

Short Communication

Mesoporous Co₃O₄ Nanosheets as Highly Efficient Sulphur Host for Lithium-Sulfur Batteries

Xun Qiao*, Fuxiang Yin, Jianshe Huang

Intelligent Manufacturing Research and Development Center, School of Mechanical Engineering, Xijing University, Xi'an, Shaanxi, 710123, China.

*E-mail: xunqiaoxijing@aliyun.com

Received: 3 December 2019 / Accepted: 30 January 2020 / Published: 10 April 2020

As an important part of the lithium-sulfur battery, the cathode material plays a key role in the electrochemical performance of the lithium-sulfur batteries. However, the traditional cathode materials have poor cycle stability and low specific capacity, which fail to adsorb the lithium polysulfide and improve the electronic conductivity simultaneously. This work prepared mesoporous Co₃O₄ nanosheets, which could strongly anchoring lithium polysulfide, thus showing remarkable improvement for cycle stability. The SEM shows that the as-prepared MCON-S composites exhibit nanosheet structure. The MCON-S displays an initial specific capacity of 1316 mAh g⁻¹ at 0.1 C. Meanwhile, the excellent capacity retention of 90% after 300 cycles at 1C was obtained.

Keywords: Li-S battery, Co₃O₄, Polysulfide, Shuttle effect.

1. INTRODUCTION

During recent decades, various energy storage systems are emerging in the market and research fields all over the world [1, 2]. This is attributed the increasing demand for the energy consumption. In addition, the traditional energy storage systems, such as oil [3], coal and gas [4], have become less and less with the development of the science and technology. Therefore, it is urgent to develop other new energy storage systems to meet the demand for the energy [5]. Only by doing this, the sustainable development could be achieved for all the countries [6]. Moreover, the traditional energy has disadvantages with great pollution and high cost. More recently, lithium-ion battery series have become hot topic for the researchers worldwide [7, 8, 9]. More importantly, Goodenough, who invents the cathode materials for the lithium-ion batteries, won the Nobel Prize, demonstrating the significant status of the lithium-ion batteries [10, 11].

Lithium-sulfur batteries are one of the lithium batteries, which used lithium as the anode and S-

based composites as cathode [12]. The specific capacity and energy density of the lithium-sulfur batteries could reach 1675 mAh/g and 2600 Wh/Kg, respectively [13, 14]. These values are much higher than those of traditional lithium-ion batteries [15]. Therefore, the lithium-sulfur batteries have drawn much attention for the researchers. However, the lithium-sulfur batteries also have some issues as one of the new energy storage system, a) the poor electronic conductivity, b) the shuttle effect of the soluble polysulfide [16, 17, 18]. To deal with these two problems, many methods have been applied. Originally, various carbon materials were prepared and used as host materials for the element sulfur, for example, carbon nanofiber, carbon nanotube and graphene. By using these carbon materials, the electronic conductivity could be greatly improved. However, the carbon materials failed to inhibit the shuttle effect of the polysulfide during the electrochemical process [19]. After that, multifunctional materials are synthesized and developed as cathode materials for the lithium-sulfur batteries. In particular, the metal oxides were considered as promising cathode materials for the lithium-sulfur batteries.

In our work, mesoporous Co_3O_4 nanosheets are successfully prepared via a solution method. The Co_3O_4 -S composites are obtained by using a heating method at high temperature. As a result, the MCON-S composites are synthesized and used as cathode materials for the lithium-sulfur batteries. Due to the presence of the metal oxide Co_3O_4 , the cycling stability of the lithium-sulfur batteries is efficiently enhanced. Moreover, the as-prepared MCON-S composites show higher specific capacity than the pristine S cathode. The superior electrochemical performance is ascribed to the employment of the Co_3O_4 , which could modify the electronic conductivity and inhibit the shuttle effect of the soluble polysulfide.

2. EXPERIMENTAL

2.1. Preparation of mesoporous Co_3O_4 nanosheets

Typically, 1.8 g cobalt acetate tetrahydrate $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved into 60 mL of ethanol and stirred for 1 h. Then, the mixture was transferred into an autoclave under 180°C for 12h. After cooling to room temperature, the product was washed with methanol for 3 times. Subsequently, the precipitate was heated at 150°C for 3 h to obtain mesoporous Co_3O_4 nanosheets.

