A superior cathode of sodium-ion battery: A V$_2$O$_5$ nanosheets anchored on carbon nanofibers

Shuang Tian, Tonghui Cai, Dandan Wang, Dongqing Kong, Hao Ren, Wei Xing*

State Key Laboratory of Heavy Oil Processing, School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, 266580, P.R. China.

*Corresponding author e-mail: xingwei@upc.edu.cn

Abstract. Vanadium pentoxide (V$_2$O$_5$) as the cathode material has caused great concern in metal-ion batteries due to the diverse valence states of vanadium. However, structural instability and poor electrical and ionic conductivity significantly limit its application as high-efficiency electrodes. Herein, V$_2$O$_5$ nanosheet is directly grown on electrospun carbon nanofibers (V$_2$O$_5$@CNFs) by a hydrothermal method as a cathode for sodium-ion batteries. The carbon fiber skeleton can improve not only the conductivity but also buffer the volume variations of the electrodes. As the cathode of NIBs, the as-prepared V$_2$O$_5$@CNFs exhibits an excellent capacity of 178 mAh g$^{-1}$ at 25 mA g$^{-1}$ and 60 mAh g$^{-1}$ at 1000 mA g$^{-1}$.

1. Introduction

Lithium-ion batteries (LIBs) are the most widely used energy storage devices in portable electronic products and electric vehicles[1]. However, due to the small reserves and uneven geographical distribution of lithium, alternative alkali metal-ion batteries such as Na$^+$ and K$^+$ with the merit of low cost, richness, and distribution throughout the world are placed high expectations. As an emerging technology, sodium-ion batteries (SIBs) has been limited in its development due to the lack of high-performance electrode materials[2]. Many of cathode candidates have been applied in SIBs, such as layered transition metal oxides, metal phosphates, and analogs of Prussian blue[3]. Among them, vanadium pentoxide (V$_2$O$_5$) is considered to be the most promising material due to its outstanding performance in SIBs. As one of the most promising candidates, V$_2$O$_5$ has the advantages of low cost, sufficient reserves, facile synthesis, and a variety of stable oxidation states (V$^{2+}$ to V$^{5+}$).

Furthermore, it is recognized that the electrochemical properties of V$_2$O$_5$ strongly depend on various factors such as preparation condition, morphology, particle size, and measurement techniques. To date, multiple V$_2$O$_5$-based nanostructured electrodes, such as nanocrystals[4], nanoribbons[5], nanowires[6], nanoparticles[7], and nanocomposites[8], have been reported. Recently, Zhou et al. reported that a sponge-like V$_2$O$_5$ nanomaterial exhibits a high capacity of 216 mAh g$^{-1}$ at a current density of 20 mA g$^{-1}$ in SIBs[9]. However, the insertion/extraction of Na$^+$ during the charging and discharging process causes the collapse of the V$_2$O$_5$ layered structure. To solve these challenge, a variety of strategies have been proposed to enhance the electrochemical performance of V$_2$O$_5$ in SIBs, such as reducing the size of V$_2$O$_5$ to nanoscale and coating it on conductive substrates[10].
Herein, we synthesized $\text{V}_2\text{O}_5$ nanosheets on the surface of electrospun carbon nanofibers (CNFs). The as-prepared $\text{V}_2\text{O}_5$@CNFs exhibit a high reversible capacity of 178 mAh g$^{-1}$ at a current density of 25 mA g$^{-1}$ and a reversible capacity of 60 mAh g$^{-1}$ at a high current density of 1000 mA g$^{-1}$. The excellent electrochemical properties of $\text{V}_2\text{O}_5$@CNF mainly attribute to the help of CNFs, which could not only increase the electronic conductivity but also buffer the volume variations of the electrodes.

2. Experiment section

2.1. Materials
Polyacrylonitrile (PAN, Mw=150000) was obtained from Sigma-Aldrich Co., Ltd. N, N-dimethylformamide (DMF, 99.5%) and isopropanol alcohol (IPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Vanadium oxytriisopropoxide (VOT) was acquired from Aladdin Biochemical Technology Co., Ltd. All the chemical reagents were analytical grade and without further purification.

