Scholars Journal of Engineering and Technology (SJET)
Sch. J. Eng. Tech., 2014; 2(6A):828-836
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(An International Publisher for Academic and Scientific Resources)
www.saspublisher.com

ISSN 2321-435X (Online)
ISSN 2347-9523 (Print)

Research Article

In-situ Deposition Route Synthesis of Graphene Oxide-Sulfur Composites as Rechargeable Lithium-Sulfur Battery Cathode

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Abstract: $Na_2S_2O_3$ was served as a source of sulfur, and graphene oxide-sulfur composites were synthesized by liquid phase in-situ deposition method. In order to observe surface morphology, phase structure and electrochemical properties of the composites, the prepared products had been characterized by X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy(SEM), charge-discharge measurements and electrochemical impedance spectroscopy(EIS). Comparing properties of composites synthesized by liquid phase in-situ deposition method and conventional method, the results showed that the former exhibited better crystal structure, more successful combination between sulfur and graphene oxide and good electrochemical performance. The in-situ composite was with first discharge capacity of 589mAh/g at the current density of 50mA/g, maintaining 241mAh/g after 20 cycles. And the reversible capacity retention was 40.9%.

Keywords: Lithium-sulfur battery cathode, Graphene Oxide-Sulfur Composites, Liquid phase in-situ deposition route

INTRODUCTION

As increasing concern about climate change, the environment, limited global energy supply, the demand of clean and efficient energy storage devices is also growing steadily. Lithium ion batteries with high energy density have become the main force of portable electronic devices market. At present, compared to the specific capacity of anode materials (graphite: 370 mAh/g, Si: 4200 mAh/g), the low specific capacity of cathode materials (layered oxide: 150 mAh/g, LiFePO4:170 mAh/g) is still an important factor to limit battery energy density [1].With low cost, environment friendly, high theoretical specific capacity ,sulfur has become a promising cathode material. However, its low electronic conductivity, soluble intermediate polysulfide and volume expansion lead to short cycle life, low specific capacity and bad energy utilization of lithium-sulfur battery, which restrict the commercial applications [2]. In this paper, on one hand, the traditional sublimed sulfur was improved, we produced sulfur with smaller size by reacting with as sulfur source; On the other hand, using in-situ deposition method ensured that the sulfur and graphene oxide combined more evenly, thus the electrochemical performance of the battery was obviously improved.

EXPERIMENTAL SECTION

Preparation of graphite oxide

Graphite oxide was prepared by modified Hummers method [3], divided into three stages.

Low temperature stage: first, weigh 200 ml of concentrated sulfuric acid in drying beaker, place it in the ice water bath to cool to about 2˚C, add 3.0g of graphite powder and 6.0g of in turn, mix well. 40 min later, add 9.0 g of slowly, keep reacting for 5 h in the ice water bath with continuous magnetic stirring, in the process, the color of solution changes from black to green.

Medium temperature stage: warm the solution to 35˚C, last for 90 min.

High temperature stage: continue to heat up to 75˚C, keep for 1 h, with bubbles generated in the process, the solution changes from green to brown.

Return the solution to room temperature, stir and slowly add a certain amount of deionized water. Then, add 30% slowly, the solution turned into bright yellow and there are a lot of air bubbles generated, stop adding until no bubbles turn up. The obtained solution was washed with 5 wt % and deionized water , until the PH of solution was close to neutral ,the brown colloidal substance was obtained, dry in the drum wind drying oven under constant 60 ˚C. At last, we got sheet graphite oxide.

Preparation of Graphene oxide / sulfur (GO/S) composite

A. The liquid phase in-situ deposition method synthesis

0.200 g of graphite oxide was dispersed into 200 ml of deionized water, ultrasonic for 2 h to form 1 mg/ml graphene oxide solution. Add isopropyl alcohol as dispersants. Slowly add 300 ml of 0.3 mol/L solution under ultrasonic. After 10 min, 100 ml of 0.3 mol/L was added drop wise, quickly the solution changed from brown to grayish white, continue ultrasound for 30 min. Then transfer to the magnetic stirrer, stir for 24 h at room temperature. At last, we heated the as-synthesized samples in an argon (Ar) environment at 155˚Cfor 12 h. The liquid phase in-situ composite was obtained.

