



Polypyrrole-encapsulated vanadium pentoxide nanowires on a conductive substrate for electrode in aqueous rechargeable lithium battery



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ABSTRACT

Precursors of ammonium vanadium bronze ($\text{NH}_4\text{V}_4\text{O}_{10}$) nanowires assembled on a conductive substrate were prepared by a hydrothermal method. After calcination at 360°C , the $\text{NH}_4\text{V}_4\text{O}_{10}$ precursor transformed to vanadium pentoxide (V_2O_5) nanowires, which presented a high initial capacity of 135.0 mA h g^{-1} at a current density of 50 mA g^{-1} in 5 M LiNO_3 aqueous solution; while the specific capacity faded quickly over 50 cycles. By coating the surface of V_2O_5 nanowires with water-insoluble polypyrrole (PPy), the formed nanocomposite electrode exhibited a specific discharge capacity of 89.9 mA h g^{-1} at 50 mA g^{-1} (after 100 cycles). A $\text{V}_2\text{O}_5@\text{PPy} // \text{LiMn}_2\text{O}_4$ rechargeable lithium battery exhibited an initial discharge capacity of 95.2 mA h g^{-1} ; and after 100 cycles, a specific discharge capacity of 81.5 mA h g^{-1} could retain at 100 mA g^{-1} .

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1. Introduction

Aqueous rechargeable lithium ion (Li^+) batteries have attracted significant attention because of their advantages like low cost, operation safety, high power density, and no specific requirement regarding humidity level during cell assembly [1–3]. In these batteries, lithium intercalation compounds are used as one or two electrodes based on redox reactions, with a lithium-containing aqueous solution as the electrolyte [4]. As an anode material for aqueous Li^+ battery, vanadium-oxide (V-O) compounds hold promising selectivity. VO_2 (B) was used for the first time as an anode material of an aqueous Li^+ battery in 1994 [5], while it suffered from serious capacity fading resulted from V dissolution. LiV_3O_8 was used as the anode material in an aqueous battery system without causing the kinetic electrolysis of water [6]; however, similar to VO_2 , it was slowly dissolved during charge–discharge process [7]. $\text{H}_2\text{V}_3\text{O}_8$ [8] and $\text{NaV}_6\text{O}_{15}$ [9] also can be used as an anode material of an aqueous Li^+ battery. Vanadium pentoxide (V_2O_5) is another promising candidate material for both Li^+ batteries and

supercapacitors in aqueous electrolyte solutions [10,11]. Stojkovic et al. [12] reported V_2O_5 xerogel with an initial discharge capacity of 69 mA h g^{-1} in an aqueous LiNO_3 solution. Yang et al. [13] found that hollow spherical V_2O_5 had a high capacitance of 479 F g^{-1} at 5 mV s^{-1} in a solution of 5 M LiNO_3 . However, its poor electronic conductivity and high dissolution rate in aqueous electrolyte are detrimental to the demands for high-rate and long-term cycling performance in electrochemical devices [14].

The traditional preparations of electrodes for Li^+ batteries involve multiple procedures, including mixing active materials with binders and conductive carbon additives such as carbon black, and then casting the mixture onto a metal foil. The presence of binders causes issues such as decreasing electrical conductivity, resistance for ions to access the surface of the active materials, and increasing the polarization of the electrodes to lower down its performance. Therefore, the elimination of binders could simplify the electrode preparation process and thus significantly improves the electrochemical performance of Li^+ batteries [15–17]. On the other hand, nanowires with high specific surface areas could provide more active centers along with shortened path length for Li^+ transport, and the space between the nanowires could accommodate larger volume expansion during the redox action of the electrodes, which is ideal for the application in Li^+ batteries [18–20].

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In this work, precursors of $\text{NH}_4\text{V}_4\text{O}_{10}$ nanowires are assembled on a conductive substrate, which transform to V_2O_5 nanowires after calcination at 360°C . To resolve the problems of poor electronic conductivity and high dissolution rate of V_2O_5 , polypyrrole (PPy) is coated uniformly on the surfaces of V_2O_5 nanowires to obtain PPy- V_2O_5 ($\text{V}_2\text{O}_5@\text{PPy}$) nanocomposite. Electrochemical results demonstrate that the $\text{V}_2\text{O}_5@\text{PPy}$ nanocomposite has good cycling behavior and high rate performances, which is a promising candidate as an anode material for aqueous Li^+ battery.

