Short communication

A Ni₃S₂-PEDOT monolithic electrode for sodium batteries

Chaoqun Shanga,b,1, Shanmu Donga,1, Shengliang Zhanget al.

1. Introduction

Rechargeable Na batteries have attracted tremendous attention because of their low cost and natural abundance of sodium [1,2]. To realize Na technology, a variety of cathodes and electrodes have been explored for Na-storage capability [3–8]. As a promising electrode candidate of sodium batteries, Ni₃S₂ has many advantages including rich in natural resources, low cost, environmental friendly and high theoretical capacity [9–11]. However, the poor conductivity of Ni₃S₂ hampers its potential application [12–14]. To address this issue, designing monolithic electrodes with well electronic conductivity is a promising strategy [15]. One of the most attractive concepts is to directly grow Ni₃S₂ on electroactive substrates as binder-free electrodes [12]. In this design, many competitive benefits such as short ion transport pathways, superior electron transport efficiency and rich accessible electroactive sites are simultaneously achieved to exhibit desirable electrochemical performance [16–18]. On the other hand, the large volume change during discharge and charge caused by the inherent large size of Na ion (35% much larger than Li ions in radius) may lead to rapid capacity fading [19]. This problem can be alleviated if an electroactive polymer layer with good binding compatibility was introduced to protect Ni₃S₂. Therefore, much attention has been paid to Poly(3,4-ethylenedioxythiophene) (PEDOT) because of its high stability, mechanical flexibility and excellent conductivity [20–22].

In this communication, we adopt a facile strategy to design monolithic Ni₃S₂-PEDOT electrode for sodium-ion batteries. Ni₃S₂ is directly grown on Ni foam substrate and the PEDOT protective layer was electrodeposited subsequently. The monolithic Ni₃S₂-PEDOT electrode displays a high reversible specific capacity of 400 mAh g⁻¹ even at 600 mA g⁻¹ and high initial coulombic efficiency.

2. Experimental

2.1. Hydrothermal preparation of Ni₃S₂

All the chemicals are used directly without further purification. In a typical synthesis process, 0.142 g Na₂SO₄ and 0.048 g Na₂S₂O₃ are dissolved into 40 mL deionized water to obtain a transparent solution. The solution is transferred into Teflon stainless steel autoclave with a piece of Ni foam (5 cm × 3 cm) in it. The autoclave is kept in an oven at 150 ℃ for 3 h. After cooled down to room temperature, the Ni foam in the autoclave changes into black that Ni₃S₂ is obtained. This black Ni₃S₂ is washed with deionized water and absolute ethanol for three times, then dried at 120 ℃ in vacuum oven for 8 h. The active Ni₃S₂ is about 1 mg cm⁻² on Ni foam, which is calculated from \( \Delta m = M_{\text{NiS2}} \times \Delta \text{mass} / 2M_{\text{Ni}} \). \( \Delta m \) is the mass difference of Ni foam before and after hydrothermal synthesis (3Ni → Ni₃S₂). The mass is carefully weighed by a microbalance with an accuracy of 0.01 mg.

2.2. Electrodeposition of PEDOT on Ni₃S₂

PEDOT is synthesized at 1 V for 60 s in 40 mL aqueous solution that contained 0.45 g EDOT (3,4-ethylenedioxythiophene), 0.426 g LiClO₄ as well as 1.6 g SDS (sodium dodecyl sulfate), where potentials are measured relative to an Ag/AgCl reference electrode using a Pt foil as a counter electrode and Ni/Ni₃S₂ as a working electrode. After electrodeposition, monolithic Ni₃S₂-PEDOT electrode is finally obtained. PEDOT is
about 0.1 mg cm$^{-2}$ after comparing the mass of electrode before and after electrodeposition, which is about 10% of active Ni$_3$S$_2$.

2.3. Characterization

XRD patterns were recorded with a Bruker-AXS Microdiffractometer (D8 Advance) using Cu Kα radiation ($\lambda = 1.5406 \text{ Å}$) from 5 to 90° at a scanning speed of 3° min$^{-1}$. Morphological information and Energy Dispersive X-ray Spectroscopy (EDX) elemental analysis were attained from field emission scanning electron microscopy (FESEM, HITACHI S-4800).

