24ml of the

upper-layer pellucid solution was then transferred into a PVDF vial after 18h quiescence with 74ml distilled water as the dilution solvent. The vial was then sealed in a stainless steel sheath and heated at 130° C for 24 hours in oven for hydrothermal reaction to get microporous phenol resin. After hydrothermal reaction, the collected products were washed with distilled water for several times and then dried in a vacuum oven at room temperature for 48 hours, followed by heat-treatment in Ar atmosphere at 900° C for 3 hours to make the products carbonized . The carbon matrix with microporous structure was finally obtained.

2.2. The preparation of sulfur/carbon composite

The sulfur/microporous carbon composite was prepared by a facile heat-diffusion method. Differential scanning calorimetry (DSC) was used to detect the mixed precursors of sulfur and microporous carbon so as to determine the temperature for heat-treatment. The ratio of sulfur and as-prepared microporous carbon was 4:1. The two exothermal peaks appearing at about 120 °C presented in figure 1 are corresponding to the melting processing of sulfur. The exothermal peak at 164 °C is related to the viscosity change of sulfur in agreement with other reports. The lowest viscosity of melted sulfur at 164°C is beneficial to the diffusion of sulfur into the micropores of carbon matrix by the capillary imbibitions.

According to the results of DSC analysis, the heat-treatment of the mixed precursors consisting of sulfur and microporous carbon was executed at 164°C for 6h to make sulfur fully imbibed into the micropores of carbon matrix, which was followed by the processing of removing excessive sulfur coated on the surface of carbon particles at 300°C for 3 hours. The preparation processing including heating-up and cooling down was protected by Ar gas all the time to avoid the oxidation of samples. The sulfur/carbon composite obtained by heat-treatment was ultrafine powder in black.

2.3. The electrochemical evaluation of as-prepared sulfur/carbon composite

The composite electrode was composed of 70wt% as-prepared sulfur/ carbon composite, 20wt% carbon black and 10wt% PTFE. The active cathode material and the carbon black were mixed in PTFE latex solution to make homogeneous slurry. Then the slurry was casted onto nickel foam disks with a diameter of 14mm, followed by heating under vacuum at 100 °C for 24 hours.

The as-prepared sulfur composite electrode disks were mounted in 2032 coin cell case with lithium metal foil as the opposite electrode and 1M LiPF₆ electrolyte with EC and DMC as the solution with same volume. The cycling properties were executed under static constant current with the same charge-discharge current of 0.2 mA.

3. RESULTS AND DISCUSSION

Although it is very difficult to get ultrafine nanosulfur particles directly, the micropores of the carbon matrix could limit the sulfur active center into a compacted space against its agglomeration during electrochemical reacting [10-18, 20-25].