B. The conventional method synthesis

By contrast, we synthesized pure sulfur by the same method, the difference only lied in that the method first drop into solution, after the complete reaction, add graphene oxide solution. Herein, we prepared the conventional method composite.

Structural characterization

The synthesized samples were examined by an X-ray diffractometer (Tokyo Rigaku Ultima IV-185 type) with Cu-Kα radiation（λ=0.15406nm）between 10°and 80°at a scan rate of 5°/min. The microstructure and morphology of the samples were characterized by scanning electron microscopy(SEM,JSM-7500F).More detailed structural information on the composites were obtained by using a Fourier transform-infrared spectrometer(FT-IR,Varian640).The sulfur content in the composite was determined by thermogravimetric analyzer (TGA,SETARAM LABSYS).

Cell assembly and electrochemical measurements

The composite was mixed with acetylene black conductive agent and poly(vinylidene fluoride)(PVDF) binder in a weight ratio of 80:10:10 in N-methyl pyrrolidone(NMP) solution with a magnetic stirrer for 8h.Then, the well-mixed slurry was uniformly pasted onto an Al foil with a blade and dried in a electro-thermostatic blast oven at 60˚C for 12h,followed by pressing with a roller under a pressure of 20MPa and punching out circular electrodes of 1.1cm in diameter. The cathode electrodes were dried in a vacuum oven at 60˚C for 3h before transferring into an Argon-filled glove box. The active material loading density of the electrode is ca. 3.0mg•cm-2 .The electrolyte was 1M LiPF6 dissolved in a mixture of dimethyl carbonate (DMC) and ethylene carbonate(EC)(1:1,v/v) .The CR2016 coin cells were assembled with the prepared cathode disks, the electrolyte ,the microporous polypropylene separators(Celgard2300),nickel foam current collectors and lithium sheets as counter electrode and reference electrode in a glove box filled with argon.

The charge-discharge profiles, cyclability and rate capability were assessed with Land cell test system. Parameter Settings are as follows:

Let stand for 30 s, voltage range from 1.0 V to 3.0 V, galvanostatic charge/ discharge current density of 50mA/g (25 mA/g, 100 mA /g).

Electrochemical impedance spectroscopy (EIS) was achieved with an amplitude of 10mV at the applied frequency range from 1MHz to 10MHz on electrochemical workstation (CHI660C).

RESULTS AND DISCUSSION

Structure analysis

Fig.1 compared the X-ray diffraction (XRD) patterns of the graphite, graphite oxide, sublimed sulfur and composite prepared by liquid phase in-situ deposition method. The graphite showed sharp crystalline peak at 2θ=26.4°, the corresponding graphite interlayer spacing was 0.3364nm. Graphite oxide, with original characteristic diffraction peak of graphite disappearing, a new wider diffraction peak appeared at 2θ= 11.9 °.The corresponding interlayer spacing became 0.739 nm, indicating that graphite was completely oxidated by oxidant, the insertion of oxygen-containing functional groups (carboxyl, carbonyl, hydroxyl group, epoxy group) made the interlayer spacing increase. In the composite, characteristic diffraction peak of graphite oxide disappeared, maintain the characteristic diffraction peak of sulfur, but the peak intensity weakened, peak shape was not simple accumulation of graphite oxide and sulfur diffraction peaks, graphite oxide reacted with part of sulfur to form new chemical bonds (the later FT-IR characterization also confirms this).There were still a part of elemental sulfur scattered on the graphite oxide. Dispersion effect of graphite oxide prevented the accumulation of sulfur largely, thus peak intensity was reduced, showing that elemental sulfur was with smaller particle size.

Fig. 2 showed the FT-IR graph of graphite, graphite oxide and the composite prepared by liquid phase in-situ deposition method. In graphite oxide spectrum, we found that a weak absorption peak was at 1720 cm-1, it corresponded to C=O stretching vibration of carboxyl and carbonyl. Absorption peak at 1390 cm–1 attributed to the C- OH stretching vibration. Strong absorption peak at 1080 cm-1 corresponded to the C-O stretching vibration. All above indicated polar groups significantly increase after the graphite oxidation, the surface of graphite oxide did exist a large number of oxygen-containing functional groups. This provided favorable conditions for the preparation of composite using graphene oxide to fix sulfur later [4]. There was an obvious absorption peak at 1206 cm–1 for composite, which did not appear in graphite oxide spectrogram. It agreed with C-S absorption peaks, this also proved that the composite was not only the mixture of graphite oxide and pure sulfur but also they reacted chemically simultaneously. Sulfur replaced part of oxygen on functional groups, forming C - S bond [5].