2.2. Preparation of MCON-S composites

The MCON-S composites were prepared by using heating method. The as-prepared mesoporous Co_3O_4 nanosheets and pristine sulfur were mixed with ratio of 3:1. Then, the mixture was heated at 155°C for 12 h and 200°C for 2 h. Finally, the product was ground for 30 min to obtain the MCON-S composites.

2.3. Materials Characterization

The morphology of the mesoporous Co_3O_4 materials and MCON-S composites were observed by using scanning electron microscopy (SEM, EM-30 plus). The diffraction peak about the crystal structure was tested by using X-ray diffraction (XRD, TD-5000X) at the angles between 3° and 80° . The sulfur content in the MCON-S composites was judged by conducting TG analysis (TGA, Mettler) at the temperature from room temperature to 800°C .

2.4. Electrochemical Measurements

The electrochemical performance of the pristine S and MCON-S composite electrodes was tested by using coin 2016 half cells at the battery tester (LAND CT2001A). Pristine S and MCON-S electrode were used as cathode, respectively. The lithium film was used as anode. The cathode slurry was prepared by mixing pristine S or MCON-S with SP and PVDF with mass ratio of 90:5:5 with NMP as solvent. The cathode slurry was uniformly coated on the surface of the Al film. The separator was Celgard 2300. The electrolyte was consisted of 1M LITFSI and DOL:DME (1:1). The electrochemical impedance spectra was tested on the electrochemistry station (CHI660E).

3. RESULTS AND DISCUSSION

To observe the morphology of the as-prepared samples, SEM images were conducted. As shown in Figure 1a, the as-prepared Co_3O_4 materials show nanosheet structure, which are consisted of great amounts of nano-layers. The diameter of the MCON is about 50-60 nm, which is helpful for the storage of the pristine sulfur. Figure 1b shows the SEM image of the MCON-S composites. It can be seen that the as-prepared MCON-S composites have the same morphology comparing with the MCON. This indicates that the element sulfur is immersed into the MCON, showing a uniform distribution. To further demonstrate the uniform distribution of all elements in the MCON-S composites, EDS was conducted for the MCON-S composites. As shown in Figure 1c-f, it can be clearly seen that elements Co, O and S are uniformly distributed in the SEM images, which proves that the successful preparation of MCON-S composites. This could ensure the capacity release when the MCON-S composites are used as cathode materials in the lithium-sulfur batteries. This is attributed the presence of the active materials of sulfur in the MCON-S composites.

Figure 2a shows the XRD patterns of the MCON, pristine S and MCON-S composites. The as-prepared MCON show typical diffraction peaks, showing superior purity. This is consistent with the previous literatures. The pristine S shows monoclinic structure. After compositing with the element sulfur, the as-prepared MCON-S composites exhibit similar diffraction peak with the pristine sulfur. The only difference between the pristine sulfur and MCON-S composites is that the MCON-S composites show weaker diffraction peak than the pristine sulfur [20]. To determine the sulfur content in the MCON-S composites, TG analysis was conducted for the MCON-S composites. As shown in Figure 2b, the as-prepared MCON-S composites display weight loss between 250°C and 320°C , which

is related to the sublimation of the element sulfur. Therefore, it can be obtained that the sulfur content in the MCON-S composites is about 73.28%. Recently, the sulfur content in the S-based materials is all more about 60%. This is beneficial for the improvement of the energy density for the lithium-sulfur batteries. The less sulfur content is not helpful for the application of the lithium-sulfur batteries.

