

Co₃O₄ modified graphene aerogel for high-performance lithium-sulfur batteries

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Abstract. Designing a sulfur host material that possesses rapid sulfur redox kinetics and effectively curtails the shuttle effect, while maintaining desirable gravimetric performance, represents a formidable hurdle in the development of practical lithium-sulfur batteries. Herein, 3D Co₃O₄/graphene aerogel composite was synthesized via a facile one-pot hydrothermal method. The composite combines the advantages of graphene aerogel's lightweight, high conductivity and Co₃O₄ nanowires' high catalytic activity and adsorption capacity. Hence the lithium-sulfur cell with prepared host material exhibited excellent electrochemical performance, with a reversible capacity of 1075 mAh g⁻¹ at 0.1 C, a high rate capacity of 177 mAh g⁻¹ at 2 C and a long-term capacity retention of 46% after 500 cycles.

Keywords: Co₃O₄ nanowires; graphene aerogels; lithium-sulfur battery.

1. Introduction

At present, the most prevalent lithium-ion batteries are extensively used in diverse domains including electric vehicles, portable electronic devices, and other applications owing to their impressive energy density and well-established industrial system.[1,2] However, due to the limitations of their own energy storage principles, the energy density of commercial lithium-ion batteries is unable to meet the increasing demand for high specific energy secondary batteries in constantly developing human society.[3] Therefore, the search for and development of high energy density battery materials and systems has become a current research hotspot. Lithium-sulfur batteries, owe to the exceptional theoretical energy density, eco-friendliness, and comparatively modest manufacturing expenses, are deemed to be among the most auspicious next-generation high-specific-energy secondary batteries that could potentially displace lithium-ion batteries. As such, they are the subject of extensive investigation by researchers both domestically and internationally. [4,5] Despite the numerous benefits of lithium-sulfur batteries, their commercial viability has been impeded by various hurdles and obstacles, including "shuttle effect", positive electrode material expansion, as well as the inadequate conductivity of active components. These problems have hindered the advancement of lithium-sulfur batteries towards widespread commercialization. [6] The aforementioned issues often coexist in lithium-sulfur batteries, resulting in poor discharge capacity, cycle life, as well as rate performance. Rationally designing host materials with high conductivity, strong adsorption ability for lithium polysulfides, and exceptional catalytic efficacy to the conversion of lithium polysulfides is regarded as one of the effective approaches to address the aforementioned issues.[7]

Among various host materials, graphene aerogel, a 3D carbon material cross-linked by 2D graphene sheets, combines the advantages of graphene and aerogel.[8] Due to its physical properties such as high porosity, lightweight, high conductivity, and good mechanical properties, graphene aerogel has been widely studied.[9] However, a single nonpolar carbon material has weak anchoring ability for lithium polysulfides, leading to low composite electrode capacity and rapid performance degradation. Therefore, researchers have introduced polar materials to modify carbon materials to enhance their chemical adsorption capacity for lithium polysulfides. Introducing transition metal sulfides[10], oxides[11], and nitrides[12] has been proven to effectively alleviate the shuttle effect.

In our work, the Co_3O_4 nanowires were anchored on the graphene aerogel forming a 3D composite (Abbreviated as $\text{Co}_3\text{O}_4/\text{GA}$) via a one-pot hydrothermal method. On one hand, the strong affinity and catalytic activity of Co_3O_4 nanowires towards lithium sulfides effectively inhibit their shuttle between positive and negative electrodes as well as their dissolution in the electrolyte. On the other hand, the high conductivity and substantial specific surface area of GA significantly reduce the electrochemical impedance of the composite material and provide sufficient active reaction sites. Hence, the cell with $\text{Co}_3\text{O}_4/\text{GA}$ delivered excellent electrochemical performance, with a reversible capacity of 1075 mAh g^{-1} at 0.1 C, a high rate capacity of 177 mAh g^{-1} at 2 C and a long-term capacity retention of 46% after 500 cycles.

2. Experiment

2.1 Synthesis of graphene solution

The graphene solution was prepared via a modified Hummer method. First, 180 mL of H_2SO_4 is placed in a 1000 mL three-necked flask and stirred uniformly at 200 rpm. Then, 2 g of graphite flakes and 20 mL of H_3PO_4 are slowly added. Next, 9 g of KMnO_4 are added slowly in several portions. The mixture is stirred in a 48°C water bath for 12 hours. After stirring, 800 mL of water and 12 mL of H_2O_2 are slowly added to the three-necked flask, causing the solution to change from dark brown to golden yellow. The product is then centrifuged and washed multiple times, and the supernatant is adjusted to near-neutral pH. The product is dissolved and made up to volume to obtain a 1g/L graphene solution.

