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Short communication

Mixed-valent VO_x /polymer nanohybrid fibers for flexible energy storage materials

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Abstract

A large-scale production process composed of the novel Forcespinning® technology followed by relatively low-temperature calcination (450 °C) was developed in this report for a flexible/bendable energy storage material of heterogeneous vanadium oxide/polyvinylpyrrolidone derivative nanofibers with bark-like topography. It overcomes the low fabrication-efficiency and cost-performance shortcomings of previous techniques, such as tedious synthesis and high carbonization/growth temperature. The mechanical flexibility from moderately cross-linked polymeric backbones and the mixed valence-induced high electronic conductivity (4.48×10^4 S m^{-1}) from vanadium oxide concurrently endow these nanohybrid fibers as high performance flexible electrode materials for lithium-ion batteries.

Keywords: Forcespinning; Flexibility; Energy storage; Vanadium oxide; Mixed-valence

1. Introduction

Flexible/bendable supercapacitors and lithium-ion batteries (LIBs) have become promising for the next generation of electronic devices in a variety of sectors such as rollup displays, paper-like gadgets, miniature biomedical and wearable devices [1–3]. Hence a plethora of research efforts has been prompted to exploit new fabrication routes for lightweight, facile and high yielding flexible energy storage materials. In particular, the superior performance of flexible energy storage materials resorts to high mechanical resilience and stable electronic conductivity. In this point of view, carbon materials have been used as backbones or substrates in combination with electroactive transition metal oxides (TMOs) [4–6]. However, these hybrid materials are not yet incorporated into devices due to several remaining engineering challenges. These challenges include micro-batch processes necessitated by precise control of reactants, long reaction duration, multi-step hybridizing procedures and, frequently, low availability of expensive carbon nanostructures (including carbon nanotubes, graphene and conductive polymers) commonly prepared by inevitable high temperature treatment and/or tedious synthesis contradicting the requirements of ease manufacture on large-scale of these materials [7,8].

Here, a high throughput protocol was developed for making composite fibers from vanadium fluoride/polyvinylpyrrolidone (PVP) precursor with water as the only solvent through the Forcespinning® (FS) technology to produce fibers via centrifugal force. The following low temperature calcination of these forcespun fibers yields heterogeneous bark-textured VO_x /PVP derivative hybrid systems with superior mechanical flexibility and high electronic conductivity. The nonwoven nanohybrid fiber networks demonstrate fast kinetics, and the nanostructured mixed-valent VO_x nanorods exhibit rapid electron transport and ion percolation at high scan rates. This effort is envisioned for developments of various hybrid materials that will bring them closer to widespread production and potential energy storage applications for LIBs and supercapacitors.

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2. Experimental

2.1. Preparation of nanohybrid fibers

The precursor solution was prepared by mixing polyvinylpirrolidone (PVP, M_W=1,300,000, Sigma-Aldrich), vanadium (IV) fluoride (VF_4, 95% metal basis, Alfa Aesar), and deionized water in a Teflon beaker with varying polymer, VF_4 and water ratios. The mixture was then magnetically stirred for approximately 45 min, allowed to degas for 3 h to remove any trapped air-bubbles, and spun in a Cyclone 1000-M FS apparatus (Fiberio Technology Corp., TX, USA) equipped with a Teflon-coated spinneret (with 3 equally circumferentially spaced orifices) at 7000–12,000 rpm with an 8 cm orifice-to-collector distance to create a one-square-foot mat of precursor fibers. The as-spun precursor fibers were calcined in air at 420–600 °C for 1–6 h to generate the nanohybrid fibers. The most desirable product was achieved by heating the precursor fibers made from a precursor solution with a PVP/VF_4/water weight ratio of 1:1:3 to 450 °C at a ramp rate of 2 °C/min and held isothermally for 1 h.

