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Synthesis of Porous Carbon Materials Based on Reduced Graphene Oxide and Their
Application in Lithium-Sulfur Batteries

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Materials Science and Engineering

by

Hao Tang

June 2022

Thesis Committee:

Dr. Juchen Guo, Chairperson

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The Thesis of Hao Tang is approved:

Committee Chairperson

University of California, Riverside

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Dedication

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ABSTRACT OF THE THESIS

Synthesis of Porous Carbon Materials Based on Reduced Graphene Oxide and Their Application in Lithium-Sulfur Batteries

by

Hao Tang

Master of Science, Graduate Program in Materials Science and Engineering
University of California, Riverside, June 2022
Dr. Juchen Guo, Chairperson

In this paper, MnO_2 /reduced graphene oxide (rGO) composite is prepared by a one-step hydrothermal method. The extraordinary structure provides MnO_2 /rGO composite with a large specific surface area and numerous channels for rapid diffusion of electrolyte ions, electron transport and high conductivity due to the presence of rGO.

Electrochemical results demonstrate that MnO_2 /rGO composite has good capacitive performance with a specific capacitance of $794 \text{ mAh}\cdot\text{g}^{-1}$ at a current of 0.1 mA.

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1. Introduction

1.1 Battery

A battery, in essence, is a device that converts stored chemical energy into electrical energy. Basically, a battery is a small chemical reactor that reacts to produce high-energy electrons that are injected into external devices.

In 1938, the director of the Baghdad Museum found the original battery, now known as the "Baghdad Battery", in the basement of the museum. Analysis showed that the original battery dated back to 250 B.C. and belonged to the Mesopotamian civilization. This earliest battery has generated a lot of controversy. There are conflicting opinions about its use, with possible hypotheses including its use for electroplating, pain relief or the religious experience people had through the tingling sensation they experienced when they came in contact with it. The American inventor Benjamin Franklin first used the term "Battery" in 1749. At that time, he used a set of series-connected capacitors to conduct electrical experiments. The real modern battery was invented by Italian physicist Alessandro Volta in 1800. He constructed a small cell by sandwiching a copper sheet and a zinc sheet with a piece of cloth soaked in saltwater, and then stacked these small cells to obtain a "voltaic pile".

Today, batteries can be as large or as small as megawatts, used to store electricity from solar power plants or substations to ensure a stable energy supply in a certain area, or as small as a button to power the electronic watch you wear.

The different cells are based on different chemistry, which makes each small cell have a different open-circuit voltage, usually between 1.0 and 3.6V. By connecting these small cells in series we are able to increase the voltage, and by connecting them in parallel we are able to increase the current. This law is used to increase the voltage and current to provide the current and voltage we need, even for megawatt-class batteries, which are obtained by this most basic law.

Now it is predicted that battery technology will take another leap forward. The new battery model will be able to take enough energy from home solar and wind installations and store it in sufficient capacity to provide an entire home with the power it needs for days to come at the right time (usually night). Wires connect the two ends of the pile to produce a steady current. Each small cell is capable of generating an open-circuit voltage of 0.76 volts (V). By connecting these small cells in series, we are able to obtain a voltage equal to the sum of the voltages of each small cell. The lead battery is one of the longest lasting batteries known, it was invented in 1859 and is still used in the ignition of most internal combustion engine cars. It is also the earliest rechargeable battery.

1.1.1 How a battery works

When a chemical reaction begins, additional electrons are released and the battery begins to discharge. An example of extra electrons being released is in the process of iron oxidation and rusting, where iron reacts with oxygen, releasing electrons to oxygen to form iron oxides.

The standard cell construction is to separate two metals or compounds with different chemical potentials by a porous insulator. The chemical potential is the energy stored between the atoms and bonds, which can be transferred to the moving electrons when they are free to move through the connected external device. Conductive liquids like saline are often used to transfer soluble ions that can be transferred from the surface of one metal to the surface of another in solution during a reaction, and we usually call such conductive liquids electrolytes. In the discharge process, the metal or compound that loses electrons is called the anode and the one that gains electrons is called the cathode. In an external circuit, the flow of electrons from the anode to the cathode is the "current" that we use to drive electrical equipment.

1.2. Lithium batteries

Cell phones, laptops, video cameras, cameras and other electronic products have become common high-tech consumer goods in people's modern life and work. Once you

have them, you will no longer be unfamiliar with their heroes behind the scenes - lithium batteries. In fact, the scope of application of lithium batteries has been broadened, from the information industry to energy transportation, from space to underwater, lithium batteries are entering all areas of human society, for the benefit of mankind.

1.2.1 Primary and secondary batteries

Lithium batteries are divided into two categories: primary batteries and secondary batteries. After generating current, the state of some cells cannot be reversed, and we call such cells primary cells. When one of the reactants is depleted, this kind of battery can no longer be used. The most common primary battery is the carbon zinc battery, which is mainly used in electronic products with low power consumption, such as cameras, and non-rechargeable primary lithium batteries. If the electrolyte is alkaline, this kind of battery can be more durable. This is also the alkaline batteries we usually buy in the supermarket. The difficulty in handling primary batteries is that we cannot recycle them by recharging them. In today's world of large batteries, recycling is becoming more and more important, and it is not commercially viable to replace batteries frequently.

