



A Water Based Synthesis of Ultrathin Hydrated Vanadium Pentoxide Nanosheets for Lithium Battery Application: Free Standing Electrodes or Conventionally Casted Electrodes?



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ABSTRACT

Ultrathin hydrated vanadium pentoxide (V₂O₅·nH₂O) nanosheets are fabricated via a water based exfoliation technique. The exfoliation process involves reflux of the precursor, 1:4 mixture of VO₂ and V₂O₅, in water at 80 °C for 24 h. Operando and *ex situ* X-ray diffraction (XRD) studies are conducted to follow the structural changes during the exfoliation process. The chemical and thermal analyses suggest that the molecular formula of the nanosheet is H_{0.2}V_{1.8}^{IV}V_{0.2}^VO₅ · 0.5H₂O. The V₂O₅·nH₂O nanosheets are mixed with 10% of multi-walled carbon nanotube (MW-CNT) to form a composite material assigned as (VOx-CNT). Free standing electrodes (FSE) and conventionally casted electrodes (CCE) of VOx-CNT are fabricated and then tested as a positive electrode material for lithium batteries. The FSE shows reversible capacities of 300 and 97 mAhg⁻¹ at current densities of 10 and 200 mAhg⁻¹, respectively. This is better than earlier reports for free-standing electrodes. The CCE delivers discharge capacities of 175 and 93 mAhg⁻¹ at current densities of 10 and 200 mAhg⁻¹, respectively.

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1. Introduction

Since the discovery of graphene [1], the research interests in synthesis of the inorganic graphene analogues (IGAs) two dimensional (2D) materials has become tremendously significant [2,3]. The 2D materials possess a high surface area which acquires them unique physical and chemical properties, and thus, they can be used in a variety of applications, including catalysis [4], gas sensors [5], field effect transistors [6], and energy storage [7–10]. The 2D materials can be prepared by bottom-up or top-down approaches. The former approach involves a chemical synthesis of the 2D material from its precursors which are not necessarily be a layered material [11]. For the latter approach, the precursors are commonly bulk layered materials which are exfoliated to form 2D materials. The most common method for exfoliation is the liquid exfoliation which was discovered by Coleman *et al.* in 2008 [12].

The selection of the precursors of 2D materials for liquid exfoliation has, however been limited to layered materials with weak van der Waals forces between the layers, like MoS₂, and WS₂ [3,13–15]. Recently, modifications have been introduced to the technique, so that non-layered materials [16] and layered materials with covalent bonds between the layers can be exfoliated by liquid exfoliation [17,18].

Vanadium pentoxide (V₂O₅) is a promising material for energy storage applications such as the lithium battery [19–22] and supercapacitors [23–27], because it possesses a layered structure which facilitates the insertion and extraction of ions between the layers. However, the use of V₂O₅ as a cathode material requires the use of a lithium containing anode material, such as metallic lithium which is still a challenging topic, but recent advances in the field may open the door again for the use of high capacity cathode materials such as V₂O₅ [28,29].

Alternatively, water molecules can intercalate between the V₂O₅ to form bilayered hydrated vanadium pentoxide (V₂O₅·nH₂O), which basically is composed of double layers of V₂O₅ stacked along the *c*-axis with water molecules between the layers [5,30]. According to the number of water molecules (*n*) between the V₂O₅ layers, the

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interlayer distance of $V_2O_5 \cdot nH_2O$ changes from 6.34 to 13.80 Å [31]; this large interlayer spacing enables the use of this material in a variety of rechargeable batteries such as lithium [18], sodium [32,33], magnesium [34], and zinc batteries [35]. The interlayer distance and the morphology of the $V_2O_5 \cdot nH_2O$ can be tuned by synthesis and drying methods [36–40]. For instance, supercritical drying [38] or freeze drying [32,37,41] usually produces highly porous aerogels with high surface area and large interlayer distance. To date, $V_2O_5 \cdot nH_2O$ nanosheets can be prepared via methods which involve hydrolysis and condensation reactions of a vanadium (V) alkoxide precursor [5], or a mixture of V_2O_5 powder and H_2O_2 [31,41,42]. However, the majority of these approaches involve the use of harmful reducing reagents. Recently, we have developed a green method to synthesize $V_2O_5 \cdot nH_2O$ nanosheets using the bronze phase vanadium dioxide ($VO_2(B)$) as a precursor [18], but the exfoliation process requires a few days, and the precursor ($VO_2(B)$) is available only on a lab scale.