2.2 Synthesis of $\text{Co}_3\text{O}_4/\text{GA}$ and GA

Firstly, 2 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into 25 mL as prepared graphene solution. Subsequently, 25 mmol of urea was introduced into the solution and mixed for 30 minutes. The resulting blend was then moved into a 40 mL Teflon-lined stainless steel vessel and heated to 200°C for a duration of 12 hours. Once the aerogel had cooled to room-temperature, it was harvested and submerged in deionized water three times. Following the washing process, the product was then dried in a vacuum freezing dryer for 24 hours. Finally, the $\text{Co}_3\text{O}_4/\text{GA}$ was obtained through an anneal process at 400°C for 2h in air with a heating rate of $10^\circ\text{C min}^{-1}$. The GA was obtained through the similar process of $\text{Co}_3\text{O}_4/\text{GA}$ without the addition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

2.3 Fabrication of cathodes

Sublimated sulfur was ground with as-prepared $\text{Co}_3\text{O}_4/\text{GA}$ with the mass ratio of 7:3 and the mixture was then transferred into a closed vessel and heated to 155°C for a duration of 12 hours to obtain $\text{Co}_3\text{O}_4/\text{GA-S}$. Then 80 wt% of $\text{Co}_3\text{O}_4/\text{GA-S}$, 10 wt% of electroconductive carbon black and 10 wt% polyvinylidene fluoride (PVDF) were mixed in N-methylpyrrolidone (NMP) forming a homogeneous slurry. Subsequently, the resulting slurry was applied onto aluminum foil and dried in a vacuum oven at 60°C for an entire night. The coated aluminum foil was then sectioned into circular pieces with a diameter of 15 mm. The sulfur loading of the cathodes was approximately 1.5 mg cm^{-2} .

2.4 Cell assembly and electrochemical measurements

CR2032 coin cells were used for the electrochemical assessments. The anode and separator were made of lithium metal disks and polypropylene (Celgard 2500), respectively. The electrolyte consisted of 1.0 M lithium bis-(tri-fluoromethanesulfonyl)imide (LiTFSI) in a mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), with a 2 wt% LiNO_3 additive. The cells were assembled in an Ar-filled glovebox. Galvanostatic charge/discharge (GCD) measurements, including rate and cycle performance, were conducted using a battery test system (NEWARE

CT-4008Q). Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) measurements were performed using a three-electrode electrochemical workstation (RST5000F).

3. Discussion

The $\text{Co}_3\text{O}_4/\text{GA}$ was synthesized through a facile one pot hydrothermal method. During the hydrothermal reaction process, the oxygen-containing functional groups on the layers of oxidized graphene are gradually removed, and the three-dimensional structure of the aerogel is constructed by utilizing the interlayer π - π stacking interaction. To observe the morphology of $\text{Co}_3\text{O}_4/\text{GA}$, the Scanning Electron Microscope (SEM) images are shown in Figure 1. Figure 1a and b exhibit the morphology of GA, the graphene sheets are thin and wrinkled, and are highly cross-linked between layers. Figure 1c and d show the morphology of $\text{Co}_3\text{O}_4/\text{GA}$. The Co_3O_4 nanowires with a diameter of 60 nm are evenly distributed across the graphene sheets. The length of Co_3O_4 nanowire is approximately 520 nm. The interlocking structure of Co_3O_4 nanowires is conducive to stabilize the structure and provide sufficient catalytic sites during the charging and discharging process.