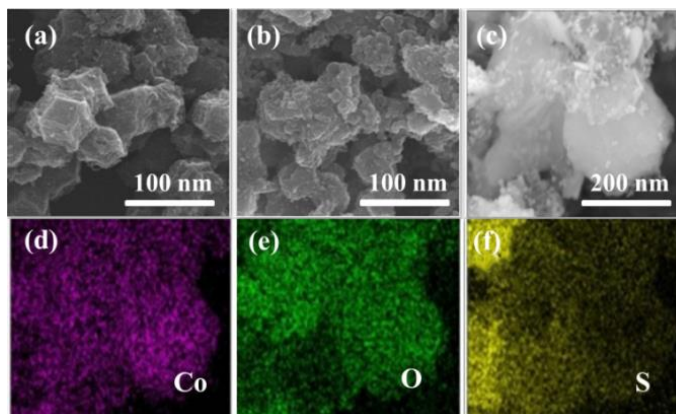


Figure 1. (a) SEM image of MCON, (b) and (c) SEM image of MCON-S composites, (d-f) Corresponding elemental mapping of Co, O and S for the MCON-S composites.

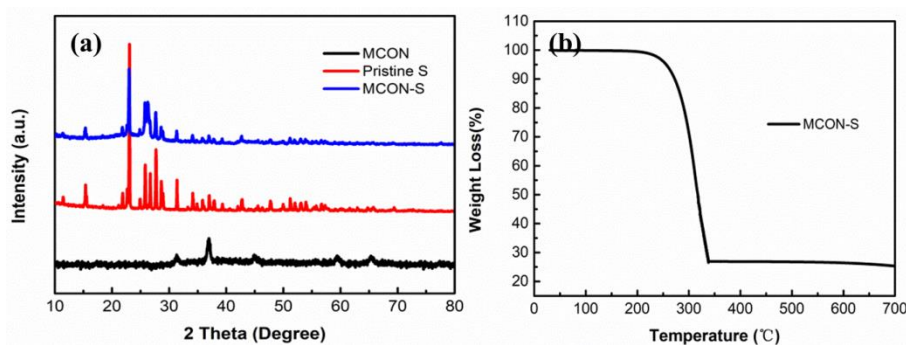


Figure 2. (a) XRD patterns of MCON, pristine S and MCON-S composites. (b) TG analysis for the as-prepared MCON-S composites.

Figure 3a shows the constant discharge and charge profiles of the MCON-S composites and pristine S electrodes. The as-prepared MCON-S composites exhibit an initial specific capacity of 1316 mAh g⁻¹ at the current density of 0.1 C. However, for the pristine S electrode, the initial specific capacity is only about 1002 mAh g⁻¹ at the current density of 0.1 C. Therefore, the as-prepared MCON-S composites show much higher specific capacity value than the pristine S electrode, thus demonstrating superior electrochemical performance. The higher capacity value of the MCON-S composites is ascribed to the superior electronic conductivity of the MCON-S composites. To investigate the electrochemical mechanism of the MCON-S composite electrode, CV test was made for the MCON-S composite electrode. As shown in Figure 3b, the CV curve of MCON-S composites

display two reduction peaks at 2.05 V and 2.3 V, respectively [21]. The peak at 2.3 V is related to the transformation of elemental sulfur to high soluble polysulfide [22]. The peak at 2.05V is corresponding to the further reaction of soluble polysulfide to Li_2S . This two steps reactions are consistent with the voltage plateaus in the discharge and charge curves (Figure 3a). In all, the obtained results are similar with the reported works in the literature [23].

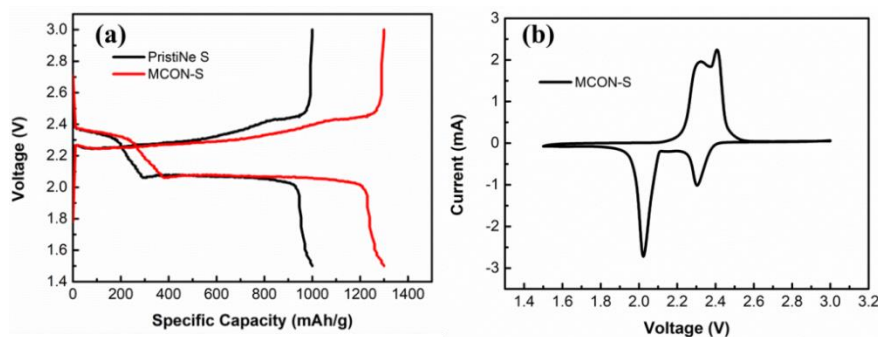


Figure 3. Discharge and charge curves of the pristine S and MCON-S composite electrode at the current density of 0.1 C. (b) CV curves of the MCON-S composite electrode at the scan rate of 0.1 mV s^{-1} .