In this paper, we report on the synthesis of $V_2O_5 \cdot nH_2O$ nanosheets using commercially available vanadium oxides (V_2O_5 and monoclinic vanadium dioxide ($VO_2(M)$)) via a one-step water based approach under mild conditions (pressure ≈ 1 atm, and temperature $\approx 80^\circ C$). The $V_2O_5 \cdot nH_2O$ nanosheets was mixed with 10% of MW-CNT to form a composite material referred to as (VOX-CNT). Free standing electrodes (FSE) and conventionally casted electrodes (CCE) of VOX-CNT were prepared and then examined for lithium battery application.

2. Results and discussion

2.1. Synthesis and structural characterization of $V_2O_5 \cdot nH_2O$ nanosheets

The synthesis of $V_2O_5 \cdot nH_2O$ nanosheets via our recently reported method, showed some limitations when applied for V_2O_5 [18]. For example, the nanosized V_2O_5 with a plate like morphology (obtained by annealing of $VO_2(B)$) can be readily exfoliated to $V_2O_5 \cdot nH_2O$ nanosheets; however the commercial V_2O_5 powder can hardly be exfoliated using this approach, and the yield is quite low (see Figure S1). Therefore, the synthesis strategy needs to be modified, so that the commercial V_2O_5 powder can be exfoliated.

Providing the fact that $V_2O_5 \cdot nH_2O$ always contains a specific amount of V^{IV} [43–45], thus the addition of V^{IV} oxide or a reducing agent to the commercial V_2O_5 during the reflux process can probably facilitate its conversion to $V_2O_5 \cdot nH_2O$ nanosheets. For instance, when 10% of $VO_2(B)$ was added to 90% of commercial V_2O_5 , it results in a partial conversion of the vanadium oxides to the $V_2O_5 \cdot nH_2O$ after refluxing at $80^\circ C$ for 8 h (see Figure S2a). However, we still have excess of V_2O_5 powder, as indicated by the sharp diffraction peak corresponding to the 001 reflection of V_2O_5 at $2\theta = 20.36^\circ$ (see Figure S2a). The prolongation of the reflux time to different time intervals (30 and 54 h) did not significantly change the amount of $V_2O_5 \cdot H_2O$, which indicates that the process is not time dependent. However, when the amount of $VO_2(B)$ was increased to 20%, the oxide mixture was completely converted to $V_2O_5 \cdot nH_2O$ after refluxing with water at $80^\circ C$ for 5–24 h, as indicated by the changes in the powder XRD patterns in Figure 1 a collected after 5, 18, and 24 h. The powder XRD pattern collected after 24 h matches quite well with the standard pattern for $V_2O_5 \cdot nH_2O$ (JCPDS No. 74-3093). The resolved peaks in the XRD pattern of $V_2O_5 \cdot nH_2O$ nanosheets are broad with d -spacing values of d/n (where n is an integer = 1, 2, 3, ..., n) and can be indexed as $00l$, which reflect the preferred orientation of the nanosheets with a few layers thickness. Similarly, the use of $VO_2(M)$ instead of $VO_2(B)$ results in a complete conversion of oxide mixture to $V_2O_5 \cdot nH_2O$, which indicates that the initial structure of VO_2 does not play a significant role in the exfoliation process (see Figure S2b). From a commercial point of view, the following study in this paper

will deal only with mixture of commercially available oxides (i.e. $VO_2(M)$ and V_2O_5).

