Research Article

The Comparative Study of Electrochemical Capacitance Performance between Sulphur-Doped Co_3O_4 and CoS Anodes

Wei Xu,¹ M. A. Khan,² Jiahui Chen,¹ Yongbing Long,³ Gui Xu,⁴ Yu Bai,¹ Xiaodong Zhang,¹ Zhenmin Qiu,¹ Sennian Lin,¹ and Donghua Fan¹

¹School of Applied Physics and Materials, Wuyi University, Jiangmen, Guangdong 529020, China

²Department of Physics, Hi-Tech. Laboratory, University of AJK, Muzaffarabad 999010, Pakistan

³School of Electronic Engineering, South China Agricultural University, Guangzhou 510642, China

⁴Baotou Power Supply Bureau, Jianshe Road, Baotou, Inner Mongolia 014030, China

Correspondence should be addressed to Wei Xu; weixugreat@126.com and Yongbing Long; yongbinglong@126.com

Received 5 May 2016; Accepted 12 June 2016

Academic Editor: Gongming Wang

Copyright © 2016 Wei Xu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Anode materials with high capacitance performance are highly desirable for supercapacitors (SCs). In this work, nanomaterials cobalt sulfide (CoS), sulphur-doped Co_3O_4 (S- Co_3O_4), and Co_3O_4 were fabricated on a carbon cloth substrate by hydrothermal method. The composition and morphology of the material were characterized by X-ray diffraction (XRD) patterns and Scanning Electron Microscope (SEM). The electrochemical measurements were performed in a three-electrode system. The result shows that CoS nanomaterial as anode is of the best electrochemical performance, achieving areal capacitance of 1.98 F/cm^2 at 2 mA/cm^2 in a 5 M LiCl solution. Moreover, the CoS anode has long-term cycling stability with more than 85.7% capacitance retention after 10000 cycles, confirming its larger capacitance, good redox activity, and electrochemical stability.

1. Introduction

With the ever increasing energy depletion and aggravating environmental issue, considerable attention was paid to energy storage and conversion and intense research has been concentrated on this field [1, 2]. Of them, supercapacitors, with their advantages of high-power density, excellent reversibility, fast recharge ability, and long cycle life and their potential application in the field of high-power electronic devices, emergency power supplies, and hybrid electric vehicles, have attracted significant research attention [1–6]. However, the relatively low energy density of SCs impeded their further development and application. Therefore, based on not sacrificing the power density and cycle life, it is highly desirable to increase the energy density of SCs. According to the equation of energy density, $E = 0.5 \text{ CV}^2$, the energy density of a SC can be improved if the output voltage and/or the capacitance is increased [7]. An

effective approach to increase the voltage is to use organic and ionic liquid electrolytes [8–10], such as tetraethylammonium tetrafluoroborate in acetonitrile [9] or lithium perchlorate in propylene carbonate [10]. Although the voltage window of up to 3 V can be reached, the disadvantages such as high cost, poor ionic conductivity, and high toxicity prevent SCs from further applications. A hopeful alternative is to develop asymmetric supercapacitors (ASCs) based on the environmentally friendly aqueous electrolyte. As compared with symmetric supercapacitors (SSCs), ASCs combined two electrodes with different voltage to increase the operating voltage in aqueous electrolyte which is up to 2 V [11, 12]. Great efforts have been made to research various materials, such as graphene- MnO_2 //activated carbon nanofiber, Ni(OH)_2 -graphene and graphene, V_2O_5 //active carbon, and MnO_2 // FeOOH [11, 13, 14], for their application on ASCs. However, previous studies have been mainly focused on the development of high-performance cathode materials [15]. By

FIGURE 1: SEM images of (a) Co_3O_4 nanomaterials, (b) $\text{S-Co}_3\text{O}_4$ nanomaterials, and (c) CoS nanomaterials on a carbon cloth.

comparison, explorations for anode materials have been very few as yet. The most common anode materials are carbon-based nanomaterials, yet they suffer from the relatively low capacitance which prevents ASCs from further enhancement in energy density. Therefore, it is necessary to explore novel anode materials to advance the performance of ASCs.

As promising, environmentally friendly, and low-cost candidates, cobalt sulfides can also be grown on a flexible conductive substrate, but they have not been systematically studied as anode materials yet [16]. In this paper, we reported the fabrication of Co_3O_4 , sulphur-doped Co_3O_4 , and CoS and compared their electrochemical performance as anodes of ASCs. The result shows that CoS nanomaterial is of the best electrochemical performance when used as anode, achieving areal capacitance of 1.98 F/cm^2 at 2 mA/cm^2 and excellent long-term cycling stability in a 5 M LiCl solution.