To observe the cycling stability of the MCON-S and pristine S electrode, cycle performances of the two electrodes are conducted. As shown in Figure 4a, the as-prepared MCON-S composites display specific capacity of 856 mAh g^{-1} at the current density of 1 C. The capacity value remains at 768 mAh g^{-1} after 300 cycles at 1 C. The capacity retention for the MCON-S composites is about 90 after 300 cycles at the high current density of 1 C. However, for the pristine S electrode, the pristine S electrode suffers from severe capacity fade during the electrochemical cycles. Overall, the as-prepared MCON-S composites show more excellent cycling stability than the pristine S electrode. To further investigate the electrochemical performance of the MCON-S composites, rate capabilities for the two electrodes were tested at various current densities from 0.1 C to 2 C. This is attributed to the perfect polar metal oxide Co_3O_4 , which could provide chemical adsorption. Moreover, the unique nanosheet structure is beneficial for the storage of the polysulfide. As shown in Figure 4b, it can be clearly observed that the as-prepared MCON-S composites electrode shows superior rate performance even at the high current density of 2 C. Besides, when the current density returns back to 0.2 C, the capacity values could recover back for the MCON-S composites. However, for the pristine S electrode, it exhibits bad rate capability with the increase of the current densities. To study the charge and ion transport of the MCON-S composites, EIS was conducted. As shown in Figure 4c, the semicircle in the high frequency represents the charge transfer resistance, the line in the low frequency is related to the ion transport ability. Therefore, the as-prepared MCON-S composites have more superior charge transfer ability than the pristine S electrode. This is consistent with the higher specific capacity value (Figure 3a). The higher capacity could be assigned to the improved the electronic conductivity of the MCON-S composites [24].

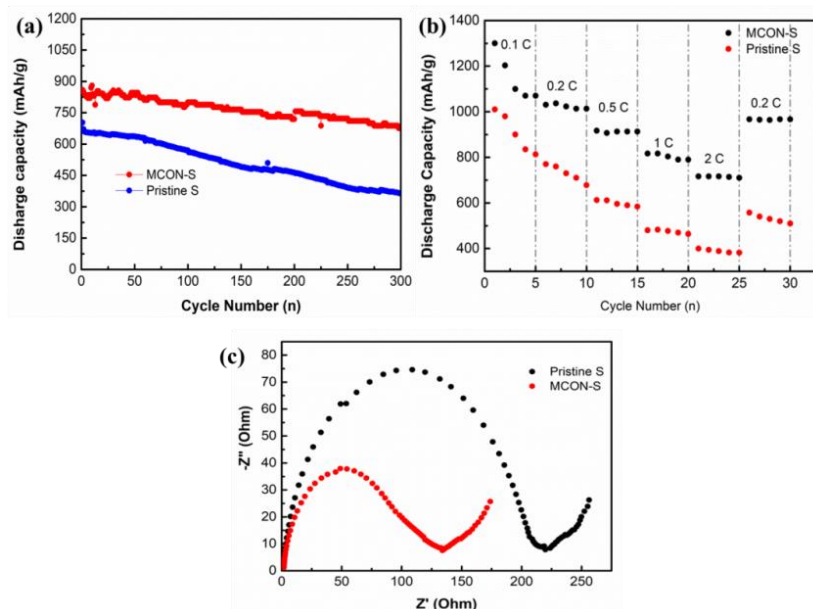


Figure 4. (a) Cycle performance of the pristine S and MCON-S composite electrode at 1 C. (b) Rate capability of the pristine S and MCON-S composite electrode. (c) Electrochemical impedance spectra of the pristine S and MCON-S composite electrode.