Operando XRD studies were conducted to investigate the exfoliation process. Figure 1 b shows a color map for the variation of X-ray intensity with reaction time in a given 2θ range. We can see from the color map that a new phase is formed after 90 min at $2\theta = 0.65^\circ$ and d -spacing = 18.0 Å ($\lambda = 0.20759$ Å). Figure 1 c displays individual selected XRD patterns with 2θ normalized to copper wavelength (to facilitate the comparison of these XRD patterns with the *in house ex situ* XRD patterns) at time intervals 0, 30, 60, 90, 120, 150, and 250 min. It can be seen from the plots that the intensities of the 200 ($2\theta = 15.38^\circ$, and d -spacing = 5.76 Å) and 001 ($2\theta = 20.36^\circ$, and d -spacing = 4.36 Å) reflections of V_2O_5 keep decreasing as the reaction proceeded, in addition to the appearance of a low angle peak after 90 min at $2\theta = 5.0^\circ$ (d -spacing = 18.0 Å). The intensity of this low angle peak keeps increasing as the reaction time increases; which was attributed to the 001 reflection of $V_2O_5 \cdot nH_2O$. However, the *ex situ* XRD of $V_2O_5 \cdot nH_2O$ powder showed that the 001 reflection has a d -spacing of about 13.63 Å. The difference in d -spacing values is probably due to the presence of larger number of water molecules between the layers of $V_2O_5 \cdot nH_2O$ nanosheets when they are dispersed in water. Interestingly, the 002 reflection of $V_2O_5 \cdot nH_2O$ nanosheets can be resolved after 250 min at $2\theta = 10.0^\circ$ (d -spacing = 9.0 Å). It is worth mentioning that the peak which appears at $2\theta = 2.5^\circ$ probably originates from the setup or the background, because it is already present at zero reaction time, and neither V_2O_5 nor $VO_2(M)$ have peaks at this 2θ value.

The mechanism of $V_2O_5 \cdot nH_2O$ nanosheets synthesis using a mixture of VO_2 and V_2O_5 is quite complicated, and the presence of VO_2 is crucial to have a successful and fast exfoliation process. Probably, VO_2 facilitates the hydrolysis of V_2O_5 [46], and/or stabilizes the formation of solution intermediates. In the meantime, VO_2 itself is partially oxidized during the reflux process and converts to $V_2O_5 \cdot nH_2O$ nanosheets [18]. However, the final product XRD pattern does not show any VO_2 reflections (see Figure 1 a) and the yield is about 99.0%. Therefore, VO_2 does not act as a real catalyst because it reacts during the synthesis process and goes to the final product.

2.2. Chemical composition and morphology of $V_2O_5 \cdot nH_2O$ nanosheets

The X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA) showed that the chemical composition of the nanosheets at $120^\circ C$ is $H_{0.2}V_{1.8}^{IV}V_{0.2}^{IV}O_5 \cdot 0.5H_2O$ [43–45]. For simplicity we will refer to it as $V_2O_5 \cdot 0.5H_2O$ (the detailed analysis is described in the supporting information). The electron microscopy showed that the exfoliated material has typical nanosheet morphology (see Figure 2 a, and e). The AFM (Figure 2 b and c) indicated that the nanosheet thickness is about 4.0 nm, which represent about 3 layers (based on the fact that the d -spacing of the 001 reflection = 13.63 Å, as obtained from XRD). In addition, the high resolution TEM (HRTEM) in Figure 2 d displays the lattice fringes of the 001 plane, which suggests that the $V_2O_5 \cdot 0.5H_2O$ nanosheet consists of 3–4 layers. Furthermore, the selected area electron diffraction (SAED) in Figure 2 f displayed powder rings, which indicates the high degree of randomness in the nanosheets arrangement. Interestingly, the freeze drying improves the morphology of the nanosheets by increasing the number of wrinkles, as shown by SEM images in Figure 2 g, h, and i.

2.3. Electrochemical characterization of $V_2O_5 \cdot nH_2O$ nanosheets in a lithium battery

The $V_2O_5 \cdot nH_2O$ nanosheets are a promising high capacity positive electrode material for lithium battery. We presented in our

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