2. Experimental

All reagents used in the experiment are up to the standard of analytical grade that were used without any further purification. Co_3O_4 were fabricated on a carbon cloth substrate by using hydrothermal method. First, 5 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mmol of NH_4F , and 25 mmol of $\text{CO}(\text{NH}_2)_2$ were dissolved in 50 mL of DI water under stirring, respectively. After 10 minutes of slight stirring, a Teflon-lined stainless-steel autoclave of 25 mL capacity was filled with 20 mL of homogeneous solution prepared above. Then, carbon cloth ($2 \text{ cm} \times 3 \text{ cm}$) was cleaned by ethanol, deionized water, and using ultrasonic treatment in turn and then immersed into the reaction solution. Subsequently, the autoclave was sealed and heated at 120°C for 5 h and allowed to cool down to room temperature. After the reaction, a layer of Co_3O_4 film was grown on the carbon cloth substrate and then washed with DI water and dried at 60°C . The $\text{S-Co}_3\text{O}_4$ was prepared by immersing a piece of Co_3O_4 ($2 \text{ cm} \times 3 \text{ cm}$) into a 25 mL autoclave containing 0.1 M of $\text{C}_2\text{H}_5\text{NS}$, which was then sealed and heated at 80°C for 3 h . After cooling down to room temperature, the sample was washed and then dried at 60°C . The CoS was prepared by immersing a piece of Co_3O_4 ($2 \text{ cm} \times 3 \text{ cm}$) into a 25 mL autoclave containing

0.3 M of NaS , which was then sealed and heated at 120°C for 36 h . After cooling down to room temperature, the sample was washed and then dried at 60°C .

3. Material Characterization and Electrochemical Measurement

The composition morphology and structure of the electrode materials were characterized by X-ray diffraction patterns, field-emission SEM (FE-SEM, JSM-6330F), and CV, and galvanostatic charge/discharge measurements were conducted using an electrochemical workstation (CHI 760D). The electrochemical measurements were performed in a three-electrode cell, with the individual sample used as working electrode, a Pt mesh as counter-electrode, and a SCE as reference electrode.

4. Results and Discussion

The SEM images of Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS on carbon cloth are shown in Figures 1(a), 1(b), and 1(c), respectively. It can be seen that the individual carbon fiber was uniformly wrapped by many nanowires with a diameter between 300 and 500 nm and length up to $4 \mu\text{m}$. The obvious difference in morphology between the SEM images of Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS can be observed. The SEM images of the $\text{S-Co}_3\text{O}_4$ and CoS are much rougher compared with that of Co_3O_4 ; furthermore, the SEM image of CoS is rougher than that of $\text{S-Co}_3\text{O}_4$ (Figures 1(b) and 1(c)).

Figure 2 shows the X-ray diffraction (XRD) patterns of the Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS samples. The peaks of Co_3O_4 and $\text{S-Co}_3\text{O}_4$ samples can be indexed to the standard card (JCPDS Card no. 42-1467), which are in good accordance with cubic spinel Co_3O_4 phase. In addition, the peak shift can be observed in $\text{S-Co}_3\text{O}_4$ as compared to the peak of Co_3O_4 , especially for (311) crystal face, confirming the S doping in the material. Energy dispersive spectrometry (EDS) elemental spectrum was performed to provide the doping amount of S ($26.08 \text{ wt\%}$). The peaks of CoS sample can be indexed to the standard card (JCPDS Card no. 65-3418), which are in good agreement with spinel CoS structure.

FIGURE 2: XRD spectra collected for Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS anodes.

The electrochemical properties of the Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS electrodes were investigated in a three-electrode cell in 5 M LiCl aqueous electrolyte, with a Pt counter-electrode and a SCE reference electrode. Cyclic voltammogram (CV) curves of Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS electrodes at a scan rate of 100 mV/s were compared in Figure 3(a). It is obvious that the current densities of $\text{S-Co}_3\text{O}_4$ and CoS electrodes are substantially higher than that of Co_3O_4 electrode, indicating that substantial enhancement of electrochemical capacitance of $\text{S-Co}_3\text{O}_4$ is originated from the sulphur doping into the Co_3O_4 , and the most significant enhancement of electrochemical capacitance appeared in CoS sample, which is due to the specific surface structure of CoS that can be proven by the rough surface in Figure 1(c). Moreover, the CV profiles of the CoS electrode at various scan rates are rectangularly shaped and remain similar as the scan rate increases from 10 to 200 mV/s (Figure 3(b)), demonstrating the excellent capacitive properties and high-rate capability of the CoS electrode.