And in the camera, digital cameras, cell phones and laptops and other electronic products with high power consumption can be charged and discharged secondary lithium batteries, that is, lithium-ion batteries. Compared with other secondary batteries, its working principle is also relatively simple. The reason why it is called lithium-ion battery

is that this battery, whether in the anode and cathode or in the battery diaphragm, lithium is in the form of ions, lithium-ion battery negative electrode is a carbon material, such as graphite, etc.. The cathode is a transition metal oxide containing lithium, such as LiCoO_2 , LiMn_2O_4 , etc. The electrolyte is an organic solution containing lithium salts. During the operation (charging or discharging) of lithium-ion battery, lithium ions move in a directional manner in the anode and cathode and electrolyte diaphragm. When charging, lithium ions are removed from the anode material driven by the electric field, pass through the electrolyte and are inserted into the cathode. When discharging, the process is reversed, i.e., the lithium ions return to the anode and the electrons pass through and power the electronic product that uses electricity.

Compared to the former, the demand for lithium-ion batteries is growing substantially year by year. Compared with other batteries, lithium-ion batteries have the advantages of high open-circuit voltage (commercially available batteries are mostly 3.6V NiMH and NiCd secondary batteries open-circuit voltage of 1.2V), large specific capacity (2.5 times that of NiCd secondary batteries, 1.5 times that of NiMH secondary batteries), low self-discharge rate (<8% / month, much lower than 30% of NiCd batteries and 40% of NiMH batteries), long life (usually can reach more than a thousand times). No memory effect is also the outstanding advantage of lithium-ion batteries are very popular, is not available in other secondary batteries, people do not have to consider whether the power in the lithium-ion battery before charging has been used up.

1.2.2 The first leap: lithium-ion batteries

Today, most new technologies require batteries with more compact design, more power, better safety, and the ability to recharge and reuse. In 1980, John Goodenough, an American physics professor, invented a new type of lithium battery. In this lithium battery, lithium is able to travel between two electrodes in the battery in the form of lithium ions.

Lithium is one of the lightest elements in the periodic table and has an extremely high electrochemical potential, two advantages that allow it to provide the highest voltage in the smallest volume.

And this is the basis of the lithium-ion battery. In this new battery, a compound of lithium and transition metals (such as cobalt, nickel, manganese and iron) with oxygen serves as the cathode. After the applied voltage, recharging begins and the positively charged lithium ions migrate from the cathode to the anode made of graphite material, changing back to lithium metal.

Because lithium metal has a very strong electrochemical driving force, it is easily oxidized and it migrates to the cathode and becomes lithium ion again, giving the outer electrons to transition metal ions (such as cobalt ions). The movement of electrons in this cycle provides us with the current we need.

1.2.3 The Second Leap: Nanotechnology

Thanks to the addition of transition metals, lithium ions are able to deliver higher energy per small cell, but the increased reactivity also has the negative effect of making the battery more susceptible to a phenomenon known as "heat dissipation.

In the 1990s, Sony produced a lithium-cobalt oxide battery, but severe "heat dissipation" caused many of these batteries to catch fire. If this problem cannot be solved, then the idea of using nanomaterials to make battery cathodes in order to obtain better reactivity will not be able to talk.

This time, it was Goodenough who stepped forward to introduce a new lithium-ion battery cathode composed of lithium, iron, and phosphate, a stable electrode that represents another major leap forward in battery technology.

Along with the continued development of new batteries, many new applications have emerged. From power tools to hybrid and electric vehicles, we can find lithium-ion batteries, perhaps the most important application will be to provide domestic electricity for residential use.

There are currently a variety of brands of lithium-ion batteries on the market for small electronic products, these batteries are usually organic solutions, it is possible to commercialize solid-state lithium batteries or lithium polymer batteries actually still contain a certain amount of organic liquid electrolyte, its main components and its working principle and liquid secondary lithium batteries are almost the same, only the packaging has been greatly improved. We should not dissect the battery when using lithium-ion batteries to avoid accidents.

At present, the hot research in the field of lithium-ion battery research is to use it in vehicles, made of electric cars or hybrid electric cars with gasoline, while people are also developing a real sense of solid-state lithium batteries, completely abandoning the organic liquid in lithium-ion batteries, so that lithium batteries become the safest and most reliable batteries.

1.3. Lithium-Sulfur Batteries

With the development of portable electronic devices and electric vehicles, the energy density of commercial lithium-ion batteries has become difficult to meet the increasing demand for electrical energy storage. Long-endurance secondary batteries have become the focus of researchers' research. Among various candidate electrochemical energy storage systems, lithium-sulfur batteries based on the multi-electron electrochemical conversion of sulfur and lithium have significant advantages:

high theoretical specific capacity of $1675 \text{ mAh}\cdot\text{g}^{-1}$; high theoretical specific energy of $2567 \text{ Wh}\cdot\text{kg}^{-1}$ (much higher than the $387 \text{ Wh}\cdot\text{kg}^{-1}$ of commercial lithium cobaltate graphite lithium-ion batteries); low operating voltage (2.2 V) makes them relatively safe; at the same time, single-mass sulfur storage Abundant, low-cost and environmentally friendly, so that lithium-sulfur batteries have great prospects for commercial application [1-4].