2.2. Characterizations

The morphological, structural properties and elemental composition of the resultant product were characterized using a Zeiss Sigma VP SEM equipped with a Kleindiek micromanipulator and back-scatter detector, a FEI Tecnai F30 HRTEM, a Bruker AXS D8 QUEST XRD, a TA Instrument Q500 TGA and a time-of-flight secondary ion mass spectrometer (TOF-SIMS).

2.3. Electrochemical evaluations

The electrochemical performance was studied in a three-compartment cell using a Potentiostat/Galvanostat/ZRA (Gamry Reference 600). 1 M $LiClO_4$ ethylene carbonate (EC)/diethyl carbonate (DEC) (volume ratio=1:1) solution was employed as electrolyte. For the galvanostatic charge/discharge testing, the as-calcined free-standing nanohybrid fiber mat was used directly as working electrode, and was charged and discharged at 100 mA g^{-1} to the potentials of 2.0 V and 4.0 V versus Li/Li^+. For comparative cyclic voltammetric evaluations at 50 mV s^{-1}, the electrode was fabricated by grinding fibers and polyvinylidene fluoride (PVDF) with a weight ratio of 85:15 in ethanol and then pasting the mixture on alumina foil before thoroughly drying at 60 °C overnight in a vacuum oven. The electrode can be readily rolled up with a tweezer to a rollup electrode.

3. Results and discussion

The FS method (Fig. 1A) was employed to prepare VF_4/PVP fiber mat (Fig. 1B). The as-spun precursor fibers have smooth surface and diameter ranged from 500 nm to 2 μm. After feeding the precursor solution into the spinning reservoir of spinneret, the high-speed rotational force drove the viscous fluid through orifices, provided the capillary force was exceeded by the centrifugal force and hydrostatic pressure [9–11]. The FS process generates submicron/nanofibers regardless of the complex controlling parameters affecting Taylor cone and jet instability of widely used electrospinning process, i.e. high electrical field strength, intrinsic solution/melt conductivity, electrostatic and ionization fields [12]. In the FS process, solution viscosity and orifice-to-collector

