Hollow Ni-Co-S Nanocubes as Superior Sulfur Host for High-Performance Lithium-Sulfur Batteries

Zhiyu Zhou1,2, Zexiang Chen1,2*, Huifang Lv1,2, Yang Zhao1,2, Hualiang Wei1,2 and Yan Wang1,2*

1 School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China, Chengdu, Sichuang, 611731, China
2 Sichuan Province Key Laboratory of Display Science and Technology, Jianshe North Road 4, Chengdu, Sichuang, 610054, China
*E-mail: zxchen@uestc.edu.cn (Zexiang Chen); wangyan127@uestc.edu.cn (Yan Wang)

Abstract. In this work, hollow Ni-Co-S nanocubes were designed and successfully prepared as a superior sulfur host for lithium-sulfur batteries (LSBs) by means of facile synthesis methods. The prepared hollow Ni-Co-S nanocubes possess multiple merits, including good electrical conductivity, sulfur encapsulated nanostructure and LiPS adsorbability. By employing Ni-Co-S nanocubes as the sulfur host, the electron transfer efficiency is increased and the volume expansion during repeated cycling can be buffered. Besides, the shuttling effect is limited effectively due to the strong lithium polysulfides (LiPS) adsorbability. As a result, the sulfur utilization is significantly improved for better performance. Benefiting from these advantages, the LSBs exhibited a fairly high initial capacity of 1482 m Ah g⁻¹, a retained capacity of 669 m Ah g⁻¹ over 200 cycles and impressive discharge capacities of 710, 565, 370 and 186 m Ah g⁻¹ even at 1C, 2C, 3C and 4C, respectively.

1. Introduction
In the background of global environmental crisis and depletion of energy resources, exploiting high-efficiency sustainable energy has been a research focus due to the great demands for energy in rapidly developing industries[1]. Among various practical applications of sustainable energy sources, wind, solar, and hydroelectric power generation as well as electrochemical devices are the most widely utilized clean energy conversion technologies[2]. Portable power resources are even more concerned due to the convenience and irreplaceability for flourishing electronic equipments and electromobiles industries. LSBs with satisfactory capacities and cycling stability are promising energy-storage systems after the current used lithium-ion batteries, on account of the extremely high theoretical performance of a specific capacity of 1675 mA h g⁻¹ and a energy density of 2600 W h kg⁻¹[3-4]. In addition, LSBs are cost-effective and sustainable because of the abundant sources of sulfur. However, LSBs have been suffering from serious challenges such as severe shuttling effect and large volum change, which lead to fast capacity decay and unstable cycling[5]. In addition, the intrinsic insulating property of sulfur leads to a low utilization of active materials, which notably decreases the practical performance of LSBs[6]. In order to overcome these stubborn obstacles, multitudinous strategies have been proposed. The capacity retention and cycling stabability of LSBs are significantly elevated by means of a varity of methods, such as protecting lithium metal, integrating sulfur species with host
materials. Beside, materials with electrocatalytic properties for LiPS conversion are much attractive and focused because the high efficient catalytic conversion between sulfur and the final discharge product Li_{2}S could result in a elevated sulfur utilization[7]. For example, a interlaced network of carbon nanotubes reinforced hollow CoS nanostraws was designed to serve as a flexible sulfur host, which possess high conductivity, LiPS adsorbability and electrocatalytic ability, resulting a excellent electrochemical properties[8]. Other strategies such as imbedding a functional interlayer between the cathode and the anode are also adopted. A microporous C_{3}N_{4} framwork was fabricated wherein the pyridinic nitrogen ensured abundant LiPS binding sites to supress the shuttling effect[9]. The modified LSBs employing the C_{3}N_{4} framwork as a cathode host and an functional interlayer concurrently demonstrated a significantly improved capacity and cycling life[10].

A widely adopted strategy is combing sulfur (or Li_{2}S_{n}, n ≤ 6; if using LiPS as the active materials) with host materials which commonly feature with electrical conductivity, LiPS adsorbability or catalytic properties. The morphologies of the selected host materials prefer to be a box that can encapsulate sulfur-related species during repeated charge/discharge. A series of metallic oxides such as Co-TiO_{2-x}/CNF[11], sulfides such as nitrogen-doped Co_{9}S_{8}[12], and nitrides such as TiN-VN[13] are explored for such sulfur hosts. However, numerous of nanocomposites are undurable to maintain the nanostructure stability under a high electric potential versus Li/Li^{+} when employed as sulfur hosts[14]. In addition, the fragmentary hosts suffer from passivation and deformation which lead to unsatisfactory LiPS perservation and electrochemical performance. Although a varity of sulfur hosts have been exploited to mitigate those inherent issues of LSBs, there are scarce candidates can make up all the intrinsic deficiencies of LSBs.