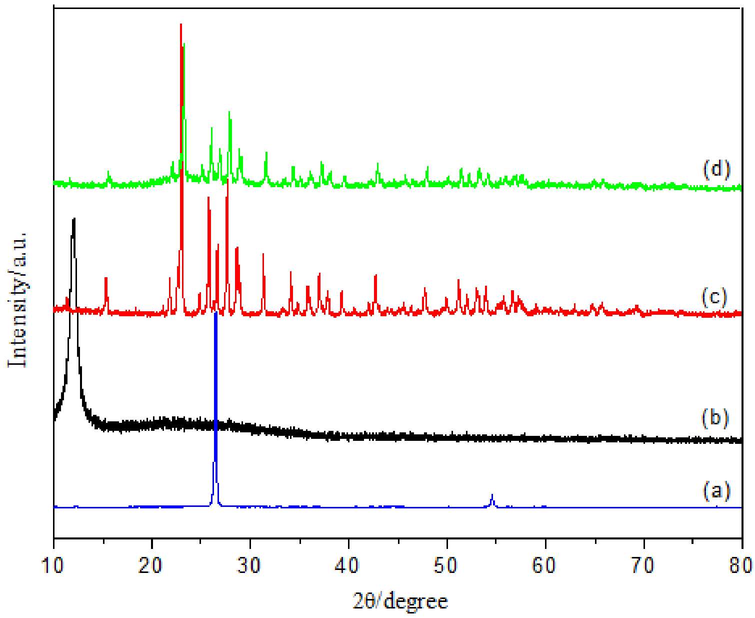

Fig.1 XRD patterns of the graphite (a), graphite oxide (b), sublimed sulfur(c) and the composite(d)

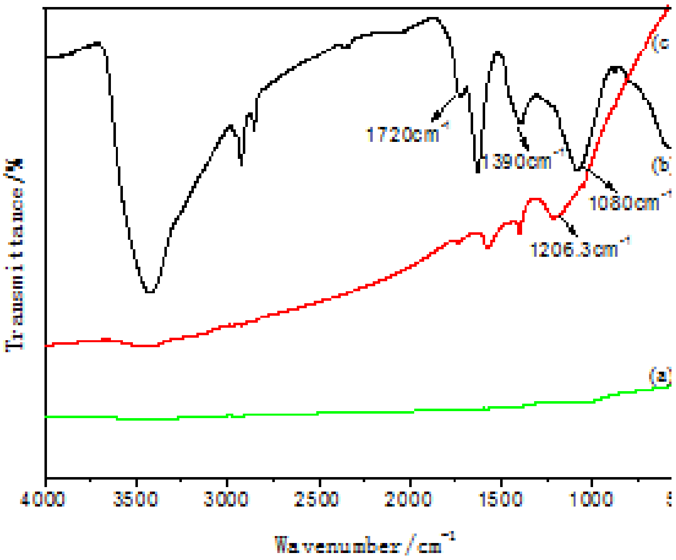

Fig. 2: FT-IR graph of graphite(a), graphite oxide(b) and the composite(c)

Fig. 3a and b illustrated the morphology of graphite and graphite oxide, typical lamellar structure can be seen in graphite. After oxidation, the layer spacing was bigger. This result indicated that oxygen-containing functional groups inserted interlayer successfully under the action of oxidants [6]. Fig. 3c and d showed the surface microstructure of the sublimed sulfur and new-made sulfur by 0.3mol/L and 0.3mol/L. Particle size distribution of sublimed sulfur was very uneven from a few microns to dozens of microns. Compared with sublimed sulfur, the particle size of new-made sulfur with chain structure decreased greatly and was uniform between 2 ~ 3 microns, some sulfur tended to reunite. Fig. 3e and f showed the SEM image of the as-prepared GO/S composite before and after heat treatment respectively. Before heat treatment, there were a lot of sulfur on the surface of the composite, the sulfur particles were fairly evenly distributed on the composite surface with less than 100nm diameter, indicating that graphene oxide can restrain reunion of new-made sulfur, the formation of small sulfur molecules was more advantageous to improve the electrochemical performance of composite. After heat treatment, As part of sulfur evaporate and the other part was fused into graphene oxide interlamination, sulfur on the surface of the composite significantly reduced [7].

