Journal of Power Sources 362 (2017) 147–159

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Core/shell nanostructured $Na_3V_2(PO_4)_3/C/TiO_2$ composite nanofibers as a stable anode for sodium-ion batteries

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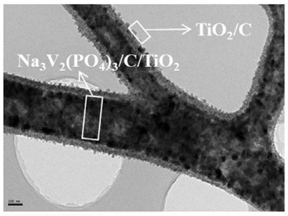
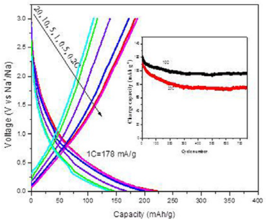
HIGHLIGHTS

- $Na_3V_2(PO_4)_3/C/TiO_2$ ($NVP/C/TiO_2$) nanofibers are prepared by coaxial electrospinning.
- The nanofibers are made of fibrous $Na_3V_2(PO_4)_3/C$ core and TiO_2/C nanoparticles shell.
- $NVP/C/TiO_2$ is of better electrochemical performance than NVP/C and TiO_2/C nanofibers.
- Even at a rate of 20C, $NVP/C/TiO_2$ is of high charge capacity and better cyclability.

GRAPHICAL ABSTRACT





ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form
6 June 2017
Accepted 2 July 2017

Keywords:
Core-shell
Sodium vanadium phosphate
Sodium-ion batteries anode
Coaxial electrospinning
Capacitive capacity

ABSTRACT

$Na_3V_2(PO_4)_3/C/TiO_2$ ($NVP/C/TiO_2$) composite nanofibers with core/shell nanostructure are prepared by coaxial electrospinning plus heat treatment method. The physical and electrochemical performances of $NVP/C/TiO_2$ nanofibers are investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and electrochemical tests. The results show that the composite nanofibers are made of TiO_2/C nanoparticles shell and $Na_3V_2(PO_4)_3/C$ nanofibers core with embedded TiO_2/C nanoparticles. $NVP/C/TiO_2$ nanofibers exhibit much better electrochemical performance than both TiO_2/C and $Na_3V_2(PO_4)_3/C$ nanofibers prepared by coaxial electrospinning method. The core-shelled $NVP/C/TiO_2$ nanofibers delivere a reversible capacity of 196.1 mAh g^{-1} at 0.2C (35.6 mA g^{-1}) in the voltage of 0.01 −3.0 V (*vs.*Na^+/Na), which is higher than the theoretical capacity of 178 mAh g^{-1} for $Na_3V_2(PO_4)_3$ and that of TiO_2/C composite. $NVP/C/TiO_2$ also displays excellent cycle stability and rate capability. Even at a high rate of 20C, it can still release a high reversible charge capacity of 109 mAh g^{-1} and retain a capacity of more than 70 mAh g^{-1} after 1500 cycles. The special microstructure and synergetic effects of $Na_3V_2(PO_4)_3$, conductive carbon and ultrafine TiO_2 are responsible for the excellent electrochemical

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http://dx.doi.org/10.1016/j.jpowsour.2017.07.004
0378-7753/

performance. This facile strategy exhibits superiority in fabricating core-shell nanostructured composite nanofibers as promising electrode materials for energy storage devices.

1. Introduction

Sodium-ion battery, a rechargeable battery with similar mechanism of energy storage and conversion to lithium-ion battery, has recently been recognized as a promising alternative to lithium-ion battery in large scale applications because sodium resources are much more abundant and more inexpensive than lithium resources [1,2]. However, compared with smaller Li^+ ($r = 0.068\ nm$), Na^+ ($r = 0.097\ nm$) plays negative impacts on electrochemical reaction kinetics and may lead to moderate electrochemical performance of sodium-ion batteries. Therefore, it is crucial to search for host materials with large channels and stable frameworks for Na^+ rapid and repeated transport. However, polyanion compounds with large channels, stable structures and excellent thermal stability have been rarely reported as anode materials because of their high potentials. Recently the intensively studied anode materials for sodium-ion batteries include oxides [3–6], sulfides [7–10], metals [11–14], alloys [15,16] and organic compounds [17,18]. Among the above-mentioned materials, oxides are the most widely investigated anodes for sodium-ion batteries and TiO_2 is a typical oxide in the previous reports [19–24]. Theoretically, TiO_2 can deliver capacity of about 335 mAh g^{-1}, unfortunately the capacity of TiO_2 was much lower than 200 mAh g^{-1} in the previous reports.