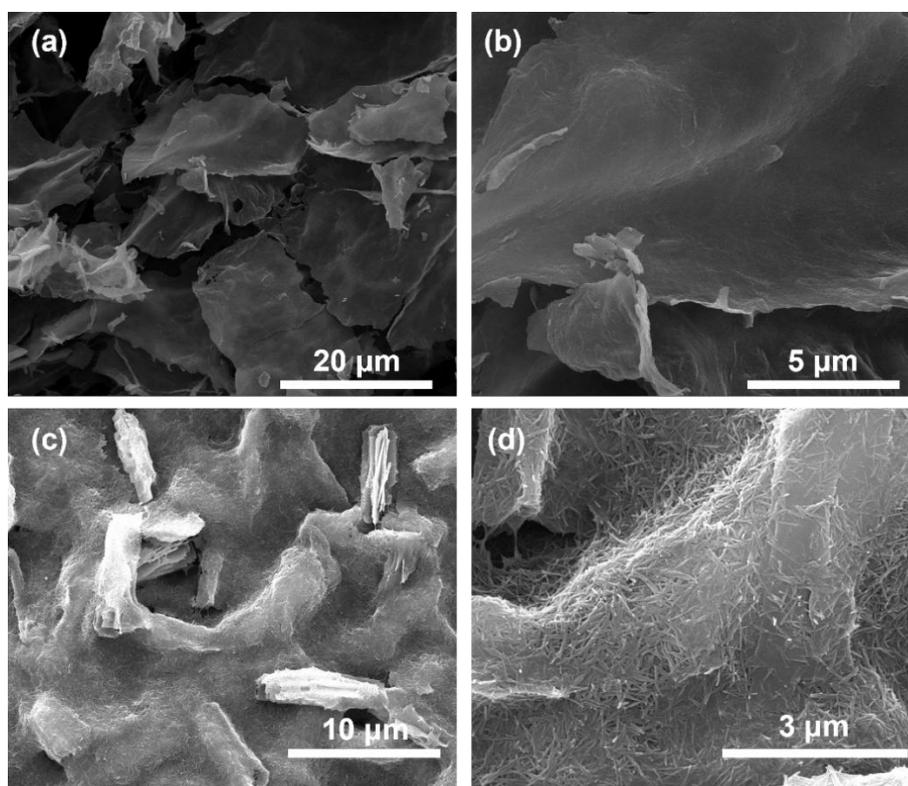


Figure 1 SEM images of (a) and (b) GA, (c) and (d) $\text{Co}_3\text{O}_4/\text{GA}$

It has been proposed that the stronger adsorption ability to lithium polysulfide of host materials, the cells deliver better cyclers performance. Hence, to confirm the adsorption ability of $\text{Co}_3\text{O}_4/\text{GA}$ to Li_2S_6 , a visualized adsorption test was performed and shown in Figure 2.

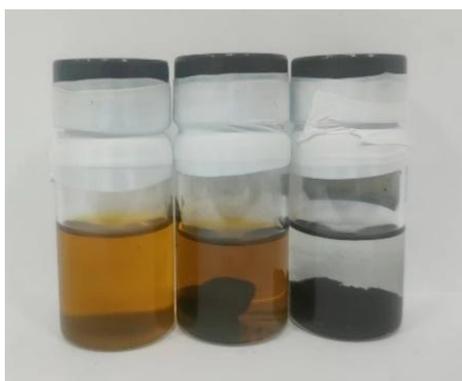


Figure 2 digital photo of visualized adsorption test

30 mg as-prepared $\text{Co}_3\text{O}_4/\text{GA}$ (right bottle) was added to 4 mL 0.05 M Li_2S_6 solution with a solvent of DME and DOL (v/v = 1:1). The two controls were imitated without host materials (left bottle) and with GA (middle bottle), respectively. As shown in Figure 2, the reddish-brown Li_2S_6 solution turned to clear after the addition of $\text{Co}_3\text{O}_4/\text{GA}$, indicating the high adsorption ability of $\text{Co}_3\text{O}_4/\text{GA}$ to Li_2S_6 . Compared with GA, it suggests that the introduction of Co_3O_4 nanowires can effectively absorb lithium polysulfide and alleviate the “Shuttle Effect”, leading to a better electrochemical stability.

The mechanism and electrochemical performance of $\text{Co}_3\text{O}_4/\text{GA}$ and GA in the lithium-sulfur battery system were studied through CV measurement, with the potential window of 1.7 to 2.7 V, and a scan rate of 0.1 mV s^{-1} . The CV curves are shown in Figure 3a. In the curve of $\text{Co}_3\text{O}_4/\text{GA}$, two obvious reduction peaks appeared at 2.01 V and 2.27 V, which can be attributed to the multi-step reactions between sulfur and lithium in the composite. The peak at 2.27 V corresponds to the process of solid S_8 to soluble Li_2S_8 , while the peak at 2.01 V is mainly attributed to the process of soluble polysulfide to solid Li_2S . The oxidation peak at 2.46 V is caused by the formation of polysulfides Li_2S_x ($2 < x \leq 6$). [13] It is obvious that the peak potential difference of $\text{Co}_3\text{O}_4/\text{GA}$ is smaller than that of GA, indicating that the $\text{Co}_3\text{O}_4/\text{GA}$ cell has less polarization, attributed to the catalytic effect of Co_3O_4 .

In addition, we conducted constant current charge-discharge tests to study the capacity, rate capability, and cycling stability of the obtained lithium-sulfur batteries, which is crucial for evaluating the electrochemical performance of the materials. As shown in Figure 3b, the cell with GA delivered the discharge capacities of 1075.39, 672.83, 422.82, 224.44, and 12.87 mA h g^{-1} at the current rates of 0.1, 0.2, 0.5, 1 and 2 C ($1\text{C} = 1672 \text{ mA g}^{-1}$), respectively. After composited with Co_3O_4 , the cell with $\text{Co}_3\text{O}_4/\text{GA}$ exhibited the discharge capacities of 1075, 685.06, 509.1, 404.9, and 176.95 mA h g^{-1} , respectively. In addition, after being subjected to high current charge-discharge at 2 C, the specific capacity still reached 782 mAh g^{-1} when returned to small current charge-discharge at 0.1 C, demonstrating good electrochemical rate performance and reversibility. These results further prove that the modified composite material has excellent electrochemical stability and can effectively improve cycle reversibility.