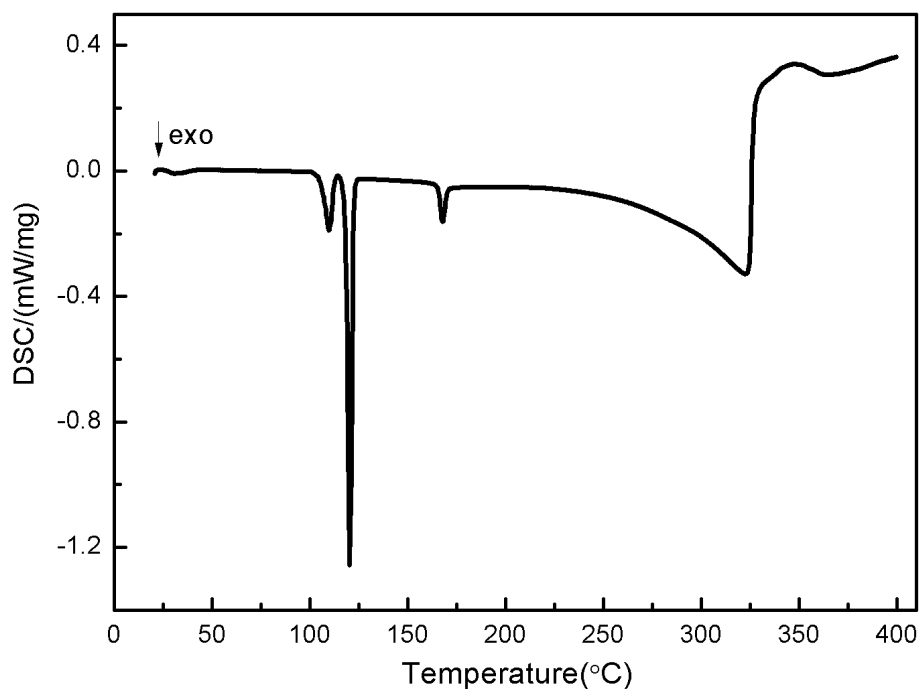


Figure 1. The DSC diagram of the mixed precursor composed of sulfur and microporous carbon

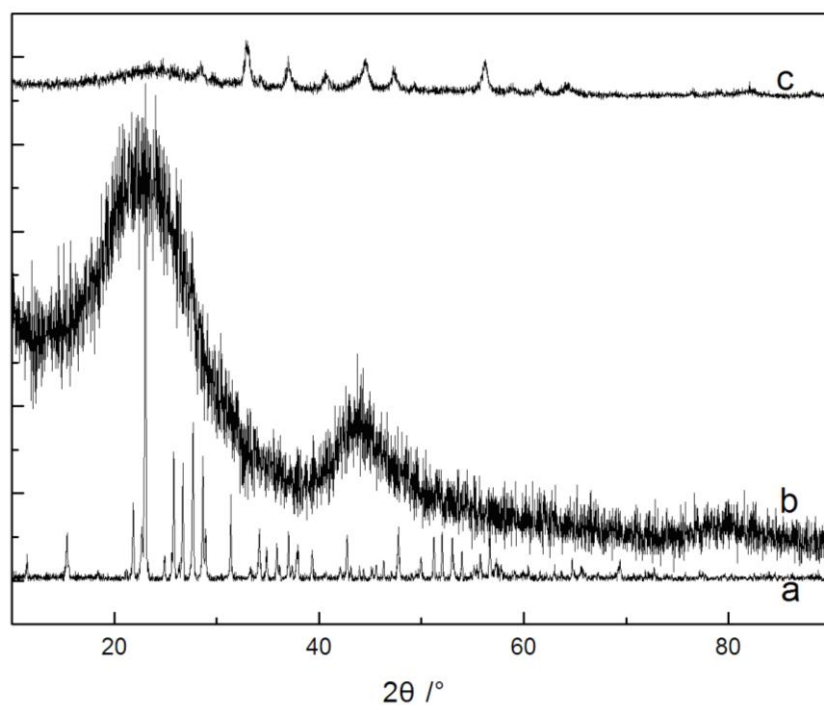


Figure 2. The XRD pattern of: a) Commercial sulfur powder used in the case; b) Porous carbon matrix prepared from purolyzed phenol resin precursor; c) Sulfur/ microporous carbon composite

In addition, closely spaced pore could impede the diffusion of intermediate Li-S products for

the capillary force. Therefore, the microstructure and morphology of carbon matrix plays an important role in the performance of sulfur/carbon composite cathode. The X-ray diffraction profiles of sulfur, carbon matrix prepared from hydrothermal method, and sulfur/carbon composite synthesized by heat-treatment are shown in figure 2, respectively. Two wide peaks appeared at 22° and 42° on curve b exhibiting the typical diffraction of carbon, and the widening peaks demonstrate the amorphous state of as-prepared carbon produced from phenol resin precursor after deoxygenating and dehydrogenation at high temperature. The sharp peaks corresponding to the strongest line of crystalline sulfur disappeared after heating with carbon matrix. Another experiment was executed to clarify the peak changes. Condensed sulfur powder stuck on the sidewall of oven tube at low-temperature region during heating was collected directly without any further treatment. The XRD results of the condensed sulfur shown in figure 2 reveal that crystalline structure was kept after heat-treatment, characterized by the strong and sharp peaks in XRD profile. That is, the disappearance of sharp peaks in curve c was not derived from the crystal transformation of sulfur for heat-treatment, demonstrating indirectly the embedding behavior of sulfur into the pores of carbon matrix.