In this study, we report a superior sulfur host which is integrated with good electrical conductivity, LiPS adsorbability, sulfur-encapsulated nanostructure and sufficient active materials contact surface. The designed Ni-Co-S composite is prepared by means of facile hot bath process and calcination which is favourable for mass production. The stacked hollow Ni-Co-S nanocubes not only exhibited improved conductivity for promotional electron conduction when introduced as a cathode host, but also provide sufficient microvoid for sulfur loading and numerous active sites for sulfur redox reactions, which can buffer the volume expansion of sulfur related species and improve the sulfur utilization. The contact area of active materials with electrolyte is elevated significantly for a more efficient electrochemical transformation. Besides, the hollow Ni-Co-S nanocubes have strong adsorbability to LiPS, which is a favorable character for the sulfur hosts. The shuttling effect is consequently supressed after introducing Ni-Co-S nanocubes as the sulfur host. As a result, the Ni-Co-S@S cathode exhibits excellent performance, including a fairly high initial capacity of 1482 m Ah g^{-1}, a capacity retention of 669 m Ah g^{-1} at 0.5 C (1 C= 1675 mA g^{-1}) over 200 cycles, and good rate capacities of 710, 565, 370 and 186 m Ah g^{-1} at the current densities of 1C, 2C, 3C and 4C, respectively. The satisfactory electochemical can be attribute to the integrated merits of Ni-Co-S nanocubes.

2. Experiments

2.1 Synthesis of Ni MOF precursors

The hollow Ni-Co-S nanocubes are prepared based on Ni metal organic framework (MOF) precursors. Typically, 2.8 g nickel acetate and 6.0 g polyvinyl pyrrolidone (PVP) are dispersed in 100 mL ethanol under continuously stirring until all the solids are dissolved. Then the obtained green solution is transferred to a flask, kept with backflow and a constant temperature of 78 °C. After 12 h, the sediments is taken out and washed with ethanol for 3 times followed by drying at 60 °C under vacuum.

2.2 Synthesis of Ni-Co-S nanocubes

Briefly, 2.0 g previously obtained Ni MOF precursors are dispersed in 750 mL ethanol under ultrasound. Then 6.3 g hexamethylenetetramine (HMT) is dissolved into the suspension under steady stirring. After that, 1.455 g Co(NO_{3})_{2}:6H_{2}O is dispersed in 250 mL ethanol and then slowly added into
the solution. The obtained solution is transferred to a flask, kept with backflow and a constant temperature of 78 °C for 12 h. The sediment is separated and washed with ethanol for 3 times followed by drying at 60 °C under vacuum to get the Ni MOF-Co composite.

Subsequently, 1.2 g Ni MOF-Co composite is dispersed in 30 mL ethanol solution which contains 20 mg thioacetamide. The solution is transferred to a teflon lining and sealed with a stainless steel vessel and then kept at 120 °C for 4 h. After that, the precipitation product is washed by deionized water for at least 5 times and then calcined at 250 °C for 2 h under N2 atmosphere with a heating rate of 4 °C min⁻¹.

2.3 Synthesis of the cathods

The sulfur loaded Ni-Co-S nanocubes (Ni-Co-S@S) are prepared by grinding and calcining Ni-Co-S nanocubes and sublimed sulfur particles in a mass ratio of 3:7 at 155 °C for 12 h in an airtight glass container. The cathods are fabricated by mixing Ni-Co-S@S, electroconductive carbon black and polytetrafluoroethylene (PTFE) in a mass ratio of 7:2:1 to a homogeneous slurry. Then the slurry is casted on a piece of Al foil and dry at 65 °C overnight. The cathods are harvested after trimming the coated Al foil into suitable disks.

2.4 Electrochemical Characterizations

CR2032 type coin cells are assembled and tested. Cyclic voltammetry (CV) profiles and electrochemical impedance spectra (EIS) are measured by means of a three-electrode electrochemical workstation (RST, Zhengzhou). Rate capacity performance and long time cycling performance are recorded by a NEWARE battery tester. The morphology of the prepared samples are investigated by using a Scanning electron microscopy (SEM, FEI Nova-Nano).

3. Results and Discussion

Figure 1. Model images and corresponding SEM photos assigned to each stage of preparing sulfur loaded Ni-Co-S nanocubes.