2.2. Synthesis the $\text{V}_2\text{O}_5$ and $\text{V}_2\text{O}_5$@CNF composites
The carbon nanofiber (CNFs) membrane was prepared through a pyrolytic decomposition PAN[11]. The $\text{V}_2\text{O}_5$@CNFs composites were synthesized using a simple hydrothermal technique. In a typical synthesis, 0.2 mL of vanadium oxytriisopropoxide (VOT) was added to 30 mL of isopropanol alcohol (IPA). After stirring 30 min, the prepared homogeneous solution and a piece of CNF substrate (2.5 cm $\times$ 4.5 cm) were transferred into a 50 mL Teflon-lined autoclave, which was heated and maintained at 200 °C for 18 h. Then, the substrate was picked out and washed by ethanol to remove surface impurities. Finally, the $\text{V}_2\text{O}_5$@CNFs composites were obtained by annealing the as-prepared precursors in the air at 320 °C for 1 h with a heating rate of 2 °C min$^{-1}$. The pure $\text{V}_2\text{O}_5$ powder was also prepared by a similar method without the CNFs.

2.3. Materials characterization
The morphologies of samples were examined by a field emission scanning electron microscope (FESEM, HITACHI, SU8010), transmission electron microscopy (TEM, FEI, Tecnai G2 20 S-TWIN). The crystalline nature of as-prepared samples was determined using X-ray diffraction patterns (XRD, Bruker, D8 Advance diffraction with Cu Ka radiation) and Raman scattering spectra (Horiba, LabRam HR spectrometer).

2.4. Electrochemical measurements
The $\text{V}_2\text{O}_5$@CNFs electrodes were prepared by directly cutting the binder-free electrode into identical pieces with 0.8×0.8 cm$^2$. The density of all electrodes is controlled about 1 mg cm$^{-2}$. All the half-cells were assembled in an argon glove box (H$_2$O and O$_2$ < 0.1 ppm, Mbraun, Unilab). Na foil was used as the counter anode and 1 M NaClO$_4$ in PC was used as the electrolyte. The sodium-ion cells used the Whatman GF/C glass fiber as the separator. Galvanostatic charge/discharge tests were performed with a battery testing system (Land CT2001A). Cyclic voltammetry was carried out on an electrochemical workstation (IVIUM technology, Netherlands) at room temperature.
3. Results and discussion

Fig. 1 (a) and (b) SEM images of CNFs. (c) SEM images of \( \text{V}_2\text{O}_5 \)@CNFs. (d) Optical image of the binder-free \( \text{V}_2\text{O}_5 \)@CNFs.

The surface morphologies of the samples were examined by scanning electron microscopy (SEM). Highly uniform electrospun CNFs with a smooth surface and average diameter of about 200 nm were prepared after electrospinning and carbonization (Fig. 1a and b). After the hydrothermal process, a large amount of \( \text{V}_2\text{O}_5 \) nanosheets were coating uniformly on the CNFs (Fig. 1c). The diameter of the \( \text{V}_2\text{O}_5 \)@CNFs fibers was about 600 nm. Besides, the as-prepared \( \text{V}_2\text{O}_5 \)@CNFs electrode is free-standing, which can be used directly as an electrode for SIBs (Fig. 1d).

Fig. 2 (a) and (b) TEM images of \( \text{V}_2\text{O}_5 \)@CNFs.

Fig. 3 (a) XRD pattern and (b) Raman spectra of \( \text{V}_2\text{O}_5 \)@CNFs.
The transmission electron microscopy (TEM) was used to investigate the morphology of V$_2$O$_5$@CNFs further. As shown in Fig. 2a, the sheet-like structure of V$_2$O$_5$ were uniformly grown on the CNFs to form a core-shell architecture. The CNFs still retained the original structure after hydrothermal and annealing treatment, indicating the excellent stability of V$_2$O$_5$@CNFs. The magnified view of the junction of V$_2$O$_5$@CNFs further demonstrated that V$_2$O$_5$ grew tightly on the surface of CNFs rather than simply stack (Fig. 2b). It is worth noting that a large number of micropores were distributed throughout the whole surface of V$_2$O$_5$ nanosheets, which could be ascribed to the release of gas during annealing treatment.