2. Methods/materials

2.1. Materials synthesis

In a typical synthesis route, NH_4VO_3 (1.2 g) and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in a molar ratio of 1:2 were dissolved in 40 mL deionized water under vigorous stirring for several hours until a dark green clear solution was produced. The obtained solution was then added into a 50 mL Teflon container, followed by addition of hexamethylenetetramine

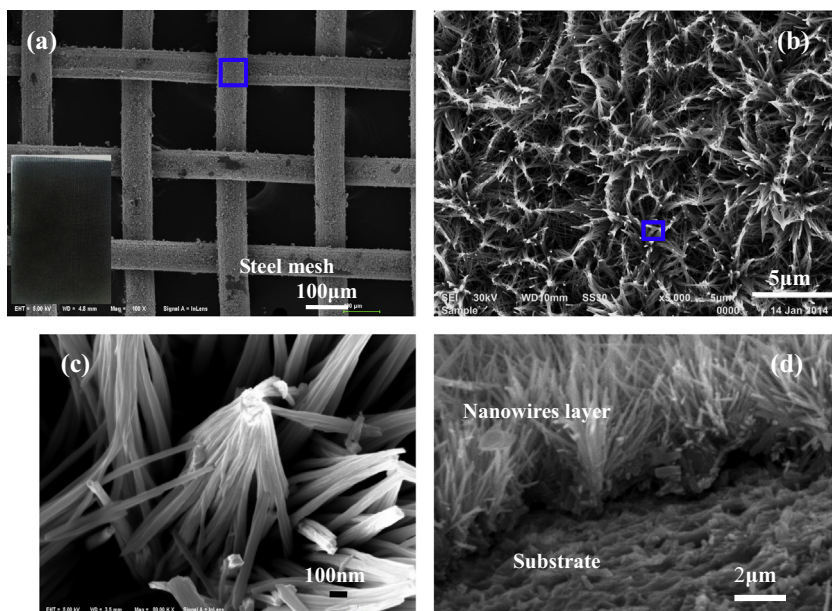


Fig. 1. SEM images of the as-prepared nanowires on a stainless steel mesh, (a–c) top view, (d) cross-section view. Inset (a) is the corresponding digital image of the sample.

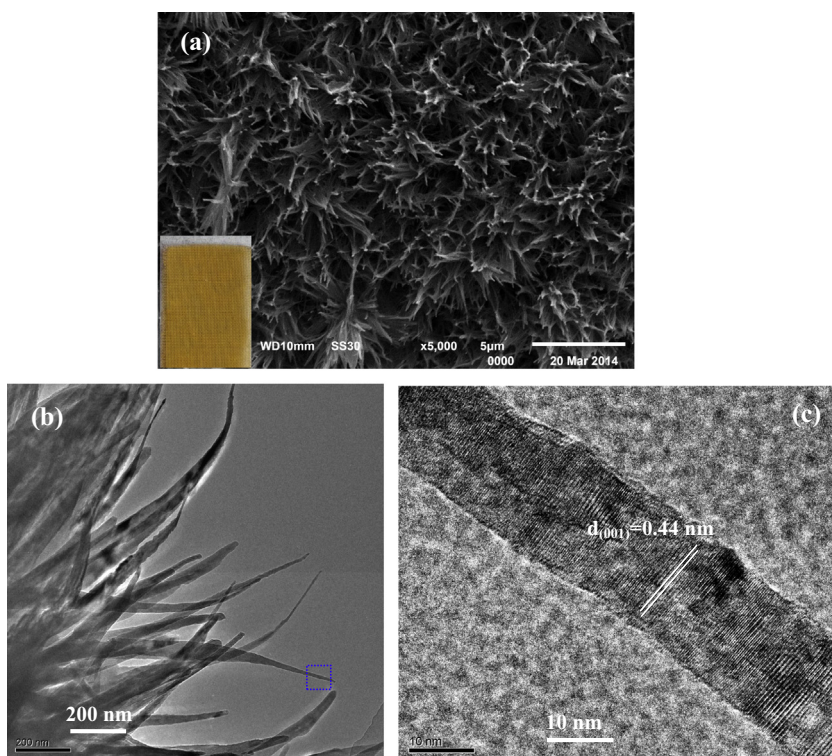


Fig. 2. SEM image (a) and TEM images (b and c) of the V_2O_5 nanowires obtained after calcination at 360°C . Inset (a) is the corresponding digital image of the sample.

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