However, there are a series of problems that limit the commercialization of lithium-sulfur batteries, such as the low conductivity of elemental sulfur and its discharge end-product lithium sulfide, which limits the utilization of the active material and the multiplier performance of the battery; the intermediate product lithium polysulfide generated during the charging and discharging process can be dissolved in the electrolyte and shuttled back and forth between the anode and cathode, resulting in the rapid decay of the battery capacity; sulfur will undergo a volume expansion of up to 80% during the discharge process, which will cause the anode to pulverize, resulting in battery failure. In addition, if lithium metal is used as the cathode, lithium dendrites may be generated during the cycling process, which may easily pierce the diaphragm and cause a short circuit in the battery, posing a safety hazard.

In order to solve the above problems, researchers have conducted extensive research in lithium-sulfur battery anode materials, cathode materials, electrolytes and diaphragms in recent years and have made a series of progress. By loading sulfur uniformly on the

conductive carrier, the electrode conductivity can be effectively enhanced; by designing a suitable pore structure or using a flexible carrier can effectively buffer the volume expansion of sulfur. In terms of inhibiting the shuttle effect of lithium polysulfide, the research work can be broadly divided into two categories: one is the physical domain limiting effect, through the design of carrier materials with large specific surface area and rich pore structure to adsorb lithium polysulfide, or add adsorption layer between the anode and the diaphragm to prevent the diffusion of lithium polysulfide to the cathode; the other is the chemisorption effect, through the chemical adsorption between polar carrier materials and lithium polysulfide to limit the dissolution and diffusion of lithium sulfide. In addition, there are also short-chain sulfur molecules and organic compounds that form sulfur bonds to avoid the shuttle effect. In the study of cathode materials, carbon-based materials (including activated carbon, carbon nanotubes, carbon nanofibers, graphene, carbon nanospheres, etc.), conductive organic polymers and metal compounds are used as carriers for loading sulfur, which can effectively enhance the performance of lithium-sulfur batteries. In terms of lithium metal anode, the growth of lithium dendrites can be inhibited to a certain extent by designing lithium storage structures or directionally inducing the generation of solid electrolyte films.

1.3.1 Working principle of lithium-sulfur battery

The working principle of lithium-sulfur battery is shown in Figure 1a [2]. During the discharge process, the negative lithium loses electrons to produce lithium ions, and the positive sulfur receives electrons from the external circuit and combines with lithium ions to produce Li_2S . The charging process is the opposite. In fact, during the charging and discharging process, the anode of the lithium-sulfur battery undergoes a complex multi-electron reaction process. As shown in Figure 1b, during discharge, the ring-like S_8 molecule first opens its ring and combines with Li^+ to form soluble lithium polysulfide (Li_2S_x , $4 \leq x \leq 8$), which is then reduced to form Li_2S_2 and Li_2S in the solid-state. This "solid-liquid-solid" conversion process poses several challenges for the anode: (1) the electron insulation of sulfur and its discharge product $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ leads to low utilization of active material; (2) the process of Li_2S generation from sulfur is accompanied by 80% volume expansion, which seriously damages the stability of the electrode structure; (3) the intermediate product lithium polysulfide is easily dissolved in the electrolyte and goes back and forth between the anode and cathode, which leads to the loss of active material in the anode and cathode, the decay of battery capacity and the reduction of coulombic efficiency [5].

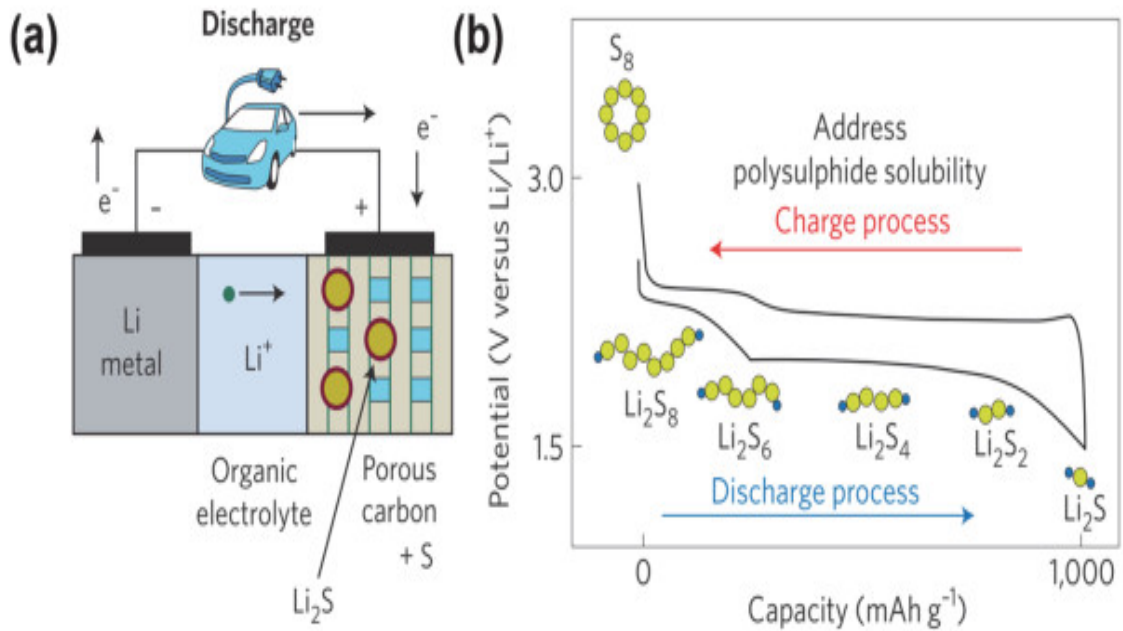


Figure 1 (a) Schematic diagram and (b) charge/discharge process of lithium-sulfur battery