Figure 5a and b show the SEM images of the as-prepared MCON-S electrode before and after 300 electrochemical cycles, respectively. As shown in Figure 5a and b, it can be clearly observed that the MCON-S composites still remain the stable morphology structure, demonstrating superior structure stability. This result could confirm the long cycle stability of the MCON-S composite electrode. The as-prepared MCON-S composite electrode exhibits excellent cycle performance even after 300 cycles at 1 C. This is mainly due to the presence of the MCON, which could keep structural stability during the electrochemical cycles in the as-prepared lithium-sulfur batteries [25]. Figure 5c and d display the stable binding energy of Li_2S_2 and Li_2S_4 by using MCON, respectively. The binding energies are -1.28 eV and -0.56 eV, showing strong adsorption ability for the polysulfide. This confirms the strong adsorption ability of the MCON and soluble polysulfide, which is beneficial for the adsorption of the polysulfide. As a result, the severe shuttle effect of the polysulfide could be effectively inhibited during the discharge and charge process [26].

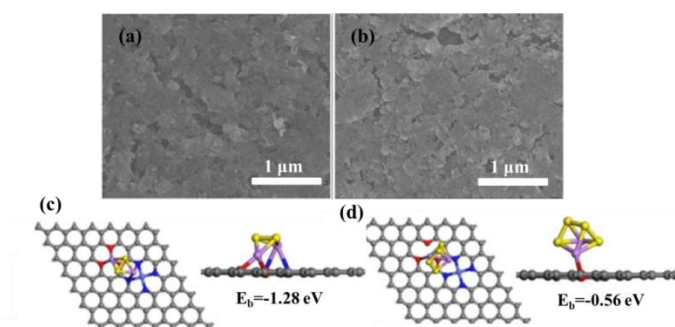


Figure 5. (a) and (b) SEM images of the MCON-S composites before and after 300 discharge and charge cycles. The stable binding energy of various polysulfides by using the MCON (c) Li_2S_2 , (d) Li_2S_4 .

Table 1 lists the electrochemical performance of the MCON-S composites and other similar cathode materials for the lithium-sulfur batteries. The as-prepared MCON-S composites exhibit superior cycle stability with high capacity retention about 90% at 1C even after 300 cycles. However, for the reported similar cathode materials, they all show severe capacity fade at the current density of 1 C after 300 cycles. Therefore, the as-prepared MCON-S composites could be used as promising cathode materials for the lithium-sulfur batteries.

Table 1. The electrochemical performances of the MCON-S composite and other similar cathode materials for the lithium-sulfur batteries.

Samples	Rate	Capacity	Ref
S@C/Co ₃ O ₄	0.5 C	86% (300 cycles)	27
NiCo ₂ S ₄ @rGO	1 C	76% (500 cycles)	28
MCON-S	1 C	90% (300 cycles)	This work

4. CONCLUSIONS

In summary, mesoporous Co₃O₄ nanosheets are successfully prepared via solution method. And the Co₃O₄-S composites are obtained by using heating method at high temperature. As a result, the MCON-S composites are synthesized and used as cathode materials for the lithium-sulfur batteries. Due to the presence of the metal oxide Co₃O₄, the cycle stability of the lithium-sulfur batteries is efficiently enhanced. Moreover, the as-prepared MCON-S composites show higher specific capacity than the pristine S cathode. The MCON-S displays initial specific capacity of 1316 mAh g⁻¹ at 0.1 C. Meanwhile, the excellent capacity retention of 90% after 300 cycles at 1C was obtained.

ACKNOWLEDGEMENT

This work is supported by the Shaanxi Provincial Education Department (Grant No. 17JK1156) and Xijing University Special Research Foundation (Grant No. XJ17T09).

References

1. J. Y. Wang, W. J. Wang, Y. G. Zhang, Z. Bakenov, Y. Zhao and X. Wang, *Mater. Lett.*, 255 (2019) 126581.
2. Y. X. Chen and X. B. Ji, *J. Alloys Compd.*, 777 (2019) 688.
3. J. X. Wang, C. Wang and M. M. Zhen, *Chem. Eng. J.*, 356 (2019) 1.
4. Y. Jiang, X. M. Yan, P. Mei, Y. Zhang, W. Xiao and H. L. Tang, *J. Alloys Compd.*, 764 (2018) 80.
5. G. Y. Jiang, N. Jiang, N. Zheng, X. Chen and Y. S. Li, *Energ. Storage Mater.*, 23 (2019) 181.
6. H. F. Long, M. Y. Zhang, Q. Wang, L. L. Xing, S. Wang and X. Y. Xue, *J. Alloys Compd.*, 701 (2017) 200.
7. W. W. Xu, X. D. Cui, Z. Q. Xie, G. Dietrich and Y. Wang, *Electrochim. Acta*, 222 (2016) 1021.
8. W. Y. Zhang, Y. S. Fu and X. Wang, *Appl. Surf. Sci.*, 439 (2018) 447.
9. X. X. Liu, R. Wu, Y. Wang, S. H. Xiao, Q. He, X. B. Niu, D. J. Blackwood and J. S. Chen,