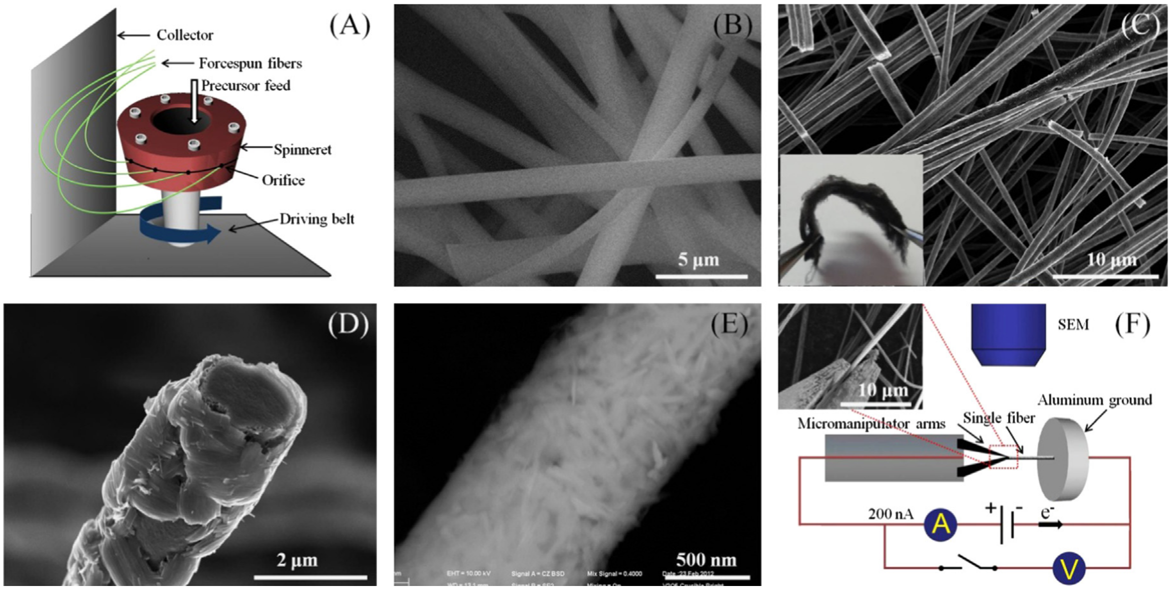

Fig. 1. (A) Schematic representation of the Forcespinning process. (B) SEM image of the as-spun precursor fibers taken under environmental conditions. (C) Low and (D) high magnification SEM images of the as-calcined nanohybrid fibers. Inset in panel C is the photographic image of the corresponding mat exhibiting good flexibility. (E) Back-scattered SEM image of the as-calcined nanohybrid fibers. (F) Schematic representation of the electrical probing setup of micromanipulator under SEM observations.

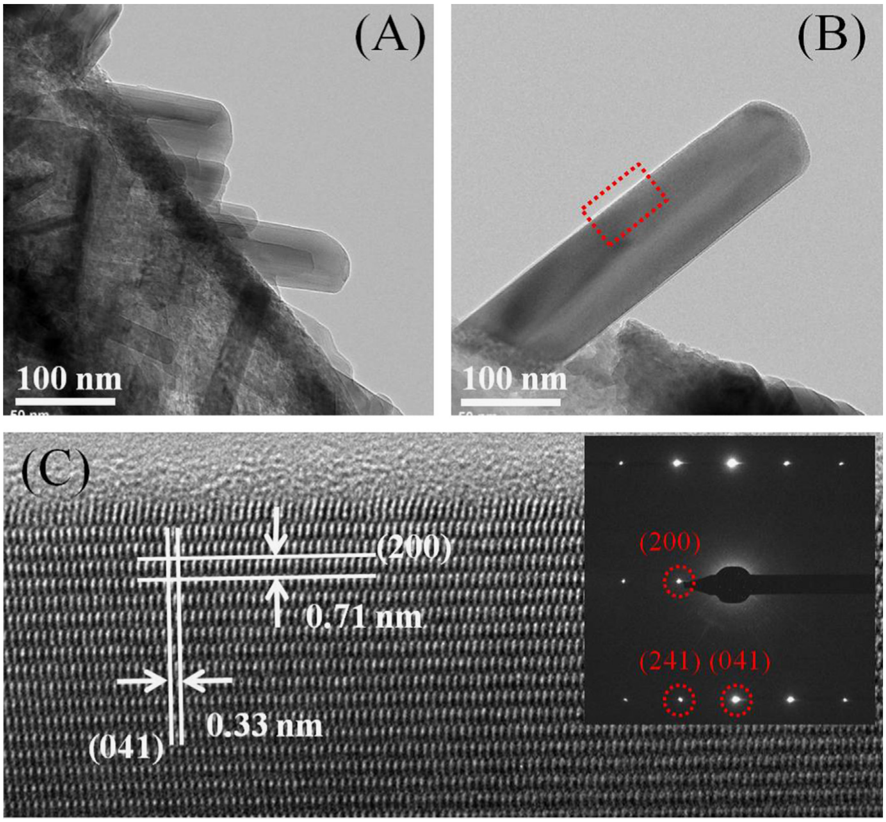

Fig. 2. (A–C) TEM of the nanohybrid fibers. (B and C) High-resolution TEM of the nanorods on the nanohybrid fibers. The inset in panel C shows the SAED pattern of the corresponding nanorod.

distance become the major contributing factors. The production rate has been estimated to be >1 g min^{-1} on a lab scale setup, a demonstration of its unique capability as a high-yield manufacturing technology of submicro/nanofibers.