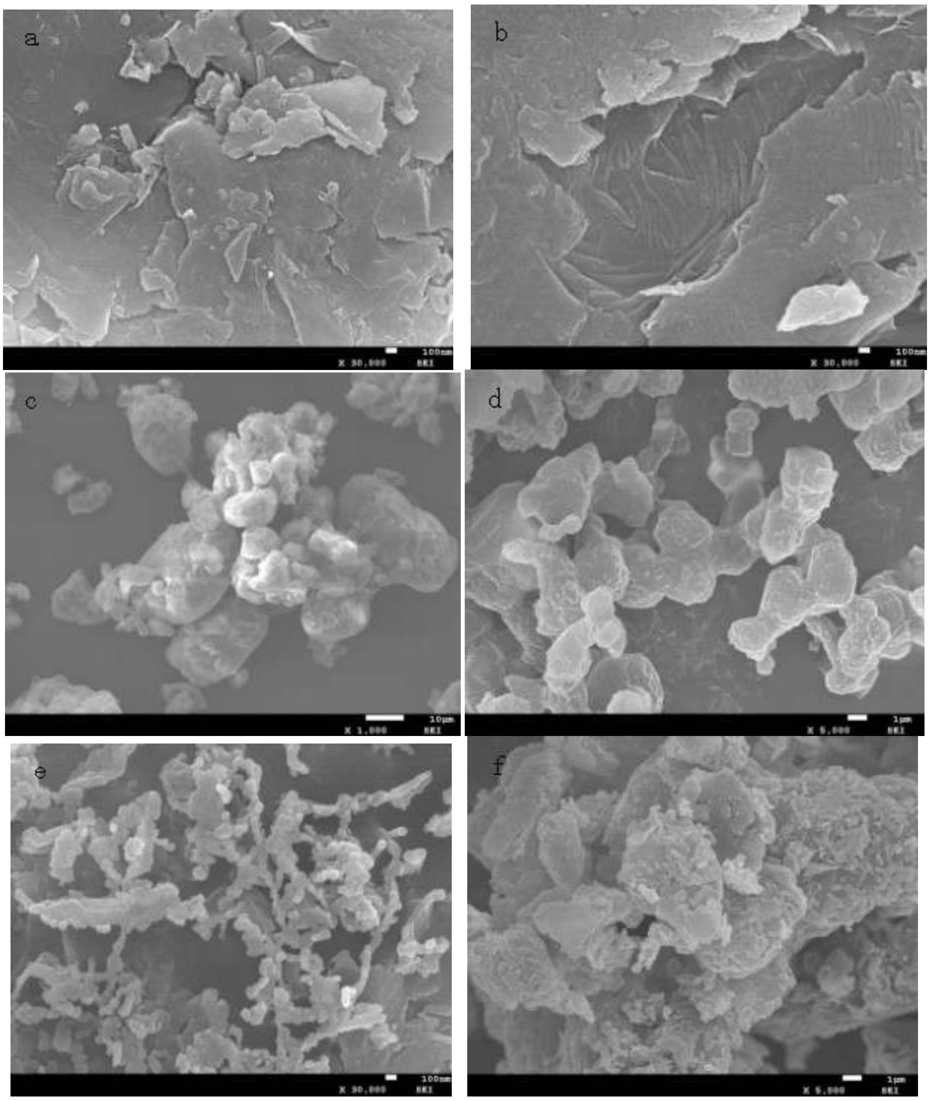

Fig. 3: SEM image of (a) graphite; (b) graphite oxide; (c) sublimed sulfur ;(d) new-made sulfur by 0.3M $Na_2S_2O_3$ and 0.3M HCl ; liquid phase in-situ GO/S composite before (e) and after（f）heat treatment in Ar environment for 12h at 155˚C.