The synthetic process of sulfur loaded Ni-Co-S nanocubes is illustrated in figure 1. As shown, the model images and corresponding SEM photos assigned to each stage are displayed. Initially, the uniform Ni MOF precursor is prepared which has smooth face and the two unobvious pyramid flanks. After treated by a hot bath process, a Ni, Co-containing outer layer in-situ grows on the surface of the Ni MOF precursor which results in distinctly rough appearance. The introduced Co element has a synergy effect to improve the electrochemical performance and LiPS adsorbability, which may accelerate the LiPS conversion during repeated charge/discharge. However, the outer layer is inseparable with the Ni MOF precursor core until this step. By means of a controlled sulfuration treatment, the Ni, Co-containing outer layer transferred to water insoluble shell. Interestingly, the Ni
MOF precursor core which is not affected by TAA in the hydrothermal treatment is soluble in water. Therefore, the preserved Ni MOF precursor core can be removed by simple water washing but the shell can be retained. We can find that the hollow nanocube structure is preserved well and the length of which is about 400–600 nm. Besides, the wall of the Ni-Co-S nanocubes are thinnish, guaranteeing a insignificant mass percentage and large specific surface area. As a result, the sublimed sulfur particles can be encapsulated well in those nanocubes, which is the critical factor for the limited shuttling effect and elevated electrical conductivity. In addition, the separated Ni-Co-S nanocubes provide numerous active sites for sulfur redox reactions and buffer the volume expansion of sulfur related species, resulting in a increased sulfur utilization.

Figure 2. Electrochemical measurement results of the Ni-Co-S@S cathode: (a) CV curves; (b) EIS; (c) rate capacities and (d) long time cycling performance.

By employing Ni-Co-S nanocubes as the sulfur host of LSBs, a superior electrochemical performance can be achieved. As shown in figure 2a, CV measurements from a small scanning rate of 0.1 mV s\(^{-1}\) to a large scanning rate of 1 mV s\(^{-1}\) are displayed. Two typical oxidation peaks at 2.35 V and 2.41 V, and two reduction peaks near 2.33 V and 2.01 V can be observed. As the scanning rate increases, the redox peaks maintained their original positions almost, indicating a excellent rate performance and electrochemical stability. EIS is also tested to investigated the conductivity of Ni-Co-S nanocubes. As shown in figure 2b, the obviously smaller semicircle in the EIS plot of the prepared Ni-Co-S nanocube cathode comparing with that of the pure sulfur cathode suggests the Ni-Co-S@S cathode has a decreased charge transfer resistance\[15\]. The result of EIS tests confirmed that the Ni-Co-S nanocubes facilitate the electronic transmission during repeated cycling, which can be ascribed to the good electrical conductivity of the prepared Ni-Co-S sulfur host. The rate performance was evaluated by measuring the specific capacities under different current densities from 0.5 C to 4 C (figure 2c). The Ni-Co-S@S cathode exhibited satisfactory discharge capacities of 710, 565, 370 and 186 m Ah g\(^{-1}\) at 1C, 2C, 3C and 4C, respectively. When the applied current was switched back, the capacities were retained well and kept stable. The long cycling performance of Ni-Co-S@S cathode was also investigated at a high current density of 0.5 C with a sulfur loading of 2.5 mg cm\(^{-2}\). As shown in figure 2d, the Ni-Co-S@S cathode exhibited excellent performance, including a fairly high initial capacity of 1482 m Ah g\(^{-1}\) and a retained capacity of 669 m Ah g\(^{-1}\) over 200 cycles. The excellent electrochemical performance can be attributed to the superior hollow Ni-Co-S nanocubes which integrates multiple merits including good electrical conductivity, sulfur encapsulated nanostructure and LiPS adsorbability, which elevated the electron transfer efficiency, accelerated the LiPS conversion and suppressed the shuttling effect significantly.
4. Conclusion
In summary, the hollow Ni-Co-S nanocubes were successfully prepared as a superior sulfur host for advanced LSBs via facile hot bath and calcining treatments. The main reasons for the improved electrochemical performance are: (a) the good electrical conductive Ni-Co-S nanocubes decrease the charge transfer resistance and facilitate charge transportation during repeated cycling; (b) the hollow nanostructure provide sufficient microvoid for sulfur loading and numerous active sites for sulfur redox reactions, which can buffer the volume expansion of sulfur related species and elevate the sulfur utilization; (c) the hollow Ni-Co-S nanocubes have strong LiPS adsorbability, which relieved the shuttling effect significantly. Benefiting from these advantages, the LSBs using Ni-Co-S nanocubes as the sulfur host exhibited excellent cycling stability and high capacity over 200 cycles. The exquisite electrochemical performance demonstrated that the prepared Ni-Co-S nanocubes is a promising material for LSBs application.