The most common strategy for optimizing the anode of lithium-sulfur batteries is to use a carbon-based material as a carrier for the active material sulfur [6-8]. The ideal sulfur carrier material should have the following characteristics: (1) high specific surface area and well-developed pore structure, which can provide sufficient storage space for sulfur and its discharge products, and provide fast transport channels for lithium ions; (2) excellent electrical conductivity, which can provide good electrochemical contact for the active material; (3) excellent structural stability, which can mitigate the electrode structure during charge and discharge strain; (4) strong adsorption effect on lithium polysulfide as well as catalytic conversion, accelerating the kinetics of the cathode redox reaction and suppressing the shuttle effect.

Graphene is a carbon material with honeycomb crystal structure formed by single layer of carbon atoms through sp² hybridization, which has rich pore structure, good electrical conductivity and high chemical stability [9]. Graphene-based materials are materials in which graphene is modified with surface functional groups, doped with heterogeneous atoms or compounded with other materials to achieve specific functions, such as graphene oxide, nitrogen-doped graphene, graphene/metal compounds, graphene/organic complexes, etc. The application of graphene-based materials in lithium-sulfur batteries can effectively enhance the electrical conductivity of sulfur electrodes, limit the diffusion of soluble polysulfides and alleviate the volume expansion of electrodes. Therefore, graphene-based materials are widely investigated for use in the anode, diaphragm coating, intermediate barrier layer, collector and anode protection layer of lithium-sulfur batteries.

1.3.2 Graphene

After graphene was exfoliated by Geim et al. in 2004 [10], researchers have developed various methods to prepare graphene, mainly including mechanical exfoliation, oxidative exfoliation, intercalation exfoliation, thermal expansion exfoliation, electrochemical exfoliation, chemical vapor deposition, epitaxial growth, etc. Since 2011, graphene has been introduced as a highly conductive carbon material for the cathode of lithium-sulfur batteries, and its good electrical conductivity and flexible structure can provide a good conductive skeleton for the cathode of lithium-sulfur batteries and buffer

the volume change of sulfur during the charging and discharging process. In the initial research, researchers tried different ways of sulfur loading, compounding graphene with monolithic sulfur, aiming to enhance the sulfur content and utilization.

As the research progressed, the researchers realized that although the cathode material with low sulfur content could achieve high sulfur utilization, the larger proportion of inactive material in the electrode material would lead to a very low overall specific capacity of the electrode, making it difficult to meet the demand for commercial applications of lithium-sulfur batteries. Graphene not only has excellent electrical conductivity, but also has good film-forming property. Using this property, a binder-free self-supporting electrode can be prepared. This design avoids the use of organic binders and collectors, which on the one hand avoids the problem of reduced conductivity of the electrode caused by binders, and on the other hand reduces the proportion of inactive components in the electrode and improves the overall sulfur content of the electrode. The active material in the composite electrode is well dispersed and provides many contact sites for sulfur and graphene to adapt to the volume change during the sulfur charging and discharging process. Meanwhile, the freeze-dried graphene film possesses a three-dimensional network structure, which can form more complete electron-conducting and ion-transporting channels. Therefore, the graphene thin film composite electrode shows good electrochemical performance while enhancing the overall electrode sulfur content.

The different structural features of sulfur/graphene-based composites can have a great impact on the electrochemical performance. Therefore, researchers have conducted extensive research on the structural design of sulfur/graphene complexes to give full play to the advantages of graphene's high electrical conductivity, high specific surface area and high flexibility through a reasonable electrode structure design to build a high sulfur-carrying and high specific energy cathode material. Considering the characteristics of graphene with good in-plane conductivity but insufficient interlayer conductivity and easy stacking of graphene sheets, graphene materials with three-dimensional structure have been widely studied and reported [11-14]. The nanosized sulfur particles are tightly attached to the graphene surface, and the porous network structure can realize rapid lithium-ion transport and reduce its diffusion distance; the fibrous graphene is cross-linked with each other to constitute a good electron transport channel, which makes the electrode exhibit excellent electrochemical performance.

In addition to morphology, pore structure is another important structural factor in materials. The rich and tunable pore structure of carbon materials, including graphene, is a major advantage for their application in lithium-sulfur batteries. The rich pore structure not only provides space for sulfur storage and volume expansion, but the appropriate pore size can also physically adsorb polysulfides. Therefore, pore structure tuning of graphene materials has also become a focus of researchers [15-17].

1.3.3 Graphene oxide

Graphene is generally used in lithium-sulfur batteries to inhibit polysulfide shuttling through physical adsorption. However, the interaction between the nonpolar surface of graphene and the polar polysulfides is weak. Therefore, researchers have tried to construct polar surfaces that can interact strongly with polysulfide ions. Graphene oxide, the most common functionalized graphene, contains many functional groups such as hydroxyl, carbonyl, carboxyl and epoxy groups on its surface, and thus is able to achieve stronger interactions with polysulfides.

Using graphene oxide as a substrate material for sulfur electrodes, despite the strong interaction with polysulfide ions, the poor conductivity of graphene oxide makes the cell polarization severe, so in subsequent work, researchers use graphene oxide more as a cladding layer to limit the diffusion of polysulfides [18-19].