Phenol resin prepared with NaOH as the catalyst could maintain its initial morphology during heat treatment [19], so the morphology and pore structure could be remained finally after carbonization. The morphological comparison of carbon matrix before and after sulfur loading is presented in figure 3. The carbon matrix possesses visible and smooth spherical shape although some of the carbon balls were interconnected with each other on the boundaries, seen in figure 3a. The average particle size of carbon balls is about 290nm calculated qualifiedly. The morphology of carbon balls after sulfur loading is similar to that of before sulfur-loading, presenting similar particle size and shape (figure 3b). We speculated that the sulfur was diffused into the inner pores of the carbon balls. The high initial pressure from BET absorption-desorption curve verified that the pore size of the carbon balls before sulfur impregnating actually is micrometer of ca. 2 nm. The specific area of the carbon balls was 377.3m²/g, but it decreased to 105.6m²/g after sulfur insertion. Sulfur/carbon composite samples were weighed before and after sulfur loading to determine the accurate weight of sulfur loading. The average sulfur contained in the composite was about 31-33 wt%, proved further again by TG analysis.

Sulfur has a high theoretical capacity for lithiation up to 1675mAh/g, but its essential characters of ionic and electronic insulation makes it difficult to be utilized completely [22]. The microporous structure of carbon matrix provided a supporting frame as well as a compacted space for sulfur active center. The volumetric minimization of dispersed sulfur active center could facilitate its utilization. The reason is not only the highly compacted sulfur-absorbing space, but also the high conductivity of carbon frame. The pore size is intimately related to the dissolubility of Li₂S_x intermediates and the interaction of electrolyte and the active material, so controlling the pore size of carbon is very important to the final performance of sulfur/carbon used as cathode materials for secondary Li-S batteries. It is deduced that the microporous structure could act as a physical barrier for the dissolution of sulfur and Li₂S_x intermediate products, and thus enhance the electrochemical performance [12, 13, 16].