The Nyquist plots of $\text{Co}_3\text{O}_4/\text{GA}$ and GA-based lithium-sulfur cells at 1.7 V were shown in Figure 3c. The Nyquist curve is primarily composed of a semicircle in the high-frequency region and a sloping line in the low-frequency region. The diameter of the semicircle is directly proportional to the charge transfer impedance. The slope of the line is related to the ion diffusion rate, where a larger slope indicates a faster diffusion rate. [14] Compared to GA, the $\text{Co}_3\text{O}_4/\text{GA}$ -based cell displays a smaller semicircle, which suggests a lower charge transfer resistance. and higher electrochemical catalytic activity. Furthermore, the cell with $\text{Co}_3\text{O}_4/\text{GA}$ also exhibits a higher slope of the line, indicating a faster lithium-ion diffusion rate. These results demonstrate that the introduction of Co_3O_4 nanowires significantly enhances the kinetics of the lithium-sulfur battery.

Figure 3d displays the cycling performance of Co₃O₄/GA and GA-based lithium-sulfur batteries at a current density of 0.5C. As shown in the figure, after 500 cycles, the specific capacity gradually decreases from 705 mAh g⁻¹ to 325 mAh g⁻¹, with a retention rate of 46%, demonstrating good cyclic stability. Additionally, the Coulombic efficiency of the lithium-sulfur battery prepared during the charge-discharge process remains around 100%, exhibiting excellent electrochemical stability.

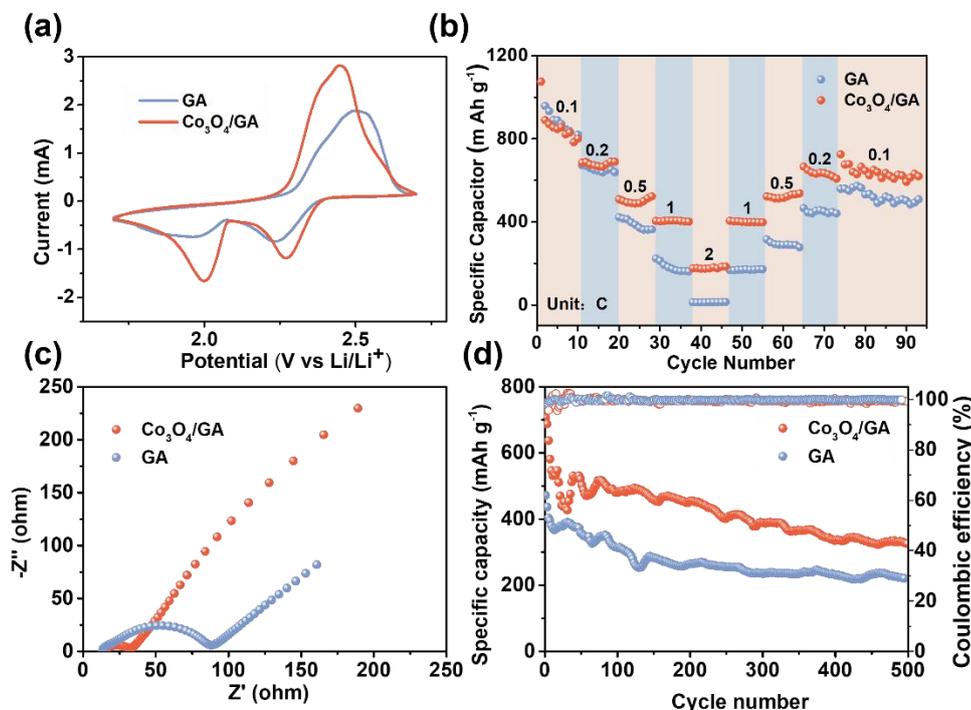


Figure 3 Electrochemical performance. (a) CV curves at 0.1 mV s⁻¹, (b) rate performance, (c) Nyquist plots, (d) long-term cycle performance of Co₃O₄/GA and GA-based cells.

4. Summary

In summary, we describe a simple one-step hydrothermal method for preparing Co₃O₄/GA composite material and have explored its potential as a host material of the sulfur species. The Co₃O₄/GA composite synergistically combines the benefits of GA's lightweight, high conductivity and Co₃O₄ nanowires' high catalytic activity and adsorption capacity, thus exhibiting good electrochemical rate capability and cycling performance. The work can produce an effective approach for satisfactory aerogel-based cathodes of lithium-sulfur batteries through a simple hydrothermal process.

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