With the increasing demand for power systems in recent decades, supercapacitors play a more and more important role [20]. Many researches have been focused on the development of different electrode materials, such as various forms of carbon materials, conducting polymers and transition metal oxides. Among all these materials, MnO_2 is a kind of transition metal oxide pseudocapacitive materials and has attracted much attention because of its low cost, high theoretical capacitance ($1370 \text{ F}\cdot\text{g}^{-1}$), high electrochemical activity and environmental friendliness [21]. However, MnO_2 usually

delivers a lower specific capacitance due to its poor electrical conductivity and low accessible surface area. To overcome the disadvantages above, graphene, a two-dimensional (2D) form of carbon, has been introduced as dispersion substrate owing to its extraordinary electronic and mechanical properties. The wrapping of transition metal oxides on graphene or reduced graphene oxide (rGO) can greatly enhance electrochemical properties of metal oxide nanocomposites.

2. Materials and methods

2.1. Materials

All the reagents were analytical grade and used without further purification, and GO was prepared from powdered flake graphite (400 mesh) by a modified Hummers method. Potassium permanganate (KMnO_4), Deionized water was used throughout in all experiments.

2.2. Synthesis of MnO₂

The MnO₂ nanorod was prepared by a hydrothermal method [22]. In a typical synthesis, the as-received manganese sulfate monohydrate (MnSO₄·H₂O, 0.1 g) and potassium permanganate (KMnO₄, 0.1 g) powders were dissolved in 40 ml deionized water successively under strong stirring at room temperature to obtain purple aqueous solution. The resulting solution was transferred into a Teflon lined stainless steel autoclave (50 ml) after magnetically stirring for 30 min. The hydrothermal process was carried out at 180 °C for 12 h. After cooling down to room temperature, the dark products were rinsed with deionized water *via* centrifuge at a rotation rate of 8000 rpm for 3 times with each time for 10 minutes. The obtained powder was dried in a vacuum oven at 80 °C for 12 hours.

2.3. Synthesis of MnO₂/rGO

The MnO₂-rGO hybrid was prepared by a hydrothermal method. In the first step, 50 mg GO were dispersed in 60 mL deionized water by ultrasonic vibration for 15 min. Then manganese sulfate monohydrate (MnSO₄·H₂O, 0.05 g) and potassium permanganate (KMnO₄, 0.05 g) powders were added into above graphene suspension and stirred by magnetic bar for 5 min. After that, the mixed solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed and put in an electric

oven at 180 °C for 12 h and then cooled to room temperature naturally. The black resultants were washed with distilled water and ethanol to remove ions remained within the final product, followed by drying at -40 °C in a vacuum freeze drier overnight.

2.4. Characterization methods

X-ray diffraction (XRD) patterns were recorded with a PANalytical Empyrean Series 2 diffractometer. The XRD patterns were recorded in the ranges of $2\theta = 5-70^\circ$. The XRD specimens were prepared by flattening the powder onto small circular trays whose radius and thickness are 10 mm and 2 mm, respectively. Surface morphology and structure of the samples were examined by scanning electron microscopy (SEM, TESCAN Vega3 SBH). Elemental analysis of as-synthesized composite material was examined by energy dispersive spectrometer (EDS).

2.5. Electrode fabrication

The sulfur-carbon (S-C) composite was prepared by mixing 80 wt % sulfur (Sigma Aldrich) with 20 wt % MnO₂/rGO, followed by a heating process at 155 °C for 10 h. The cathode slurry was prepared by mixing 80 wt % S-C composite, 10 wt % binder, 5 wt % carbon black. One polymer binder, polyvinylpyrrolidone (PVP) was used in this study. The slurry was coated onto Al foil, and the electrode was dried in a vacuum oven at 50°C

for 12 h. The electrolyte was composed of 0.4 M lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) in a mixture of 1,2-dioxolane and dimethoxyethane (DOL and DME with 50/50 vol. ratio) with 0.5 M lithium nitrate (LiNO_3) [23].

2.6. Electrochemical measurements

All electrochemical tests were carried out on a electrochemical workstation (NEWARE, China). The specific capacitances were calculated by galvanostatic charge-discharge (GCD) curves with the equation.

3. Results and discussion

3.1. Microstructure characterizations

Fig. 2 shows XRD patterns of rGO, and MnO_2/rGO composite. For rGO, there is a typical broad peak located at 25.1° , which can be indexed to the (002) plane of rGO, indicating the deoxidation of GO [24]. For the pattern of MnO_2/rGO , there are five diffraction peaks, correspond to (211), (220), (004), (400) and (424) basal reflections, respectively, which can be indexed to $\beta\text{-MnO}_2$ (JCPDS 24-0735). From the XRD pattern of the $\text{MnO}_2\text{-rGO}$, the diffraction peaks from the graphene can hardly be seen, indicating a high mass loading of MnO_2 .