Figure 3(c) shows the areal capacitances of the CoS anode at the scan rates from 10 mV/s to 400 mV/s calculated according to its CV curves. The highest areal capacitance of 0.46 F/cm² obtained at the scan rate of 10 mV/s is much better than the value (0.27 F/cm²) obtained for $\text{N-Fe}_2\text{O}_3$ negative electrode and comparable to the excellent value for other negative electrodes, such as $\text{Co}_3\text{O}_4/\text{RuO}_2$ (0.6 F/cm²) and VOS (0.56 F/cm²), demonstrating the excellent capacitive performance and a good electrical conductivity of CoS anode [3, 15, 16].

The galvanostatic charge-discharge curves of the $\text{S-Co}_3\text{O}_4$ and CoS electrodes at a current density of 2 mA/cm² are shown in Figure 3(d). Compared with the $\text{S-Co}_3\text{O}_4$ electrode, the CoS exhibits slower and more symmetrical charge and discharge curves and a more linear variation of potential versus time, which is also supported by the galvanostatic charge-discharge curves collected for CoS electrode at different

current densities from 2 to 3, 4, 5, 6, 8, and 10 mA/cm² (Figure 3(e)), confirming the enhanced capacitance, superior Coulombic efficiency, and excellent reversibility of the CoS electrode at a high current density. The areal capacitance of 0.68 F/cm² at current density of 10 mA/cm² (shown in Figure 3(e)) is also comparable to $\text{Co}_3\text{O}_4/\text{RuO}_2$ electrode (0.67 F/cm²), the best value for cobalt sulfides, proving that CoS can be a suitable candidate for anode [16].

Figure 4 demonstrates the long-term cycling performance of the $\text{S-Co}_3\text{O}_4$ and CoS as anodes, respectively. Although the capacitance retention CoS is a little lower than that of $\text{S-Co}_3\text{O}_4$, more than 85.7% of the capacitance retention after 10000 cycles at a scan rate of 200 mV/s still indicates that CoS is of excellent long cycle life.

To further find the electrochemical reason for the phenomenon that the fully converted CoS can significantly improve capacitance (Figure 3(a)), the electrochemical impedance spectroscopy (EIS) measurements on the Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS electrodes were performed (as shown in Figure 5). It is qualitatively demonstrated that the Nyquist plots of the EIS spectra show a similar semicircle in a high frequency range and a spike in a low frequency range. In a high frequency area, the intercept to the x -axis represents the bulk resistance (R_b), while the semicircle corresponds to the double-layer capacitance and charge-transfer resistance (R_{ct}). The R_b resistances of CoS and $\text{S-Co}_3\text{O}_4$ electrodes are smaller than that of pristine Co_3O_4 electrodes, especially for CoS electrode, indicating the enhanced electrical conductivity and the significantly improved capacitance of CoS electrodes.

5. Conclusion

In summary, high-performance CoS anode was demonstrated on woven carbon fabrics. The electrochemical performances of CoS were enhanced dramatically compared with that of Co_3O_4 and were better than that of $\text{S-Co}_3\text{O}_4$.

FIGURE 3: (a) CV curves collected for CoS and S-Co₃O₄ anodes at a scan rate of 100 mV/s. (b) CV curves collected for CoS anode at various scan rates. (c) Areal capacitance of the CoS anode as a function of the scan rate. (d) Galvanostatic charge-discharge curves of the S-Co₃O₄ and CoS anodes at a current density of 2 mA/cm². (e) Galvanostatic charge-discharge curves of the CoS anodes collected at different current densities. (f) Areal capacitance of the CoS anode collected from galvanostatic charge-discharge curves as a function of current density.

FIGURE 4: Cycling performance of S-Co₃O₄ and CoS anodes collected at a scan rate of 200 mV/s for 10000 cycles.

FIGURE 5: Nyquist plots of the Co_3O_4 , $\text{S-Co}_3\text{O}_4$, and CoS anodes.

Moreover, stable rate capability and cycle capability were also achieved. These encouraging performances have access to its applications in high-performance asymmetric supercapacitors, opening up a novel approach to advancing the performance of energy storage devices.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

The authors acknowledge the financial support from Guangdong Natural Science Funds for Distinguished Young Scholar (no. 2014A030306005), Natural Science Foundation of Guangdong Province, China (Grant no. S2013010012854), Foundation for High-Level Talents in Higher Education of Guangdong Province, China (Yue Cai-Jiao [2013] 246, Jiang Cai-Jiao [2014] 10), Development Program for Outstanding Young Teachers in Guangdong University (Yue Jiaoshi [2014] 108), Innovative Research Team in University of Guangdong (no. 2015KCXTD027), China's Postdoctoral Science Foundation (no. 2013M540744), Natural Science Foundation of Shanxi Province, China (2014JM7265), Degree and Postgraduate Education Reform Project of Wuyi University (no. 30641015), The Innovation Project of Department of Education of Guangdong Province (no. 2014KTSCX131), and The Mobilization Project of Scientific and Technological Equipment (Yue Cai-Jiao [2015] 356).

