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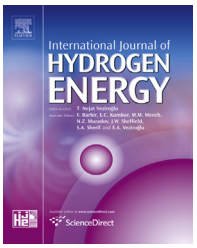

Controllable-multichannel carbon nanofibers-based amorphous vanadium as binder-free and conductive-free electrode materials for supercapacitor

Guofang Huang, Chunping Li, Jie Bai, Xingwei Sun, Haiou Liang*

Chemical Engineering College, Inner Mongolia University of Technology, Huhhote, 010051, People's Republic of China

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ABSTRACT

Multichannel carbon nanofibers-based amorphous vanadium (VMCNFs) was fabricated via electrospinning technology and calcination process. The amorphous V_2O_5 were homogeneous dispersed in the carbon nanofibers with inner hollow channels. One-dimensional structure nanomaterials with a compound inner fistulous pore construction promote the electrochemical property due to the synergistic effect between the hollow inner channels and carbon nanofibers with amorphous vanadium. With changing the addition amount of PS acting as a porogen, the optimized VMCNFs-0.5, in which the molar ratio of $VO(acac)_2$/styrene monomer (SM) was 0.5, exhibited a high specific capacitance of 739 F g^{-1} at 0.5 A g^{-1} and good cycling performance with 80.3% capacitance retention after 1500 cycles. Thus this novel method can provide an acceptable idea for practical applications in energy storage.

Introduction

The global pollution and energy resource shortages have accelerated the progress of the energy systems, including fuel cells, lithium-ion batteries and supercapacitors [1–5]. Among these energy systems, supercapacitors are potential energy storage alternative due to their performance of high power density, short charging time, long cycle stability and simple energy-storage mechanism [5–7]. Therefore, many different electrode materials have been researched for use in capacitors, including metal oxides and metal hydroxides [8,9]. Nevertheless, the capacitive property of each category is influenced by the size, morphology and electrode preparation methods [10].

Metal oxides are another promising candidate for high performance supercapacitor electrode material due to their high melting point [11]. Among them, vanadium oxides (V_xO_y) have attracted considerable attention owing to high specific capacitance and good electrical conductivity [11]. Li and co-workers synthesized tow-dimensional V_2O_5 stacks, which exhibited specific capacitance of 76 F g^{-1} [12]. Chen and co-workers prepared carbon nanotube/V_2O_5 (300 F g^{-1}) nanowire-type nanocomposites, in which the CNTs and V_2O_5 nanowires were intimately intertwined into a hierarchically porous

* *Corresponding author*. Fax: +86 471 6575722.
E-mail address: hgcp_li@126.com (C. Li).

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structure, thus enabling the electrolyte to contact with electrochemical active materials [13].

In addition, it could be found that nanomaterials applied to the electrode could enhance the capacitance of supercapacitors. One-dimensional (1D) nanostructured electrically conductive materials are alternatives for electrode materials because of their simple design and fast charge transportation network [14–23]. The 1D materials exhibit excellent cycle performance, good electrical conductivity, high surface area and long service life [22,24]. Among the 1D material, carbon-based forms, including carbon nanofibers (CNFs) and carbon nanotubes (CNTs), all conform to the above features and offer several beneficial features. The 1D structure facilitates electron transport along the longitudinal direction and the 1D hollow inner-pore structure increases transmission rate with the electrolyte because of the intrinsic large surface to volume [25–28]. So the 1D structure with a more inner hollow pore might promote the transport of ion between the electrode and electrolyte [29].