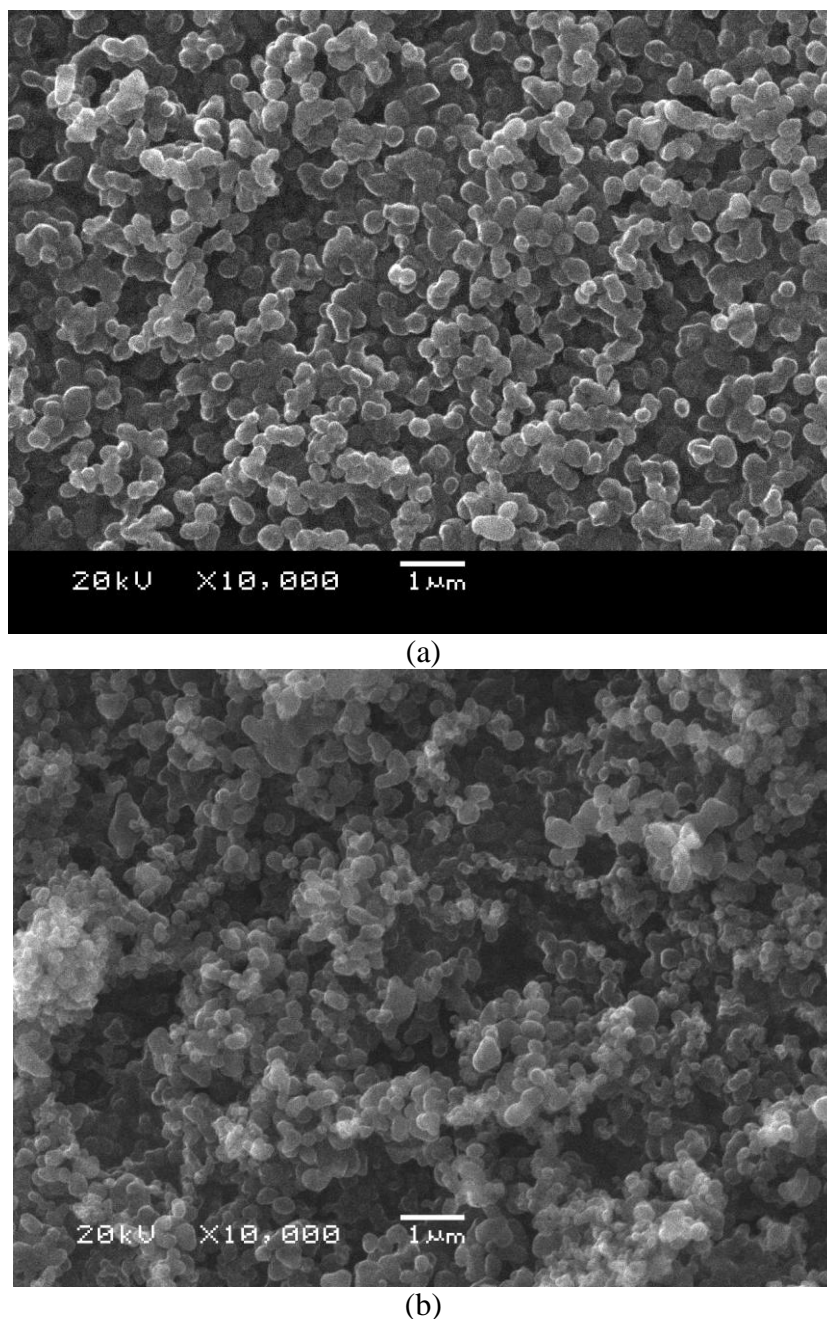


Figure 3. The SEM images of a) The carbon matrix produced from pyrolyzed phenol resin; b) The sulfur/carbon composite

The electrochemical performance of sulfur/carbon cathode material was investigated by constant current method. Figure 4a shows the charge-discharge profile of a sulfur/carbon cathode with lithium foil as the counter electrode at 0.1C rate within the voltage cutoff windows of 1 V-3 V vs. Li metal reference electrode. The as-prepared composite cathode carried a charge capacity (lithium insertion) range up to 484 mAhg^{-1} and discharge capacity of 385 mAh g^{-1} for the first cycle, yielding a coulombic efficiency of ca. 80% (figure 4a). It is worth noting that the specific capacity of sulfur involved in the composite was actually close to 1467 mAhg^{-1} based on the weight fraction of sulfur, ignoring the possible lithium insertion into carbon matrix. In our case, this utilization value is higher

than most reports related to sulfur cathode [10, 12, 13], achieving 90% of its theoretic capacity based on 32 wt% of sulfur involved in this sample. This high utilization efficiency is likely attributed to the closely spaced micropores and interconnected inner structure of the carbon matrix pyrolyzed from hydrothermal phenol resin, which provides interconnected tunnels for electrons and also structured a compacted space for insulation region. After the first and second cycles, the shape of the charging and discharging curves became reproducible with a discharging plateau at 2.1-2.5V, similar to other reports. The retained capacity is 352mAhg^{-1} after 100 cycles, delivering 99% columbic efficiency and 91% of its first discharging capacity (figure 4b). Electric and ionic isolation of the sulfur can occur unavoidably with the formation of Li_2S_x intermediates, but the closely spaced micropores could be saturated transient and Li_2S_x intermediate was restricted tightly in the space by capillary force, which could impede the continuous dissolution of Li-S_x , resulting in the enhancement of electrochemical performance [16-18, 23, 24].