Fig.4 was thermogravimetric analysis (TGA) curve of graphite oxide (a) and in-situ GO/S composite(b) after heat treatment. As shown in the figure, the weight of graphite oxide after calcination in the tube furnace reduced by about 5% in the TGA temperature range, considering moisture loss, mass loss caused by the decrease of functional group was less. Besides, graphite oxide would not burn in the temperature range. Some oxygen-containing functional groups in composite were replaced by sulfur, ignoring the mass loss caused by the decrease of functional groups, the result indicates that sulfur burning leads to a decrease of composite mass. Therefore, we can directly read the sulfur content of GO/S composite from the TGA [5]. And at calcination temperature of 155 ˚C, the mass of the composite had no change, showing that excess sulfur and part of oxygen-containing functional groups have been removed in the previous tube furnace burning and the composite is stable. The composite began weightlessness at 220 ˚C and sulfur combusts completely at about 360 ˚C, after that, the mass remained constant. It was concluded that sulfur content of the composite was 74.4%.

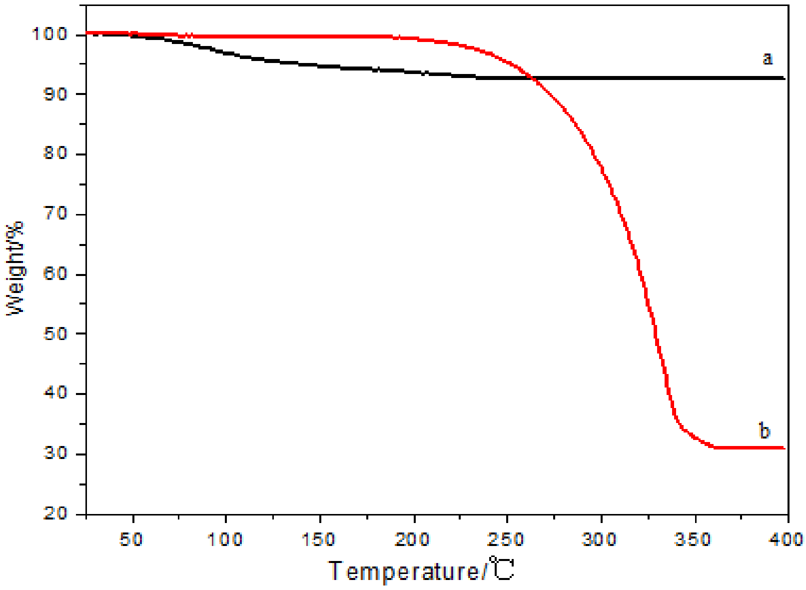

Fig. 4: TGA curve of graphite oxide (a) and in-situ GO/S composite (b) after heat treatment recorded in N_2 with a heating rate of 5°C/min.

Electrochemical performance

The first discharge profiles of liquid phase in-situ deposition composite, conventional method composite and pure sulfur cathodes at a current density of 50mA/g were shown in Fig.5. The first discharge plateau of in-situ composite was at around 2.26V and relatively stable, specific capacity reached 589mAh/g. The initial discharge plateau of conventional method composite was at around 2.21V and falls faster, at the end of the discharge, exhibiting specific capacity of 429mAh/g. In contrast, the first discharge plateau of pure sulfur cathode was slant, the average voltage was 2.15 V or so, the first discharge specific capacity was only 385mAh/g, which was lower than the previous two methods composite. Discharge platform voltage was closely related to the battery discharge mechanism [8]. Discharge plateau differences between in-situ deposition composite and the conventional method composite might result from different crystal shapes and particle sizes of sulfur synthesized by the two methods and the combination of graphene oxide and sulfur in different ways and so on. Pure sulfur cathode utilized sublimed sulfur with larger particle size and uneven distribution as sulfur source directly, only add the acetylene black as conductive agent, no graphene oxide served as conductive and support role. As shown in the figure, its first discharge capacity was the lowest of the three. Thus new-made sulfur based on the aqueous reaction can improve battery performance greatly [9], and in-situ deposition reaction based on aqueous solution can produce smaller sulfur molecules which were better dispersed on the graphene oxide with excellent performance, even interacted with graphene oxide to form strong chemical bonds. These can not only improve the conductivity of sulfur but also fix intermediate polysulfides to prevent them dissolve in the electrolyte.