The vanadium doped carbon nanofibers obtained at carbonization temperature of 500 °C (VCNF-500) exhibited the highest specific capacitance of 606 F g^{-1} among a series of samples which were annealed at different carbonization temperature (400 °C, 500 °C, 600 °C, 700 °C and 800 °C). In this paper, on the basis of previous experimental results, multichannel carbon nanofibers-based amorphous vanadium (VMCNFs) was prepared by electrospinning technique and high-temperature calcination process, in which the carbonization temperature was 500 °C. The amount of the inner channels in the composite nanofibers was controlled by adjusting the molar ratio of polystyrene (PS). The molar ratio among the $VO(acac)_2$/SM/AN ranged from 1/0.25/10 to 1/2/10, including 1/0.5/10, 1/0.75/10 and1/1/10, and the as-prepared samples were named VMCNFs-0.25, VMCNFs-0.5, VMCNFs-0.75, VMCNFs-1 and VMCNFs-2, respectively. Then the composite samples were directly applied to electrode material without the introduction of binder and conductive. A series of electrochemistry tests were carried out to demonstrate the electrochemical performance of composite.

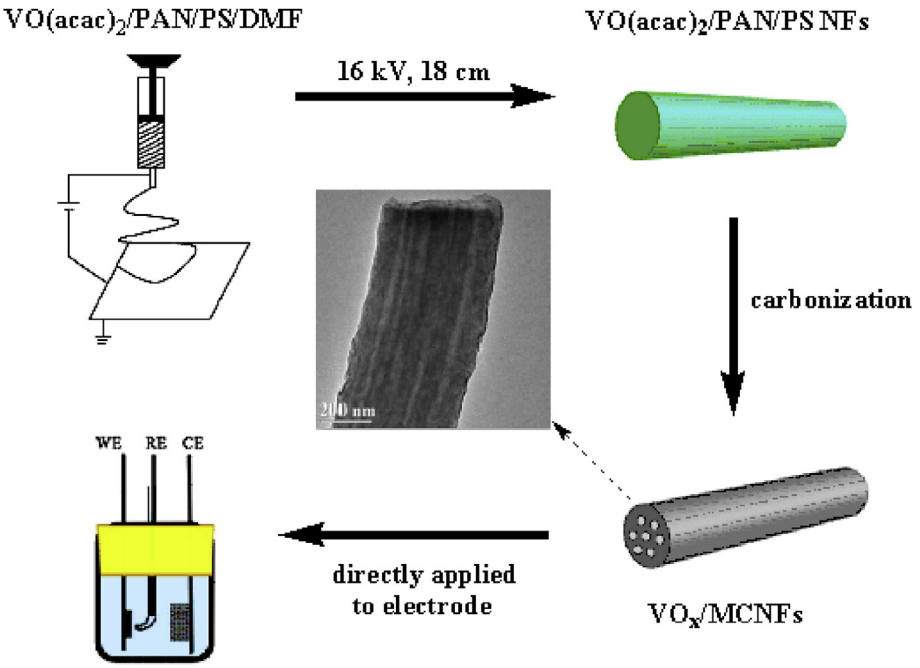
Experimental

Materials

Polyacrylonitrile (PAN, M_w = 80, 000) was provided by Kunshan Hongyu Plastics Co., Ltd. Polystyrene (PS, M_w = 110, 000) was purchased from Xindahui Chemical Company in Tianjin. N, N-Dimethyformamide (DMF, AR, 99.5%) was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Vanadly acetylacetonate ($VO(acac)_2$, GR, 99%) was from Sinopharm Chemical Reagent Co., Ltd. Potassium hydroxide (KOH, GR, 99.5%) was from Sinopharm Chemical Reagent Co., Ltd. All of these chemical reagents were used with further purification.

Synthesis of VMCNFs

The fabrication processes of multichannel carbon nanofibers-based amorphous vanadium (VMCNFs) were depicted as follow. A hyaline and homogenous PAN/DMF solution containing 10 wt % PAN was acquired at room temperature under continually stirring for 24 h. $VO(acac)_2$ was added into PAN/DMF solution with a molar ratio of 1/10 between $VO(acac)_2$ and AN under the same stirring condition. Then different PS was dissolved into the above mixture solution with different molar ratio of 0.25, 0.5, 0.75, 1 and 2 between styrene monomer (SM)



Scheme 1 – Schematic illustration of the fabrication steps for the multichannel carbon nanofibers-based amorphous vanadium.

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