Unexpectedly, it was reported in 2015 that $Na_3V_2(PO_4)_3$ was used as an anode material and exhibited low discharge voltage plateau about 0.3 V and high capacity in the voltage range of 3.0–0 V [25,26]. $Na_3V_2(PO_4)_3$ (NVP) possesses a NASICON (Na super ionic conductor) structure and this three-dimensional network structure facilitates fast Na^+ diffusion, possibly resulting in better cyclability and rate capability. However, its theoretical capacity is only 178 mAh g^{-1} on the basis of assumption that 3 mol of sodium ions can be reversibly inserted into per mole of $Na_3V_2(PO_4)_3$. In view of high theoretical capacity of TiO_2 and better cyclability and rate capability of $Na_3V_2(PO_4)_3$, nanocomposites of TiO_2 and $Na_3V_2(PO_4)_3$ are expected to display much better electrochemical performance due to synergistic effects. It was reported that $Na_3V_2(PO_4)_3$/C nanofibers and TiO_2/C nanofibers exhibit better electrochemical performance than conventional $Na_3V_2(PO_4)_3$/C and TiO_2/C nanocomposites [27,28], respectively, so construction of core-shelled composite nanofibers containing $Na_3V_2(PO_4)_3$, carbon and TiO_2 may be a better strategy to optimize electrochemical performance of $Na_3V_2(PO_4)_3/TiO_2$ composites. While coaxial electrospinning method is a better way to prepare core-shell nanofibers electroactive materials with high surface area and consequently better electrochemical performance. However, to our best knowledge, composite anode material of $Na_3V_2(PO_4)_3$ and TiO_2 has not been reported up to now.

In this work, core-shelled composite nanofibers of $Na_3V_2(PO_4)_3$, carbon and TiO_2 (NVP/C/TiO_2) were prepared by a coaxial electrospinning method and following heat treatment, and the composite nanofibers exhibited high capacity, better cyclability and rate capability in the voltage range of 3.0–0.01 V (vs Na^+/Na). In addition, the control samples of TiO_2/C composite nanofibers and $Na_3V_2(PO_4)_3$/C (NVP/C) composite nanofibers were also prepared by the similar coaxial electrospinning method, and comparisons of physical and electrochemical of NVP/C/TiO_2, TiO_2/C and NVP/C composite nanofibers were carried out.

2. Experimental

Nanofibrous composite of $Na_3V_2(PO_4)_3$, carbon and TiO_2 was prepared by calcination of electrospun precursor fibers in inert gas atmosphere. The precursor fibers were prepared by a coaxial electrospinning method and the typical procedure was as follows: 4.2 mmol NH_4VO_3, 6.3 mmol NaH_2PO_4 and 4.2 mmol citric acid were dissolved in 10 mL hot distilled water. Then the resulted solution was added to 20 mL 15 wt% poly (4-vinyl) pyridine (PVP) (Alfa Aesar, $M_w = 1{,}300{,}000$) aqueous solution and stirred for 2 h to obtain sheath solution. The core solution consisted of 5 mL tetrabutyl titanate and 10 mL paraffin oil. Both two electrospinning solutions were loaded into a plastic syringe equipped with inner and outer nozzles, and ejection rate of sheath and core solutions was 0.2 and 0.3 mL/h, respectively. The applied voltage was 20 kV, and the distance between coaxial nozzles and steel collector was 15 cm. The precursor fibers were collected, dried at 90 °C for 12 h under vacuum, calcined at 150 °C for 4 h at a ramp rate of 1 °C min^{-1}, sintered at 850 °C for 8 h in nitrogen atmosphere at a ramp rate of 2 °C min^{-1}, and cooled to room temperature to obtain the final nanofibrous product. The product was black due to the expected residual carbon and denoted as NVP/C/TiO_2. The control TiO_2/C and $Na_3V_2(PO_4)_3$/C (NVP/C) composite nanofibers were also prepared by a coaxial electrospinning method. The preparation of TiO_2/C composite nanofibers is similar to that of NVP/C/TiO_2, but the sheath solution comprises 20 mL aqueous solution containing 3 g PVP and 4.2 mmol citric acid. While sheath solution for the control $Na_3V_2(PO_4)_3$/C composite is the same as the sheath solution of the preparation of NVP/C/TiO_2 composite nanofibers, and core solution contains 15 mL paraffin oil. It is noted that preparation of the above-mentioned three samples was carried out by the same electrospinning and heat treatment conditions.

The phase identification of composite nanofibers was performed by a D/Max III X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 0.15418$ nm). The carbon content of the composite was determined by a carbon-sulfur analyzer (Mlti EA2000). Microstructure of the composite was investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2100F). N_2 adsorption/desorption measurement for the composite nanofibers was performed by a Nova Station B (Quantachrome). The specific surface area was determined using the Brumauer-Emmett-Teller (BET) method and the pore diameter was obtained from the adsorption branch based on Barrett-Joyner-Halenda (BJH) method. Electronic conductivity measurements were carried out on compacted pellets of the above-mentioned composite nanofibers by using four-probe conductivity technique. X-ray photoelectron spectra (XPS) of nanofibers samples were recorded by PHI5700 with monochromatic Al Ka radiation, and the C1s line ascribable to the adventitious carbon located at 284.6 eV was used as a reference to determine the binding energy values.

The electrochemical tests of the composite were carried out using coin cells. In all cells, sodium foil served as counter electrode or both counter and reference electrodes, NVP/C/TiO_2, TiO_2/C and NVP/C electrodes were respectively used as working electrodes, and the electrolyte was 1 mol L^{-1} $NaClO_4$ in mixed solvents of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 by