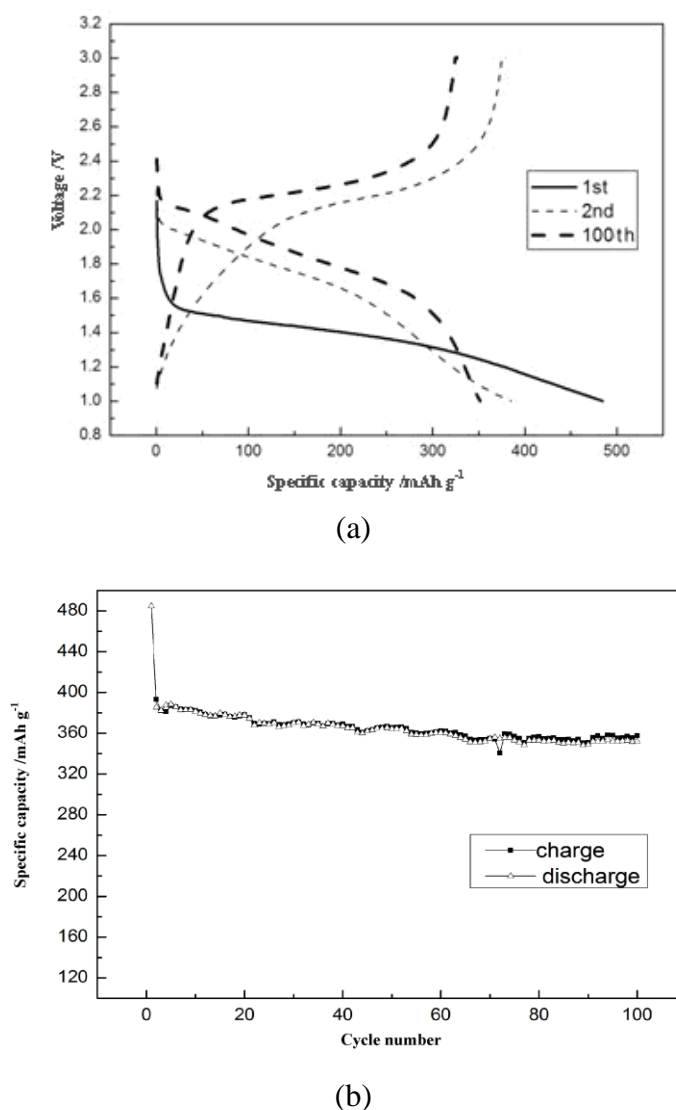
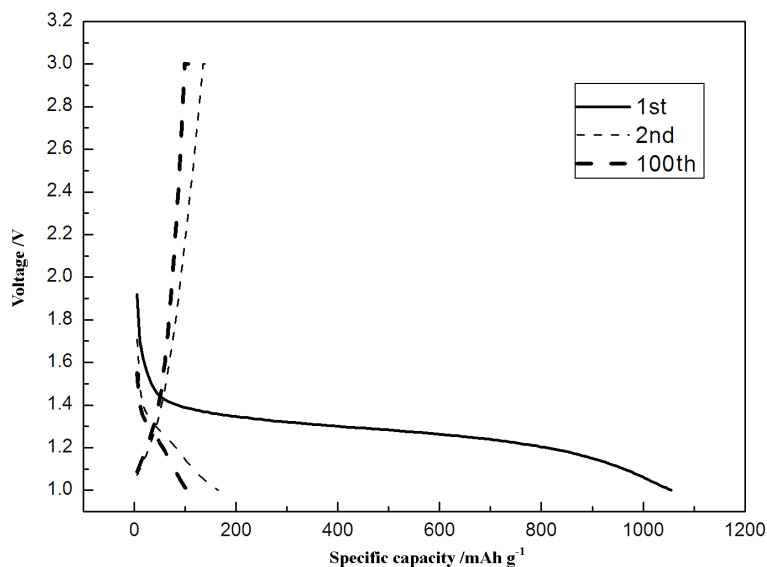
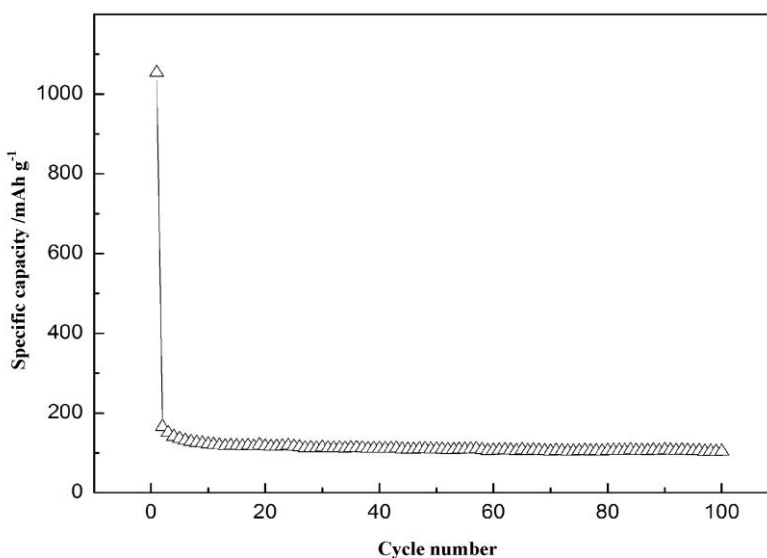