According to our previous thermal studies on forcespun PVP and corresponding composite nanofibers, the cutoff degradation temperature of PVP is 450 °C [13], therefore calcinations were performed on the as-spun precursor fibers at 450 °C in this study to thermally transform VF_4 to its oxide counterparts with high electronic conductivity and PVP to its moderately cross-linked derivatives with desirable mechanical properties [14]. Fig. 1C exhibits the randomly oriented network of the as-calcined nanohybrid fibers as free-standing mat capable of being bent readily. The nanohybrid fibers did not undergo shrinkage apparently from the precursor fibers and possess an average axial length of 200 μm. The bark-textured individual nanohybrid fiber is emphasized in Fig. 1D. The sheath of vanadium oxide and the backbone of the flexible PVP residual can be clearly identified. The formation of this interesting heterogeneous structure is ascribed to the premature rigid shell of the precursor fibers during uneven heat transmission, which causes distinct inward and outward ionic diffusion rates [15]. After excluding the influence of carbon residual, the back-scattered SEM image (Fig. 1E) indicates that the superficial sheath comprises fine vanadium oxide nanorods. Noteworthy is that the heavily-loaded "carrier polymer" in FS processes can provide adequate medium resulting in different ionic diffusion rates at low ramp rates which alleviate burst-nucleation and generate electrochemically favored fine nanostructures in comparison with electrospinning [16]. Therefore, the FS process is essential and unique to generate this type of nanohybrid fibers. We also found that a lower PVP/VF_4 ratio and/or calcination temperature could result in hybrid fibers with unassociated highly scattered vanadium oxide nanorods rooted in the polymer skeleton and therefore poor electrical transportation. In addition, the resultant product with a high PVP/VF_4 ratio and calcined at 600 °C for 6 h showed nanorod-shaped single crystals with high aspect ratio but suffered from unfavorable brittleness.

The electronic conductivity of the nanohybrid fibers was investigated by an electrical probe (Kleindiek micromanipulator) (Fig. 1F). One individual fiber was positioned by moving the robotic microgripper under the SEM. The conductivity is estimated based on the *I–V* response. The flexible nanohybrid fibers exhibited a high electronic conductivity of 4.48×10^4 S m^{-1}. The XRD pattern (Fig. S1) indicates that the vanadium oxide sheath possesses a mixed-valent characteristic and is composed of polymorphic V_2O_5 and V_6O_{13}. The incomplete oxidation of hydrolytic product of VF_4 and phase transformation were responsible for this mixed vanadium valence formation and polymorphism phenomenon. The mixed-valent vanadium oxide compounds contain both donor and acceptor sites interacting by a bridge. The electronic coupling of these two redox sites as well as the "reorganization energy" unpredictably enhances the electron transfer [17]. Consequently, the balance between mechanical flexibility and electronic conductivity could be achieved by forming mixed-valent vanadium oxides within the nanohybrid fiber. The TOF-SIMS study (data not shown here) determined an approximate vanadium/carbon atomic ratio of 19:18. Moreover, the TGA curve (Fig. S2) indicates that about 54.3% oxide residual is eventually present after heating the nanohybrid fibers to 800 °C.

Further structural information about the heterogeneous nanostructures of vanadium oxide was obtained from TEM. Fig. 2A and B clearly demonstrates the surface of nanohybrid fibers is covered with oblique nanorods ranging from 50 to 100 nm in diameter, in great accordance with back-scatter SEM image. The high-resolution TEM image (Fig. 2C) reveals that the individual nanorod is single-crystalline. The characteristic interplane spacings of 0.71 nm and 0.33 nm (corresponding to the (200) and (041) planes, respectively) and the corresponding SAED pattern confirm that these nanorods are made of tetragonal V_2O_5 (JCPDS card: 45-1074, $a = b = 1.426$ and $c = 1.258$ nm). The high density of the central fiber core constricted the nucleation sites of V_2O_5 and forced the nanocrystals to grow laterally [18]. In other words, the V_6O_{13} phase congregated in the subsurface region of the nanohybrid fibers.