The sodium coin cells are assembled in an argon filled glove box (<1 ppm H$_2$O and O$_2$) by using the Ni$_3$S$_2$-PEDOT as the active working electrode and sodium pieces as the counter and reference electrode, a glass-fiber and a polypropylene (Celgard 2400) as separators, and 1 M NaClO$_4$ dissolved in EC:DMC (1:1 in volume) with 10% FEC as the electrolyte. Galvanostatic charge–discharge experiments are tested in a LAND battery testing system at a current density of 600 mA g$^{-1}$.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the as-prepared Ni$_3$S$_2$-PEDOT, Ni$_3$S$_2$ and the used Ni foam are illustrated in Fig. 1a. As can be seen, the three strongest diffraction peaks at 44.4°, 51.7° and 76.2° in all patterns are corresponding to (111), (200) and (220) of Ni (JCPDF#44-1418). No other peak suggests the high purity of the Ni$_3$S$_2$ crystalline phase we prepared. Interestingly, where Ni$_3$S$_2$-PEDOT electrodes display high coulombic efficiency of PEDOT protective layers, which is quite different from the morphology of Ni$_3$S$_2$. PEDOT is mostly like nanoflakes (inset of Fig. 1d). This protective layer can be expected to effectively alleviate the structure destruction of Ni$_3$S$_2$ during charge–discharge. According to EDX analysis (as shown in Table 1), the main element was Ni for both Ni$_3$S$_2$ and Ni$_3$S$_2$-PEDOT electrodes owing to the Ni foam substrate. After electrodeposition, the contents of S and O increase because of the formation of PEDOT.

The monolithic Ni$_3$S$_2$-PEDOT on Ni foam is directly explored as an integrated electrode for sodium batteries. Ni$_3$S$_2$ on Ni foam without PEDOT protection is also introduced as a fair comparison. Fig. 2a exhibits the initial five galvanostatic charge–discharge voltage profiles, between 0.5 and 2.8 V, of monolithic Ni$_3$S$_2$ electrode at a current density of 600 mA g$^{-1}$. The discharge profile can be attributed to the reaction of Na$^+$ and Ni$_3$S$_2$. The reversible charge capacity of Ni$_3$S$_2$ is about 78%, which may be caused by the large volume change and irreversible side reactions. On the other hand, Ni$_3$S$_2$ electrode delivers poor cycle stability that there is only 60% capacity retention after five cycles. The effect of PEDOT protective layer to buffer the volume change during Na$^+$ insertion and extraction would probably destroy the integrity of Ni$_3$S$_2$ and Ni substrate, which would further impact the electrochemical performance. In order to protect Ni$_3$S$_2$ electrode, PEDOT is electrodeposited directly on Ni$_3$S$_2$ to form a flexible conductive layer. Fig. 1d displays the morphology of PEDOT protective layers, which is quite different from the morphology of Ni$_3$S$_2$. PEDOT is mostly like nanoflakes (inset of Fig. 1d). After the initial five cycles, between 0.5 and 2.8 V, the PEDOT/SPE electrode delivers a discharge capacity of about 77% of its initial capacity.

The sodium coin cells are assembled in an argon filled glove box (<1 ppm H$_2$O and O$_2$) by using the Ni$_3$S$_2$-PEDOT as the active working electrode and sodium pieces as the counter and reference electrode, a glass-fiber and a polypropylene (Celgard 2400) as separators, and 1 M NaClO$_4$ dissolved in EC:DMC (1:1 in volume) with 10% FEC as the electrolyte. Galvanostatic charge–discharge experiments are tested in a LAND battery testing system at a current density of 600 mA g$^{-1}$.

![Fig. 1.](image-url) (a) XRD patterns of Ni foam, Ni$_3$S$_2$ and Ni$_3$S$_2$-PEDOT. (b) Typical SEM image of Ni foam substrate. (c) Typical SEM image of Ni$_3$S$_2$ obtained from hydrothermal treatment on Ni substrate. (d) Typical SEM image of Ni$_3$S$_2$-PEDOT synthesized by electrodeposition of PEDOT on Ni$_3$S$_2$. 

---

**Table 1.** The main element was Ni for both Ni$_3$S$_2$ and Ni$_3$S$_2$-PEDOT electrodes owing to the Ni foam substrate. After electrodeposition, the contents of S and O increase because of the formation of PEDOT.
The initial charge capacity by cycling between 0.5 and 2 V is only 318.3 mAh g\(^{-1}\) with an irreversible capacity of 140 mAh g\(^{-1}\) and a capacity of 280 mAh g\(^{-1}\) after 30 cycles (Fig. 2f). As illustrated in Fig. 2c, the Ni\(_3\)S\(_2\)–PEDOT electrodes retain over 50\% of the initial discharge specific capacity after 50 cycles, while Ni\(_3\)S\(_2\) electrodes decay to only 6\% of the initial discharge specific capacity. Fig. 2d displays that the monolithic Ni\(_3\)S\(_2\)–PEDOT electrode exhibits a reversible specific capacity of 600, 503, 408 and 310 mAh g\(^{-1}\) at a current density of 150, 300, 600 and 1200 mA g\(^{-1}\), respectively. Particularly, when the current density decreased to 600 mA g\(^{-1}\) after rate cycles, the specific capacity of monolithic Ni\(_3\)S\(_2\)–PEDOT electrode recovers to 400 mAh g\(^{-1}\), indicating a strong potential for rapid Na\(^+\) insertion and extraction.