Figure 4. The profiles of a) charging-discharging behavior of sulfur/carbon cathode; b) the cycling performance of sulfur/carbon cathode



(a)



(b)

Figure 5. The profiles of a) charging-discharging performance and b) the cycling performance of sulfur/carbon cathode by direct solution absorption method

It was speculated that the residue sulfur on the surface of carbon matrix was removed by sintering. We experimentally executed another experiment to confirm it evidently. In the designed experiment, sulfur was dissolved into CS₂ solution directly to make saturated sulfur solution. Then as-prepared carbon matrix was put in this sulfur dissolution, followed by 16 hour quiescence to make dissolved sulfur absorbed completely to carbon matrix. Then the mixture was filtrated to get rid of the liquid solution. The carbon matrix loading with sulfur was then dried under vacuum at ambient temperature over 20 hours. The product was assembled as electrode and tested following the same procedure as in experimental section of electrochemical evaluation. The charging-discharging profiles

show in figure 5. It worth noting that the lithiation capacity approaches to 1054 mAh g^{-1} , but the discharging capacity declines abruptly to 165 mAh g^{-1} (figure 5a). We deduced that the absorption reaction occurred homogeneously on the surface and interior of carbon matrix by van der Waals force or capillary force. Obviously, the absorption quantity of sulfur atoms is determined by the volume capacity of micropores and the total surface area of carbon matrix [13, 19], so it could be understood that higher first-cycle charging capacity was obtained. However, a phenomenon can't be ignored is that the capacity after the first cycle dropped abruptly to 165 mAh g^{-1} . It is deduced that the sulfur loaded in the micropores functions as the main active center after the first cycle because the sulfur on the surface had high possibility to contact directly with electrolyte, which increased the risk of mass loss during cycling, and therefore, the obvious fall in capacity could be observed. It indirectly demonstrated that the sulfur diffused into the micropores plays a key role to support the long-term stability in its electrochemical performance. The further explanation will be shown in following part.