Fig.6 displayed the second charge/discharge profile of liquid phase in-situ composite and pure sulfur cathode (50mA/g). As seen from the figure, the second discharge specific capacity of liquid phase in-situ composite was 476mAh/g, representing a 80.8% capacity retention. Charging to a certain stage, the voltage rose steeply. The second discharge specific capacity of pure sulfur cathode was 278mAh/g with capacity retention of 72.2%.And when the charging voltage reached a certain value (3.2 V), the voltage never rose steeply, the battery would never reach a full charge state [10]. This was due to the fact that sulfur and intermediates had not been well fixed, so polysulfide ions dissolved in electrolyte, the battery appeared more serious shuttle effect. The shuttle current formed by shuttle effect exceeded the charging current, which lead to severe polarization phenomenon in the battery.

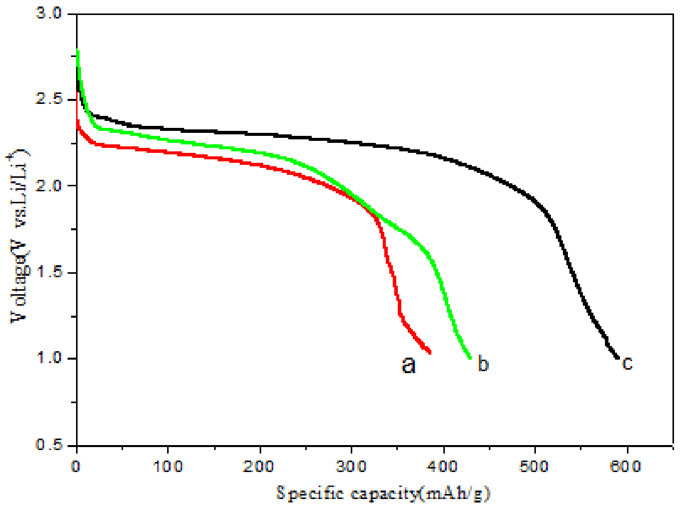

Fig. 5: The first discharge curve of liquid phase in-situ deposition GO/S composite (a); conventional method composite (b) and pure sulfur(c) cathodes at a current density of 50 mA/g

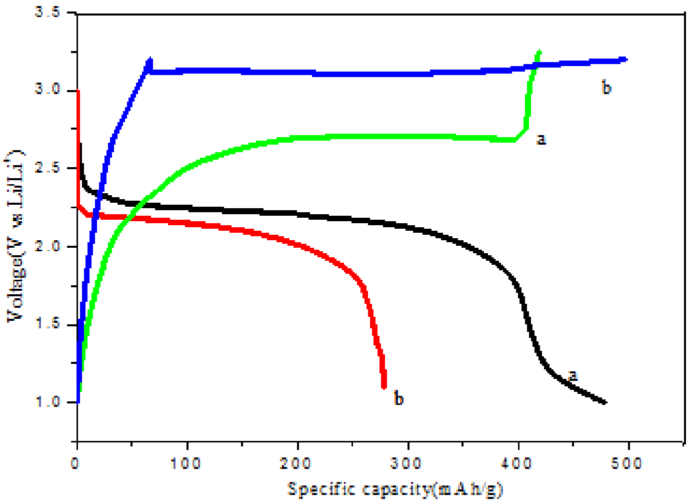

Fig. 6: The second galvanostatic charge/discharge profiles of liquid phase in-situ GO/S composite (a) and pure sulfur (b) cathode (50mA/g)

During charging, thermodynamics process of oxidizing high-order polysulfide into elemental sulfur was very slow. So at the end of the charging, a large number of active substances existed in the electrolyte in the form of high-order polysulfide. Therefore, from the second discharge on, discharge active substances had a big difference with that of the first time, only a small amount of active substances began to discharge from the elemental sulfur, other active substances discharged from ($4\leq n\leq 8$). Discharge end-products and were insoluble in the electrolyte, but deposited on the surface of the cathode structure, they themselves were insulated and can not contact with conductive materials adequately, making this part of sulfur inactive, leading to capacity irreversible decay in Li-S batteries [11-14].

The cycle life plots of liquid phase in-situ composite cathode at various current density (b.50mA/g c.25mA/g d.100mA/g) and pure sulfur cathode (a.50 mA/g) were shown in Fig.7.As previously encountered, the discharge specific capacity of liquid phase in-situ composite cathode decreased with increasing current density. But they were all much higher than that of pure sulfur cathode under the current density of 50 mA/g, representing liquid phase in-situ composite with excellent rate and cycle performance. On one hand, liquid phase in-situ method can not only synthesize small molecule sulfur with uniform particle size but also obtain more homogeneous composites. On the other hand, the addition of graphene oxide can prevent sulfur reuniting, suppress the migration of elemental sulfur and soluble intermediates, adapt to the volume changes of sulfur during the cycling process and maintain the structural integrity of the cathode [14-18].