The cycle performance of Ni\(_3\)S\(_2\) is so poor that the capacity retention is only 6\% as demonstrated in Fig. 2c. As a consequence of Na\(^+\) insertion/deinsertion during cycling, Ni\(_3\)S\(_2\) typically breaks into Ni because it can react with Na to form Na\(_2\)S, leading to large volume expansion and destruction of structure, resulting in severe loss of capacity upon cycling. Stabilizing the interface between Ni\(_3\)S\(_2\) and the electrolyte is therefore essential in improving the cycling performance. The ideal protective layer for Ni\(_3\)S\(_2\) electrode needs to be chemically stable and mechanically strong. High flexibility is also desired to accommodate the volume expansion of Na\(^+\) insertion/deinsertion without structure damage.

| Electrode     | O at\% | S at\% | Ni at\% |
|---------------|--------|--------|---------|
| Ni\(_3\)S\(_2\) | 9.7 ± 0.2 | 32 ± 0.2 | 96.8 ± 0.2 |
| Ni\(_3\)S\(_2\)–PEDOT | 9.7 ± 0.2 | 8.1 ± 0.2 | 82.2 ± 0.2 |

Table 1. Elemental composition of Ni\(_3\)S\(_2\) and Ni\(_3\)S\(_2\)–PEDOT electrodes obtained by EDX analysis.
The monolithic Ni$_3$S$_2$-PEDOT electrode delivers stable performance during cycling without any overcharging behavior, which further indicates the effective protection of PEDOT layer.

Here, we describe a flexible PEDOT coating with the aim of realizing cycle stability. The superior reversibility capacity of monolithic Ni$_3$S$_2$-PEDOT electrodes could be ascribed as follows: (i) Ni$_3$S$_2$ particles are directly grown on Ni foam, which improve the electrical contact between Ni$_3$S$_2$ active materials and Ni foam current collector. (ii) There is enough void space between the particles, which is beneficial to the contact of active materials and electrolyte. (iii) Monolithic design avoids the use of conductive additives and polymer binder and enhances the utilization of active materials. (iv) Ultrathin flexible PEDOT would encapsulate Ni$_3$S$_2$ inside the polymer shells with a buffer void, which maintains the structural integrity of Ni$_3$S$_2$ during charge–discharge process. All the desired functions of each component are efficiently utilized to realize a synergistic effect that monolithic Ni$_3$S$_2$-PEDOT electrodes exhibit desirable cycling stability for sodium-ion batteries.

4. Conclusions

In summary, a facile strategy has been developed to construct Ni$_3$S$_2$-PEDOT monolithic electrodes with stable electrochemical performance for sodium-ion batteries. The PEDOT layer would efficiently protect the Ni$_3$S$_2$ arrays from being wrecked by the severe volume change during charge–discharge process. The as-prepared Ni$_3$S$_2$-PEDOT electrodes display a reversible specific capacity of 400 mAh g$^{-1}$ even at 600 mAh g$^{-1}$ and high initial coulombic efficiency (83.6%). This monolithic design of electrodes presented here will be further investigated for the extension to fabricating other new types of materials in sodium-ion batteries.

Conflict of interest

The authors declare no competing financial interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21271180), the China Postdoctoral Science Foundation (2014M561976), the National Program on Key Basic Research Project of China (973 Program) (No. MOST2011CB935700), the Key Technology Research Projects of Qingdao (No. 13–4–1–10-gx), and the Qingdao Key Lab of Solar Energy Utilization and Energy Storage Technology.

References

[1] M.D. Slater, D. Kim, E. Lee, C.S. Johnson, Sodium-ion batteries, Adv. Funct. Mater. 23 (2013) 947–958.

[2] Y. Kim, K.H. Ha, S.M. Oh, K.T. Lee, High-capacity anode materials for sodium-ion batteries, Chem. Eur. J. 20 (2014) 11980–11992.

[3] C. Zhu, K. Song, P.A. van Aken, J. Maier, Y. Yu, Carbon-coated Na$_3$V$_2$(PO$_4$)$_3$ embedded in porous carbon matrix: an ultrafast Na-storage cathode with the potential of outperforming Li cathodes, Nano Lett. 14 (2014) 2175–2180.

[4] Y. You, X.-L. Wu, Y.-X. Yin, Y.-G. Guo, High-quality Prussian blue crystals as superior cathode materials for room-temperature sodium-ion batteries, Energy Environ. Sci. 7 (2014) 1643–1647.

[5] R. Zhao, L. Zhu, Y. Cao, X. Ai, H.X. Yang, An aniline–nitroaniline copolymer as a high capacity cathode for Na-ion batteries, Electrochem. Commun. 21 (2012) 36–38.