The phase and crystal structures of V$_2$O$_5$ and V$_2$O$_5$@CNFs were characterized by X-ray powder diffraction (XRD) analysis and Raman spectroscopy. As shown in Fig. 3a, the XRD pattern of the V$_2$O$_5$@CNFs could be perfectly matched with orthorhombic V$_2$O$_5$ (JCPDS card no.41-1426, [12], and shown sharp diffraction peaks, indicating a highly crystalline nature. In addition, there are no diffraction peaks of CNFs observed in the XRD pattern of the V$_2$O$_5$@CNFs, confirming the CNFs are entirely covered by V$_2$O$_5$ sheets. The Raman spectrum of V$_2$O$_5$@CNFs composite was shown in Fig. 3b. The V$_2$O$_5$@CNFs displays the characteristic peaks at 142, 190, 282, 303, 407, 523, 700, and 993 cm$^{-1}$. The typical vibrations are observed at 142, and 190 cm$^{-1}$ correspond to the V-O-V stretching modes. The skeleton bent vibrations of V=O are observed at 282 and 407 cm$^{-1}$. And, the 303 and 523 cm$^{-1}$ are characteristic vibrations of V$_3$-O stretching modes. The stretching vibration of V-O-V is observed at 483 cm$^{-1}$. The peaks at 700 and 997 cm$^{-1}$ are attributed to the bending vibrations of V$_2$-O and V$_2$=O bonds, respectively [13], [14]. Also, the Raman spectra of the V$_2$O$_5$@CNFs also exhibit a D-band (defect-induced band, 1343 cm$^{-1}$) and a G-band (in-plane vibrational band), which confirms the presence of CNFs in V$_2$O$_5$@CNF composites[15].

![Fig. 4](image_url)

**Fig. 4** (a) CV curves of V$_2$O$_5$@CNFs at a scan rate of 0.1 mV s$^{-1}$. (b) The first three galvanostatic discharge-charge curves of V$_2$O$_5$@CNF at a current density of 25 mA g$^{-1}$. (c) Rate performance of two different electrodes at various densities. (d) The cycling performance of two different electrodes at 25 mA g$^{-1}$.

The electrochemical performance of V$_2$O$_5$@CNFs electrode was tested by cyclic voltammetry (CV) in the voltage range of 1 to 4 V at a scan rate of 0.1 mV s$^{-1}$. As shown in Fig. 4a, there are two redox couples at 1.25/2.0 V and 1.85/2.75 V during the first CV curve. The redox couple at 1.25/2.0 V can be ascribed to the formation of the solid electrolyzed interface (SEI). At the same time, the other redox couple at 1.85/2.75 V is attributed to the insertion/extraction process of Na$^+$ ion in V$_2$O$_5$. 

The excellent reversibility of the V$_2$O$_5$@CNFs electrode was highlighted, as the first three charge and discharge curves of the V$_2$O$_5$@CNFs electrode at a current density of 25 mA g$^{-1}$ are shown in Fig. 4b. The discharge and charge capacity is 348.7 mAh g$^{-1}$ and 205 mAh g$^{-1}$ during the first cycle, respectively, corresponding to a Coulombic efficiency of 58.9%. To better evaluate the electrochemical performance of the V$_2$O$_5$@CNFs electrode, we tested the rate performance of the V$_2$O$_5$@CNFs and V$_2$O$_5$ electrodes (Fig. 4c). As expected, the V$_2$O$_5$@CNFs electrode exhibits an excellent reversible capacity of 178 mAh g$^{-1}$ at 25 mA g$^{-1}$, while the reversible capacity of the V$_2$O$_5$ electrode is only 101 mAh g$^{-1}$. Furthermore, the reversible capacity of the V$_2$O$_5$@CNFs electrode is 60 mAh g$^{-1}$ at 1000 mA g$^{-1}$, while the capacity of the V$_2$O$_5$ electrode is almost zero (just 1.8 mAh g$^{-1}$) at a current density of 500 mA g$^{-1}$. When the current density returns to 25 mA g$^{-1}$, the capacity of the V$_2$O$_5$@CNFs electrode can be maintained as high as 146 mAh g$^{-1}$, which fully demonstrates the good rate performance of V$_2$O$_5$@CNFs. The cycle performance of the two samples was carried out at a current density of 25 mA g$^{-1}$ and is presented in Fig. 4d. The initial capacities of the V$_2$O$_5$@CNF electrode and the V$_2$O$_5$ electrode were 200 mAh g$^{-1}$ and 95 mAh g$^{-1}$, respectively. However, after 50 cycles, the capacity of the V$_2$O$_5$@CNF electrode remained to 110 mAh g$^{-1}$, while the V$_2$O$_5$ electrode only had a capacity of 40 mAh g$^{-1}$. In our view, the excellent electrochemical performance of the V$_2$O$_5$@CNF electrode should be attributed to its unique structure. The presence of CNFs is sufficient to provide many active sites for Na$^+$, enable more Na$^+$ insertion with V$_2$O$_5$ nanosheets. On the other hand, the good electrical conductivity of the binder-free CNFs is beneficial for the fast transmission of the electron[12]. In this way, even at high rate continuous cycles, the V$_2$O$_5$@CNF electrode can still show good electrochemical performance.