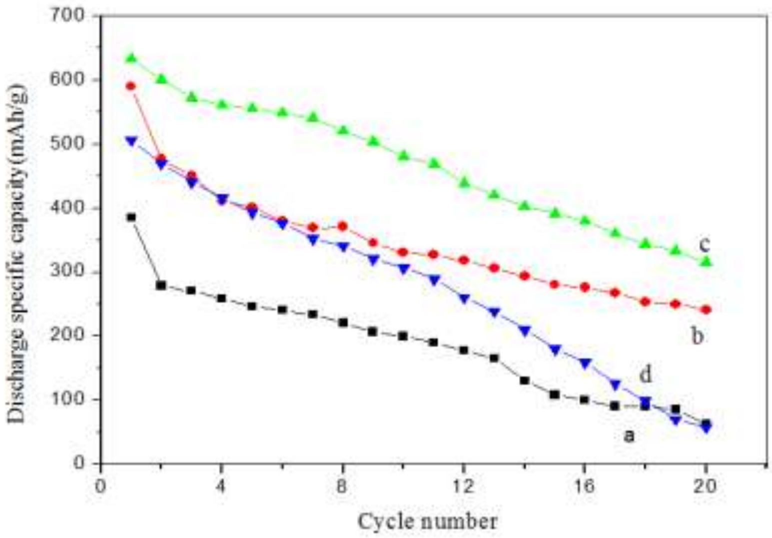

Fig. 7: The cycle performance of liquid phase in-situ composite cathode at various current density(b.50mA/g c.25mA/g d.100mA/g) and pure sulfur cathode(a.50 mA/g)

To understand the reason for superior electrochemical performance of liquid phase in-situ composite, EIS measurements were carried out with coin cells. The Nyquist profiles of liquid phase in-situ composite, conventional method composite and pure sulfur cathode and the equivalent circuits were shown in Fig.8. Rel: resistance of electrolyte; Rsl: total resistance of the surface layers on the sulphur and lithium electrodes; CPEsl: distributed capacitance of the surface layers of both the sulphur and lithium electrodes; Rer: resistance to charge transfer on the sulphur electrode; CPEer: a double layer capacitance distributed on the surface of the pores in the sulphur electrode; W: the Warburg impedance. Comparing the impedance spectrum of three kinds of materials cathode before cycling, we can find that diameter of the semicircle increases in turn, the difference between the slope of the straight line was not obvious, the intersection point of the left side of semicircle with the horizontal axis was basically the same. The above results showed that the charge transfer resistance of liquid phase in-situ composite cathode was the least, which should be related that the method can synthesize uniform composite, graphene oxide and sulfur combines firmly to form a strong interaction, graphene oxide provided convenient electronic transmission channel for insulating sulfur. This was also consistent with the result that in-situ composite had the highest first discharge capacity in later cycle. And the lithium ion diffusion degree of three kinds of materials in the beginning was alike. The electrolyte impedance of three kinds of cathodes was basically the same, illustrating the composition and property of the electrolyte was stable in the process of battery assembly [19, 20].

Fig. 9 was the electrochemical impedance spectra of liquid phase in-situ composite before and after 20 cycles. As the figure shown that charge transfer impedance of the composite cathode increases, the charge transferred through electrode and electrolyte interface became difficult, but the added value was relatively small. The result showed that electrode structure was damaged to a certain extent during cycling, but generally, the structural integrity was still relatively good. The slope of the straight line decreased, indicating that irreversible deposited on the electrode and hindered the diffusion of lithium ions with the charge/discharge processing [21].