- Electrochim. Acta*, 311 (2019) 221.
10. G. F. Zhang, P. Qin and J. M. Song, *Appl. Surf. Sci.*, 493 (2019) 55.
 11. K. H. Jang, D. K. Hwang, F. M. Auxilia, J. Jang and M. H. Ham, *Chem. Eng. J.*, 309 (2017) 15.
 12. W. G. Wang, Y. J. Liu, M. Q. Wang, G. H. Ren, S. S. Wu and J. Shen, *Appl. Surf. Sci.*, 450 (2018) 66.
 13. H. Y. Wang, R. Y. Li and Z. J. Li, *Electrochim. Acta*, 255 (2017) 323.
 14. Z. Q. Ye, Y. Jiang, J. Qian, W. L. Li, T. Feng, L. Li, F. Wu and R. J. Chen, *Nano Energy*, 64 (2019) 103965.
 15. W. Zhang, J. F. Zhang, Y. Zhao and X. Wang, *Mater. Lett.*, 255 (2019) 126595.
 16. G. F. Chen, J. H. Li, N. Liu, Y. Zhao, J. G. Tao, G. Kalimuldina, Z. Bakenov and Y. G. Zhang, *Electrochim. Acta*, 326, (2019) 134968.
 17. S. J. Dai, Y. Feng, P. Wang, H. Wang, H. G. Liang, R. F. Wang, V. Linkov and S. Ji, *Electrochim. Acta*, 321 (2019) 134678.
 18. J. W. Guo and M. S. Wu, *Electrochim. Acta*, 327 (2019) 135028.
 19. W. T. Qi, W. Jiang, F. Xu, J. B. Jia, C. Yang and B. Q. Cao, *Chem. Eng. J.*, 382 (2020) 122852.
 20. Y. Jiang, X. M. Yan, P. Mei, Y. Zhang, W. Xiao and H. L. Tang, *J. Alloys Compd.*, 764 (2018) 80.
 21. W. Y. Zhang, Y. S. Fu and X. Wang, *Appl. Surf. Sci.*, 439 (2018) 447.
 22. M. T. Liu, X. Y. Hou, T. Wang, Y. D. Ma, K. Sun, D. Q. Liu, Y. R. Wang, D. Y. He and J. S. Li, *Electrochim. Acta*, 283 (2018) 979.
 23. Y. Hu, W. Chen, T. Y. Lei, Y. Jiao, J. Xiong, *Nano Energy*, 68 (2020) 104373.
 24. X. Jiao, P. H. Ji, B. Shang, Q. M. Peng and X. B. Hu, *Solid State Ionics*, 344 (2020) 115150.
 25. C. S. Chai, H. Tan, X. Y. Fan and K. Huang, *J. Alloys Compd.*, 820 (2020) 153144.
 26. L. M. Jin, J. Ni, C. Shen, F. L. Peng and J. P. Zheng, *J. Power Sources*, 448 (2020) 227336.
 27. J. Wu, Z. J. Pan, Y. Dai, T. Wang, H. P. Zhang, S. Yan, J. M. Xu and K. X. Song, *J. Alloys Compd.*, 823 (2020) 153912.
 28. C. Huang, T. T. Sun, H. B. Shu, M. F. Chen, Q. Q. Liang, Y. Zhou, P. Gao, S. Xu, X. K. Yang, M. L. Wu, J. Jian and X. Y. Wang, *Electrochim. Acta*, 334 (2020) 135658.