4. Conclusion

In summary, the binder-free V$_2$O$_5$@CNFs was prepared by electrospinning and hydrothermal method for sodium-ion batteries. The prepared V$_2$O$_5$@CNFs composite delivers an excellent electrochemical performance due to its unique structure and the existent of CNF, which is sufficient to provide many active sites for Na$^+$ and beneficial for the fast transmission of the electron.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NSFC 51877216), Taishan Scholar Foundation (tsqn20161017), Major Program of Shandong Province Natural Science Foundation (ZR201801280009), Fundamental Research Funds for the Central Universities (18CX05007A, 19CX05001A, 19CX05002A).

References

[1] R. Córdoba, A. Kuhn, J.C. Pérez-Flores, E. Morán, J.M. Gallardo-Amores, F. García-Alvarado, Journal of Power Sources 422 (2019) 42-48.
[2] A. Tolosa, S. Fleischmann, I. Grobelsek, V. Presser, ACS Applied Energy Materials 1 (2018) 3790-3801.
[3] Y. Lu, L. Wang, J. Cheng, J.B. Goodenough, Chem Commun (Camb) 48 (2012) 6544-6546.
[4] M. Li, G. Sun, P. Yin, C. Ruan, K. Ai, ACS applied materials & interfaces 5 (2013) 11462-11470.
[5] Q. Qu, Y. Zhu, X. Gao, Y. Wu, Advanced Energy Materials 2 (2012) 950-955.
[6] V.A. Zheng Chen, Xilai Jia, Qiangfeng Xiao, Bruce Dunn, and Yunfeng Lu†, ACS nano (2012).
[7] C.Y. Foo, A. Sumboja, D.J.H. Tan, J. Wang, P.S. Lee, Advanced Energy Materials 4 (2014) 1400236.
[8] P. Vishnuprakash, C. Nithya, M. Premalatha, Electrochimica Acta 309 (2019) 234-241.
[9] K. Zhu, C. Zhang, S. Guo, H. Yu, K. Liao, G. Chen, Y. Wei, H. Zhou, ChemElectroChem 2 (2015) 1660-1664.
[10] D. Chao, X. Xia, J. Liu, Z. Fan, C.F. Ng, J. Lin, H. Zhang, Z.X. Shen, H.J. Fan, Adv Mater 26 (2014) 5794-5800.
[11] Q. Jiang, X. Pang, S. Geng, Y. Zhao, X. Wang, H. Qin, B. Liu, J. Zhou, T. Zhou, Applied
Surface Science 479 (2019) 128-136.

[12] X. Zhang, X. Liu, C. Yang, N. Li, T. Ji, K. Yan, B. Zhu, J. Yin, J. Zhao, Y. Li, Surface and Coatings Technology 358 (2019) 661-666.

[13] T. Kim, J. Shin, T.-S. You, H. Lee, J. Kim, Electrochimica Acta 164 (2015) 227-234.

[14] Y. Guo, J. Li, M. Chen, G. Gao, Journal of Power Sources 273 (2015) 804-809.

[15] Y. Xu, C. Zhang, M. Zhou, Q. Fu, C. Zhao, M. Wu, Y. Lei, Nature communications 9 (2018) 1720.

[16] D.W. Su, S.X. Dou, G.X. Wang, Journal of Materials Chemistry A 2 (2014) 11185.