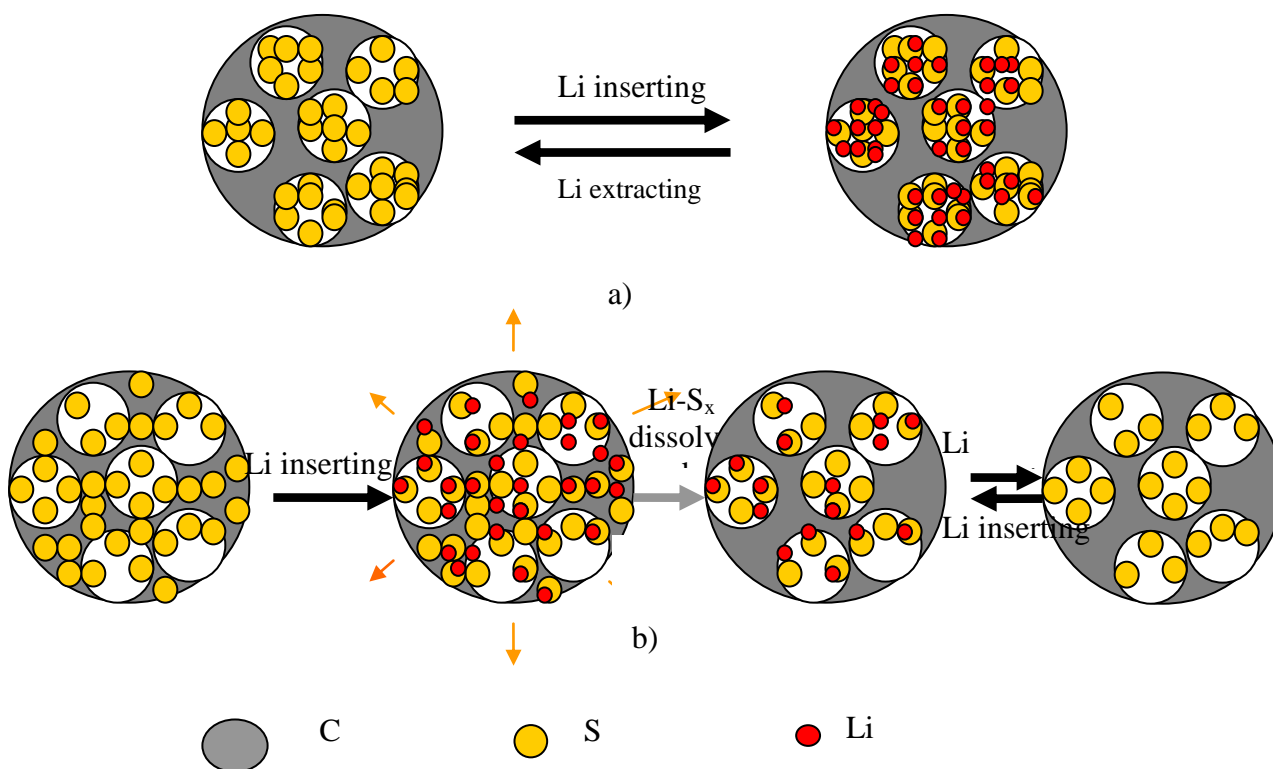


Figure 6. The schematic illustration of the inserting-extracting processing of lithium ions in sulfur/carbon composite prepared from a) melting heat-treatment; b) direct solution absorption method

The lithiation processing for sulfur/carbon composite cathode from different method was speculated as schemed in figure 6. For sulfur/carbon composite from melting heat-treatment, the lithiation process occurs mostly in the micropores in carbon host where the sulfur active center is accommodated (figure 6a), which makes it possible to decrease the direct contact between Li_2S_x intermediate compounds and a large quantitative of electrolyte so as to mitigate the mass loss of sulfur

active center, resulting in enhanced cyclability [19, 22-25]. However, for the sulfur/carbon composite from direct solution absorption method, in which sulfur is dispersed both on surface and interior, lithiation reaction takes place wherever sulfur is distributed, risking much higher dissolution of intermediate Li-S_x (figure 6b) and thus resulting in high irreversibility of the cathode. The cycling performance could become stable after the first cycle once the excessive sulfur coated on the surface of carbon matrix was exhausted for irreversible dissolution during lithiating (seen in figure 6b). This cycling performance affected by the different structure been demonstrated in our experiments (figure 5b). In addition, the quantity of sulfur active center absorbed interior during direct solution absorption processing was naturally much less than melting heat-treatment because of more solution involved in the compacted space and hence less sulfur active center impregnated in, so lower stable capacity was obtained for sulfur/carbon composite cathode from direct solution absorption method.

4. CONCLUSIONS

Sulfur/carbon composite composed of sulfur and microporous carbon matrix was prepared by heat diffusion method, in which the carbon matrix was formed from pyrolyzed phenol resin by hydrothermal reaction and sulfur was imbedded in the micropores structured in carbon hose. We demonstrated that high dispersion of nanosulfur impregnated in carbon matrix is the key factor to enhance the utilization efficiency and electrochemical reversibility of sulfur active center. The capacity of sulfur active center could achieve up to 90% of its theoretical capacity. The cyclability of the structured sulfur/carbon composite was enhanced dramatically, showing 91% and 99% capacity retention after 100 cycles, comparing to its first and second discharging capacity, respectively.

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