References

- [1] M. F. El-Kady, V. Strong, S. Dubin, and R. B. Kaner, "Laser scribing of high-performance and flexible graphene-based electrochemical capacitors," *Science*, vol. 335, no. 6074, pp. 1326–1330, 2012.

- [2] S. He and W. Chen, "3D graphene nanomaterials for binder-free supercapacitors: scientific design for enhanced performance," *Nanoscale*, vol. 7, no. 16, pp. 6957–6990, 2015.
- [3] X. Lu, Y. Zeng, M. Yu et al., "Oxygen-deficient hematite nanorods as high-performance and novel negative electrodes for flexible asymmetric supercapacitors," *Advanced Materials*, vol. 26, no. 19, pp. 3148–3155, 2014.
- [4] X. Xia, C. Zhu, J. Luo et al., "Synthesis of free-standing metal sulfide nanoarrays via anion exchange reaction and their electrochemical energy storage application," *Small*, vol. 10, no. 4, pp. 766–773, 2014.
- [5] C. Guan, Z. Zeng, X. Li et al., "Atomic-layer-deposition-assisted formation of carbon nanoflakes on metal oxides and energy storage application," *Small*, vol. 10, no. 2, pp. 300–307, 2014.
- [6] Z. Yu and J. Thomas, "Energy storing electrical cables: integrating energy storage and electrical conduction," *Advanced Materials*, vol. 26, no. 25, pp. 4279–4285, 2014.
- [7] P.-C. Chen, G. Shen, Y. Shi, H. Chen, and C. Zhou, "Preparation and characterization of flexible asymmetric supercapacitors based on transition-metal-oxide nanowire/single-walled carbon nanotube hybrid thin-film electrodes," *ACS Nano*, vol. 4, no. 8, pp. 4403–4411, 2010.
- [8] A. Lewandowski, A. Olejniczak, M. Galinski, and I. Stepniak, "Performance of carbon-carbon supercapacitors based on organic, aqueous and ionic liquid electrolytes," *Journal of Power Sources*, vol. 195, no. 17, pp. 5814–5819, 2010.
- [9] E. Frackowiak, "Carbon materials for supercapacitor application," *Physical Chemistry Chemical Physics*, vol. 9, no. 15, pp. 1774–1780, 2007.
- [10] K.-W. Nam, C.-W. Lee, X.-Q. Yang, B. W. Cho, W.-S. Yoon, and K.-B. Kim, "Electrodeposited manganese oxides on three-dimensional carbon nanotube substrate: supercapacitive behaviour in aqueous and organic electrolytes," *Journal of Power Sources*, vol. 188, no. 1, pp. 323–331, 2009.
- [11] J. Yan, Z. Fan, W. Sun et al., "Advanced asymmetric supercapacitors based on $\text{Ni}(\text{OH})_2$ /graphene and porous graphene electrodes with high energy density," *Advanced Functional Materials*, vol. 22, no. 12, pp. 2632–2641, 2012.
- [12] X. Lu, M. Yu, G. Wang et al., " H-TiO_2 @ MnO_2 // H-TiO_2 @C core-shell nanowires for high performance and flexible asymmetric supercapacitors," *Advanced Materials*, vol. 25, no. 2, pp. 267–272, 2012.
- [13] Z. Fan, J. Yan, T. Wei et al., "Asymmetric supercapacitors based on graphene/ MnO_2 and activated carbon nanofiber electrodes with high power and energy density," *Advanced Functional Materials*, vol. 21, no. 12, pp. 2366–2375, 2011.
- [14] W.-H. Jin, G.-T. Cao, and J.-Y. Sun, "Hybrid supercapacitor based on MnO_2 and columned FeOOH using Li_2SO_4 electrolyte solution," *Journal of Power Sources*, vol. 175, no. 1, pp. 686–691, 2008.
- [15] T. Zhai, X. Lu, Y. Ling et al., "A new benchmark capacitance for supercapacitor anodes by mixed-valence sulfur-doped $\text{V}_6\text{O}_{13-x}$," *Advanced Materials*, vol. 26, no. 33, pp. 5869–5875, 2014.
- [16] J. Xu, Q. Wang, X. Wang et al., "Flexible asymmetric supercapacitors based upon Co_9S_8 nanorod// Co_3O_4 @ RuO_2 nanosheet arrays on carbon cloth," *ACS Nano*, vol. 7, no. 6, pp. 5453–5462, 2013.