References
[1] M. Rana, S.A. Ahad, M. Li, B. Luo, L. Wang, I. Gentle, R. Knibbe. (2019) Review on areal capacities and long-term cycling performances of lithium sulfur battery at high sulfur loading. Energy Storage Materials, 18: 289-310.
[2] D. H. Liu, Z. Bai, M. Li, A. Yu, D. Luo, W. Liu, L. Yang, J. Lu, K. Amine, Z. Chen. (2020) Developing high safety Li-metal anodes for future high-energy Li-metal batteries: strategies and perspectives. Chemical Society Reviews, 49: 5407-5445.
[3] Z.W. Seh, Y. Sun, Q. Zhang, Y. Cui. (2016) Designing high-energy lithium–sulfur batteries. Chemical Society Reviews, 45: 5605-5634.
[4] J.M. Tarascon, M. Armand. (2001) Issues and Challenges Facing Rechargeable Lithium Batteries. Nature, 414: 359-67.
[5] W. Xue, Z. Shi, L. Suo, C. Wang, Z. Wang, H. Wang, K.P. So, A. Maurano, D. Yu, Y. Chen, L. Qie, Z. Zhu, G. Xu, J. Kong, J. Li. (2019) Intercalation-conversion hybrid cathodes enabling Li–S full-cell architectures with jointly superior gravimetric and volumetric energy densities. Nature Energy, 4: 374-382.
[6] X. Zhang, Y. Yang, Z. Zhou. (2020) Towards practical lithium-metal anodes. Chemical Society Reviews, 49: 3040-3071.
[7] G. Zhang, Z.W. Zhang, H. J. Peng, J. Q. Huang, Q. Zhang. (2017) A Toolbox for Lithium–Sulfur Battery Research: Methods and Protocols. Small Methods, 1: 1700134.
[8] L. Ma, W. Zhang, L. Wang, Y. Hu, G. Zhu, Y. Yang, R. Chen, T. Chen, Z. Tie, J. Liu, Z. Jin. (2018) Strong Capillarity, Chemisorption, and Electrocatalytic Capability of Crisscrossed Nanostraws Enabled Flexible, High-Rate, and Long-Cycling Lithium–Sulfur Batteries. ACS Nano, 12: 4868-4876.
[9] H. Wu, Y. Li, J. Ren, D. Rao, Q. Zheng, L. Zhou, D. Lin. (2019) CNT-assembled dodecahedra core@nickel hydroxide nanosheet shell enabled sulfur cathode for high-performance lithium-sulfur batteries. Nano Energy, 55: 82-92.
[10] S. Karuppiah, B. Kalimuthu, M.A. Nazrulla, S. Krishnamurty, K. Nallathamby. (2019) An effective polysulfide trapping polar interlayer for high rate Li–S batteries. Journal of Materials Chemistry A, 7: 10067-10076.
[11] J. Wang, D. Luo, J. Li, Y. Zhang, Y. Zhao, G. Zhou, L. Shui, Z. Chen, X. Wang. (2020) “Soft on rigid” nanohybrid as the self-supporting multifunctional cathode electrocatalyst for high-performance lithium-polysulfide batteries. Nano Energy, 78: 105293.
[12] Y. Liu, S. Ma, L. Liu, J. Koch, M. Rosebrock, T. Li, F. Bettels, T. He, H. Pfünir, N.C. Bigall, A. Feldhoff, F. Ding, L. Zhang. (2020) Nitrogen Doping Improves the Immobilization and Catalytic Effects of CoSx in Li-S Batteries. Adv Funct Mater, 30: 2002462.
[13] Y. Yao, H. Wang, H. Yang, S. Zeng, R. Xu, F. Liu, P. Shi, Y. Feng, K. Wang, W. Yang, X. Wu, W. Luo, Y. Yu. (2020) A Dual-Functional Conductive Framework Embedded with TiN-VN
Heterostructures for Highly Efficient Polysulfide and Lithium Regulation toward Stable Li–S Full Batteries. Adv Mater, 32: 1905658.

[14] J. He, Y. Chen, A. Manthiram. (2019) Metal Sulfide-Decorated Carbon Sponge as a Highly Efficient Electrocatalyst and Absorbant for Polysulfide in High-Loading Li2S Batteries. Adv Energy Mater, 9: 1900584.

[15] L. Yuan, H. Yuan, X. Qiu, L. Chen, W. Zhu. (2009) Improvement of cycle property of sulfur-coated multi-walled carbon nanotubes composite cathode for lithium/sulfur batteries. Journal of Power Sources - J POWER SOURCES, 189: 1141-1146.