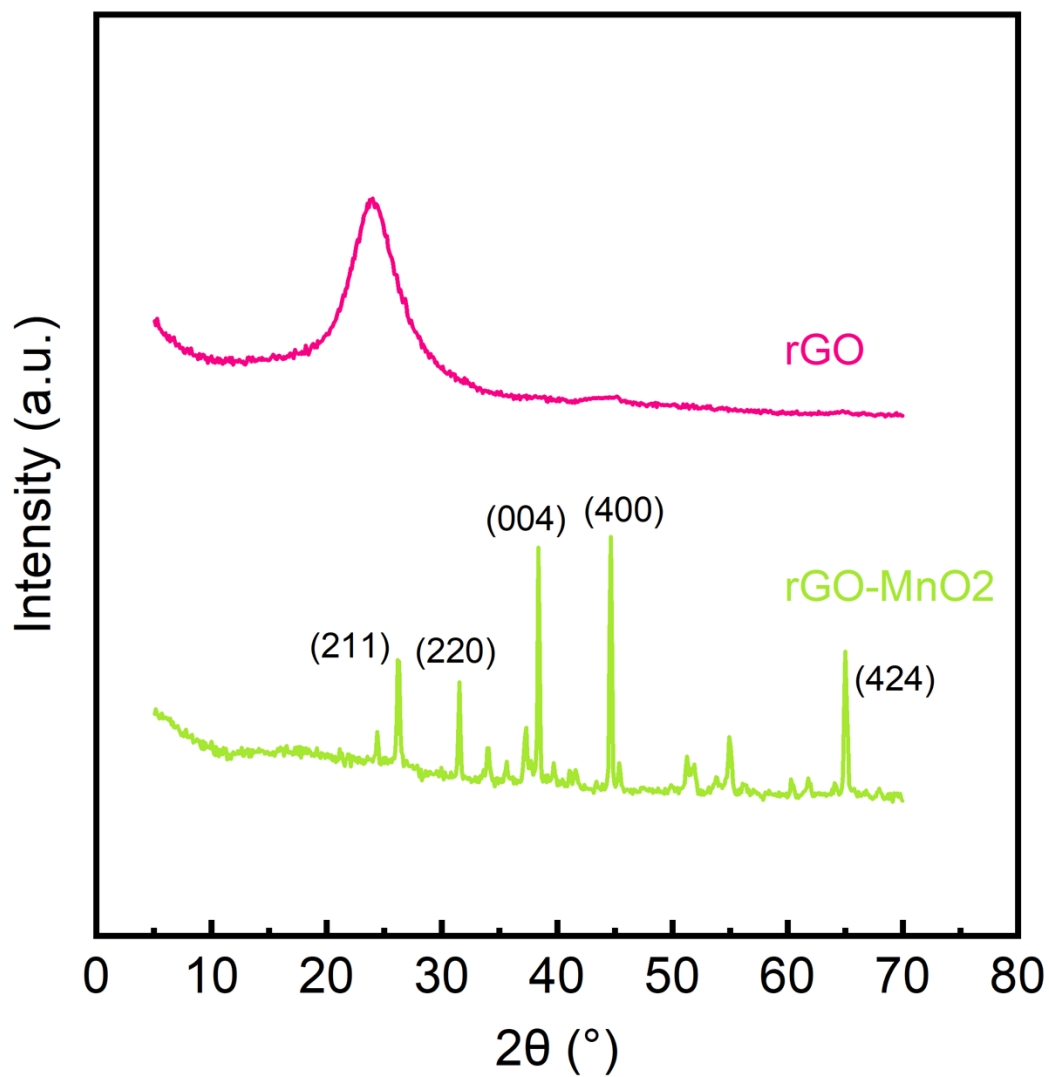


Figure 2 XRD patterns of MnO₂/rGO nanocomposites and the rGO

Fig. 3 shows the SEM image of the rGO (Fig. 3a) and MnO₂/RGO composites (Fig. 3b) displaying that the rGO surface is smooth and shows a spatial mesh structure and the MnO₂ nanorods have been completely inserted into the rGO material.

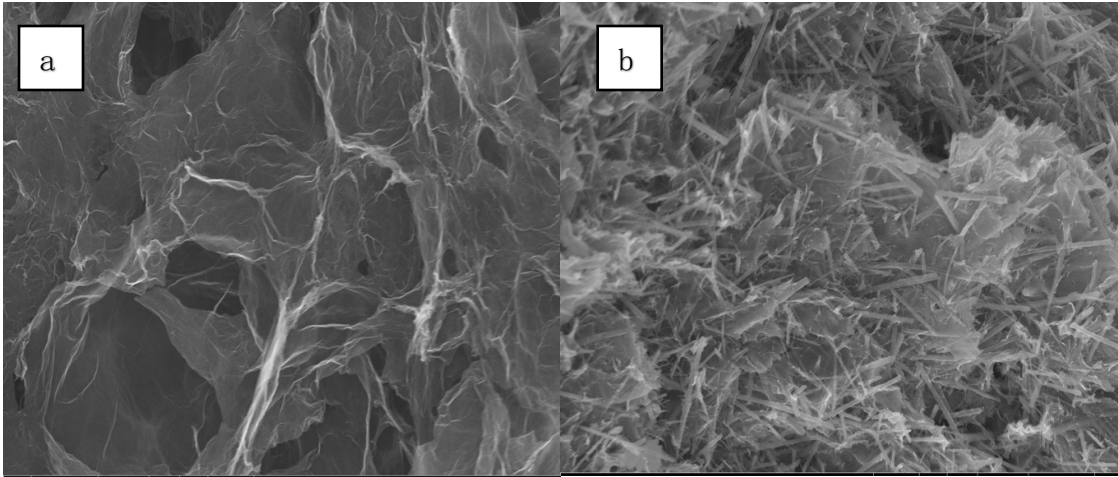


Figure 3 SEM images of (a) rGO, (b) MnO₂/rGO

EDS analysis of the nanocomposites (Fig. 4) indicates that besides manganese (Mn) and oxygen (O) originated from manganese oxide, there are other element detected such as C which can be related to rGO covering the surface of MnO₂.