[6] L. Xiao, Y. Cao, J. Xiao, W. Wang, I. Kovalsk, Z. Nie, J. Liu, High capacity, reversible alloying reactions in SnSb/C nanocomposites for Na-ion battery applications, Chem. Commun. 48 (2012) 3321–3323.

[7] L. Fei, Y. Jiang, Y. Xu, G. Chen, Y. Li, X. Xu, S. Deng, H. Luo, A novel solvent-free thermal reaction of ferrocene and sulfur for one-step synthesis of iron sulfide and carbon nanocomposites and their electrochemical performance, J. Power Sources 265 (2014) 1–5.

[8] X. Rui, H. Tan, Q. Yan, Nanostructured metal sulfides for energy storage, Nano energy 6 (2014) 9899–9924.

[9] J.-S. Kim, S.-W. Lee, X. Liu, G.-B. Cho, K.-W. Kim, I.-S. Ahn, J.-H. Ahn, G. Wang, H.-J. Ahn, Electrochemical properties of Na$_3$Ni$_2$S$_2$ cells with liquid electrolytes using various sodium salts, Curr. Appl. Phys. 11 (2011) 511–514.

[10] J.-S. Kim, H.-J. Ahn, H.-S. Ryu, D.-J. Kim, G.-B. Cho, K.-W. Kim, T.-H. Nam, J.H. Ahn, The discharge properties of Na$_3$Ni$_2$S$_2$ cell at ambient temperature, J. Power Sources 178 (2008) 852–856.

[11] H.-S. Ryu, J.-S. Kim, K. Park, J.-Y. Park, G.-B. Cho, X. Liu, I.-S. Ahn, K.-W. Kim, J.-H. Ahn, J.-P. Ahn, S.W. Martin, G. Wang, H.-J. Ahn, Degradation mechanism of room temperature Na$_3$Ni$_2$S$_2$ cells using Ni$_3$S$_2$ electrodes prepared by mechanical alloying, J. Power Sources 244 (2013) 764–770.

[12] D. Li, X. Li, X. Hou, X. Sun, B. Liu, D. He, Building a Ni$_3$S$_2$ nanotube array and investigating its application as an electrode for lithium ion batteries, Chem. Commun. 50 (2014) 9361–9364.

[13] J.-S. Kim, C.-B. Cho, K.-W. Kim, J.-H. Ahn, G. Wang, H.-J. Ahn, The addition of iron to Ni$_3$S$_2$ electrode for sodium secondary battery, Curr. Appl. Phys. 11 (2011) 5215–5218.

[14] J. Yang, W. Guo, D. Li, C. Wei, H. Fan, L. Wu, W. Zheng, Synthesis and electrochemical performances of novel hierarchical flower-like nickel sulfide with tunable number of composed nanoparticles, J. Power Sources 268 (2014) 113–120.

[15] J. Wang, D. Chao, J. Liu, L. Li, L. Lai, J. Lin, Z. Shen, Ni$_3$S$_2$@MoS$_2$ core–shell nanorod arrays on Ni foam for high-performance electrochemical energy storage. Nano Energy 7 (2014) 151–160.

[16] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan, X.W. Lou, Recent advances in metal oxide-based electrode architecture design for electrochemical energy storage, Adv. Mater. 24 (2012) 5166–5180.

[17] C. Yuan, J. Li, L. Hou, X. Zhang, L. Shen, X.W.D. Lou, Ultrathin mesoporous NiCo$_2$O$_4$ nanosheets supported on Ni foam as advanced electrodes for supercapacitors, Adv. Funct. Mater. 22 (2012) 4592–4597.

[18] L. Yu, G. Zhang, C. Yuan, X.W. Lou, Hierarchical NiCo$_2$O$_4$@MoO$_3$ core–shell heterostructured nanowire arrays on Ni foam as high-performance supercapacitor electrodes, Chem. Commun. 49 (2013) 137–139.

[19] J. Qian, Y. Xiong, Y. Cao, X. Ai, H. Yang, Synergistic Na–storage reactions in SnP$_2$, as a high-capacity, cycle-stable anode of Na-ion batteries, Nano Lett. 14 (2014) 1865–1869.

[20] R. Liu, S.B. Lee, MoO$_3$-Poly(3,4-ethylendioxypthiophene) coaxial nanowires by one-step coelectrodeposition for electrochemical energy storage, J. Am. Chem. Soc. 130 (2008) 2942–2943.

[21] X.Y. Zhang, J.S. Lee, G.S. Lee, D.K. Cha, M.J. Kim, D.J. Yang, S.K. Manohar, Chemical synthesis of PEDOT nanotubes, Macromolecules 39 (2006) 470–472.

[22] M. Culebras, C.M. Gómez, A. Cantarero, Enhanced thermoelectric performance of PEDOT with different counter-ions optimized by chemical reduction, J. Mater. Chem. A 2 (2014) 10109–10115.