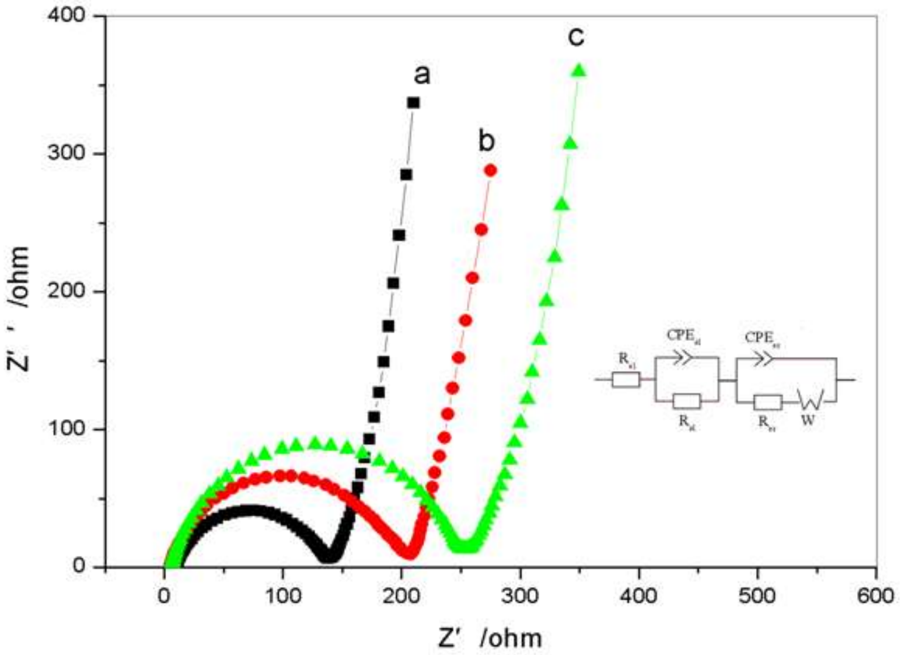

Fig. 8: EIS spectrum of liquid phase in-situ GO/S composite (a); conventional method composite (b) and pure sulfur (c) cathode before cycling and the equivalent circuits

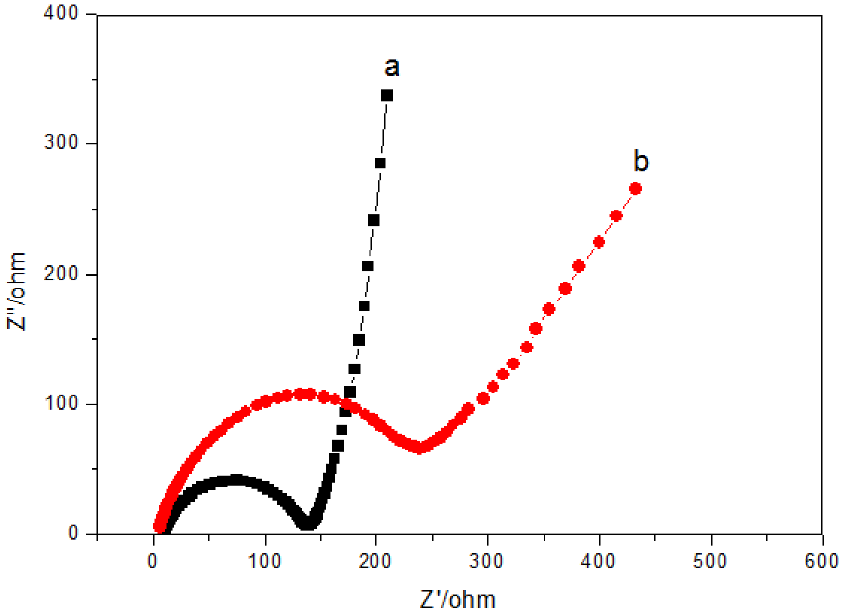

Fig. 9: EIS spectra of liquid phase in-situ composite before (a) and after (b) 20 cycles

CONCLUSION

In short, we used chemical in-situ deposition method in aqueous solution to prepare GO/S composite with the excellent performance, which not only offered a low-cost and controlled approach for large-scale production but also produced high-purity active material. Compared with the conventional method composite and pure sulfur cathode, the in-situ composite possessing uniform and stable sub-micron structure exhibited a higher specific capacity and cyclic stability. The initial discharge specific capacity was 589mAh/g under the current density of 50mA/g, the value of conventional method composite and pure sulfur cathode were respectively 429mAh/g and 385mAh/g, the specific capacity of in-situ composite after 20 cycles was also the highest. Thus, this new method improved the electrochemical performance of the Li-S battery to some extent.

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