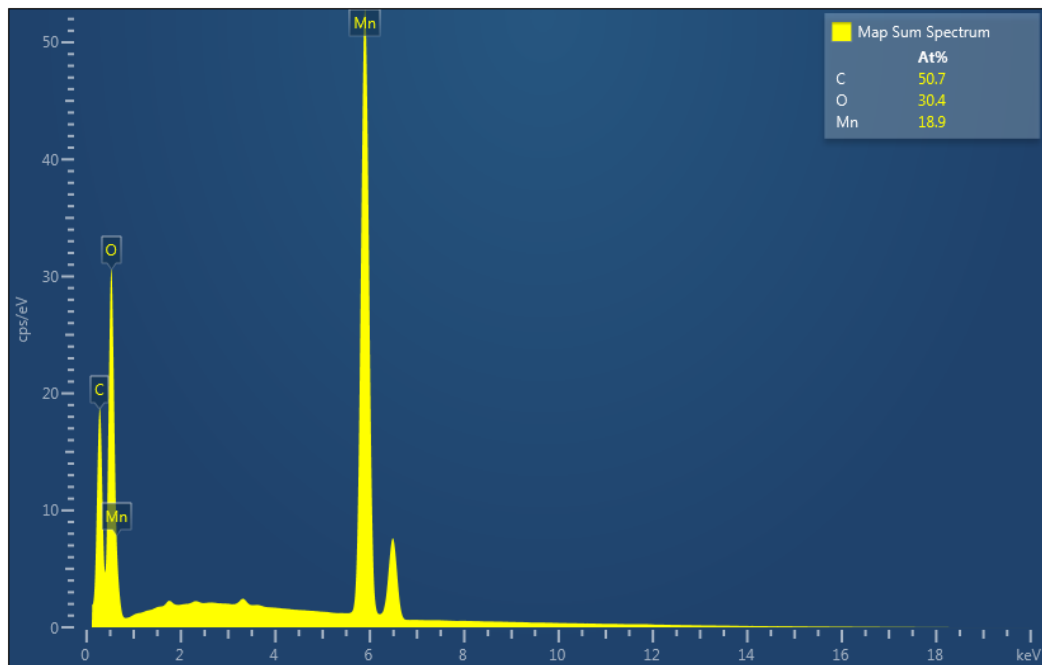


Figure 4 EDS spectra of MnO₂/rGO

3.2. Electrochemical performances

Fig. 5 shows the GO and MnO₂-rGO first circle GCD plots. The specific capacitance is 695 mAh·g⁻¹ when GO is used as the material of the electrode.

In contrast, the specific capacitance is 794 mAh·g⁻¹ when using MnO₂-rGO as the material for the electrode, which is a significant improvement in electrochemical performance compared to the rGO electrode material.