Fig. 3A shows the CV measurements of the nanohybrid fibers before and after rolling. Shape changes of the CV curves were not observed, reflecting the potential applications of these nanohybrid fibers as electrode materials for flexible electrochemical energy storage devices. Interestingly, one pair of redox peaks situated at 2.88 and 3.20 V indicating the conversion of V^{4+}/V^{5+} was still well-defined at a scan rate as high as 50 mV s^{-1}. Besides the advantages like high mechanical flexibility, electronic conductivity and tolerance of volumetric expansion caused by Li^+ intercalation, the one-dimensional networks and the nanostructured sheath of the nanohybrid fibers allow efficient ion access and shortened ion diffusions without kinetic limitations. The nanohybrid fibers exhibited a first cycle discharge capacity of 276.2 mA h g^{-1} at a current density of 100 mA g^{-1}. After the initial several cycles, they stably delivered discharge capacity of about 46.5 mA h g^{-1} once the formation of solid electrolyte interface layer. Our future endeavor includes (i) to lower carbonization temperature of the flexible cross-linked backbone and (ii) to incorporate conducting fillers to further promote the electrochemical performance of the nanohybrid fibers.

4. Conclusions

A successful preparation of hybrid VF_4/PVP precursor fibers via a novel Forcespinning process was reported here under the pursuit of a simplified approach and maximized throughput. The manipulative low temperature calcination process generates heterogeneous bark-textured VO_x/PVP derivative nanohybrid fibers. The nanohybrid fibers possess high mechanical stability, electrical conductivity and tolerance of volumetric expansion. When used as electrochemical electrode materials, they exhibit efficient ion access and shortened ion diffusions without kinetic limitations for flexible electrochemical energy storage devices due to the mixed-valent VO_x.

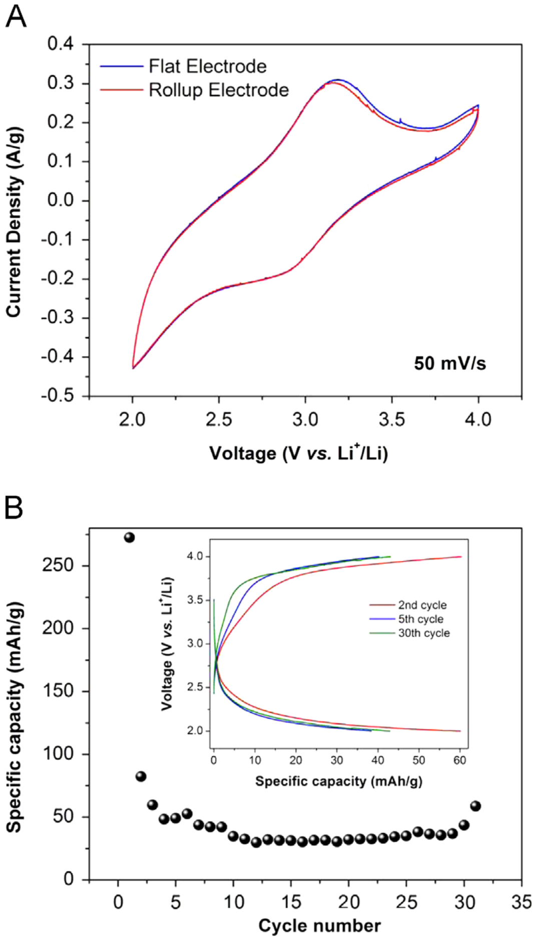

Fig. 3. (A) Cyclic voltammetric curves of the nanohybrid fibers before and after rolling at 50 mV s^{-1}. (B) Cycling performance of the nanohybrid fibers up to 30 cycles at 100 mA g^{-1}. Inset in panel B shows the galvanostatic charge/discharge curves for the 2nd, 5th and 30th cycles.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2013.09.067.

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