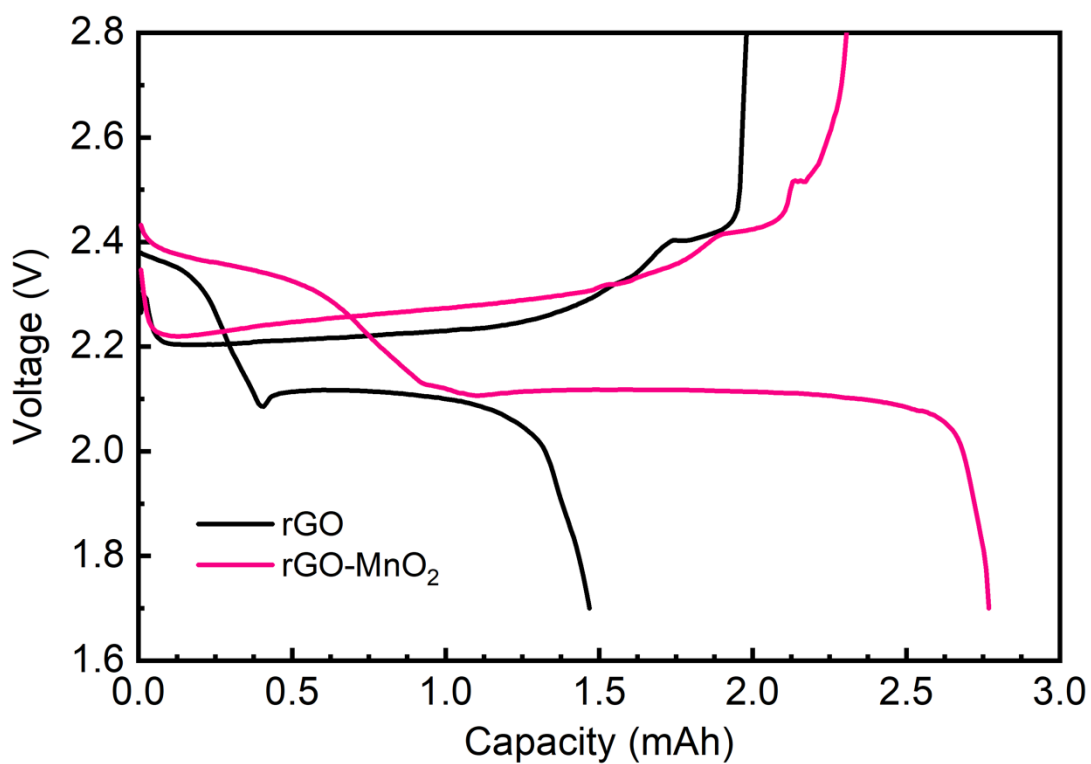


Figure 5 First circle GCD plots of the GO and MnO₂-rGO

4. Conclusions

MnO₂-rGO hybrid has been designed and synthesized by a simple hydrothermal treatment. The formation mechanism of the hybrid synthesized by the self-limiting deposition of KMnO₄ under hydrothermal reaction is discussed. Electrochemical measurements reveal that the MnO₂-rGO electrode exhibits much higher specific capacitance and better rate capability compared with rGO electrodes. Specifically, the MnO₂-rGO electrode displays a high specific capacitance of 794 mAh·g⁻¹ at current of 0.1 mA, indicating a promising potential application as an effective candidate for electrodes materials. The superior capacitive performance of MnO₂-rGO hybrid is attributed to its unique structure, which provides good electronic conductivity, fast electron and ion transport, and high utilization of MnO₂.

References

- [1] Manthiram, A.; Fu, Y. Z.; Su, Y. S. *Acc. Chem. Res.* 2013, 46, 1125
- [2] Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. *Nat. Mater.* 2011, 11, 19
- [3] Fang, R. P.; Zhao, S. Y.; Sun, Z. H.; Wang, D. W.; Cheng, H. M.; Li, F. *Adv. Mater.* 2017, 29, 1606823
- [4] Yu, M.; Li, R.; Wu, M.; Shi, G. *Energy Storage Materials* 2015, 1, 51
- [5] He, Y.; Chang, Z.; Wu, S.; Zhou, H. J. *Mater. Chem. A* 2018, 6, 6155
- [6] Xu, Z. L.; Kim, J. K.; Kang, K. *Nano Today* 2018, 19, 84
- [7] Guan, L.; Hu, H.; Li, L.; Pan, Y.; Zhu, Y.; Li, Q.; Guo, H.; Wang, K.; Huang, Y.; Zhang, M.; et al. *ACS Nano* 2020, 14, 6222
- [8] Yan, Y.; Chen, Z.; Yang, J.; Guan, L.; Hu, H.; Zhao, Q.; Ren, H.; Lin, Y.; Li, Z.; Wu, M. *Small* 2020, 16, 2004631
- [9] Geim, A. K. *Science* 2009, 324, 1530.
- [10] Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* 2004, 306, 666
- [11] Xu, C.; Wu, Y.; Zhao, X.; Wang, X.; Du, G.; Zhang, J.; Tu, J. J. *Power Sources* 2015, 275, 22
- [12] Papandrea, B.; Xu, X.; Xu, Y. X.; Chen, C. Y.; Lin, Z. Y.; Wang, G. M.; Luo, Y. Z.; Liu, M.; Huang, Y.; Mai, L. Q.; Duan, X. F. *Nano Res.* 2016, 9, 240
- [13] Xi, K.; Kidambi, P. R.; Chen, R.; Gao, C.; Peng, X.; Ducati, C.; Hofmann, S.; Kumar, R. V. *Nanoscale* 2014, 6, 5746

- [14] Lu, S.; Chen, Y.; Wu, X.; Wang, Z.; Li, Y. *Sci. Rep.* 2014, 4,4629
- [15] Shi, J. L.; Peng, H. J.; Zhu, L.; Zhu, W.; Zhang, Q. *Carbon* 2015, 92, 96
- [16] Huang, X.; Sun, B.; Li, K.; Chen, S.; Wang, G. *J. Mater. Chem. A* 2013, 1, 13484
- [17] Zhai, P. Y.; Peng, H. J.; Cheng, X. B.; Zhu, L.; Huang, J. Q.; Zhu, W.; Zhang, Q. *Energy Storage Materials* 2017, 7, 56
- [18] Xiao, M.; Huang, M.; Zeng, S.; Han, D.; Wang, S.; Sun, L.; Meng, Y. *RSC Adv.* 2013, 3, 4914
- [19] Rong, J.; Ge, M.; Fang, X.; Zhou, C. *Nano Lett.* 2014, 14, 473
- [20] M. Cakici, R.R. Kakarla, F. Alonso-Marroquin *Chem. Eng. J.*, 309 (2017), pp. 151-158
- [21] S. Zhu, L. Li, J. Liu, H. Wang, T. Wang, Y. Zhang, L. Zhang, R.S. Ruoff, F. Dong *ACS Nano*, 12 (2018), pp. 1033-1042
- [22] H. T. Guan, G. Chen, J. Zhu and Y. D. Wang, *J. Alloys Compd.*, 2010, 507, 126–132
- [23] Y.F. Zhao, J. Zhang and J.C. Guo, *ACS Appl. Mater. Interfaces* 2021, 13, 27, 31749–31755
- [24] S. Zhang, L. Sui, H. Kang, H. Dong, L. Dong, L. Yu *Small*, 14 (2018), p. 1702570