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Potassium Vanadate Nanobelt as a High-Capacity Cathode Material for Li-ion Battery

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In this paper, a potassium-deficient $K_{0.66}V_3O_8$ with nanobelt morphology was synthesized by a facile and large-scale hydrothermal method and its electrochemical performance as cathode material for Li-ion battery was investigated. As indicated by the scanning electron microscopy (SEM), the nanobelts show a width of ~80 nm and a length of less than one micrometer. Cyclic voltammetry (CV) test indicates good reversible Li ion insertion/extraction behavior. When used as a cathode material for Li-ion battery, the nanobelts exhibit a high initial discharge capacity of 268.9 mAh g^{-1} during 1.5~4.0 V at 15 mA g^{-1}. After capacity fading in the first several cycles, it maintains the capacity of 180 mAh g^{-1}. At 75 mA g^{-1}, the $K_{0.66}V_3O_8$ nanobelts still show the reversible capacity of 197.5 mAh g^{-1} with the capacity retention of 70.8% after 25 cycles.

Keywords: Li-ion battery; $K_{0.67}V_3O_8$; Nanobelt; Hydrothermal method; Electrochemical performance

1. INTRODUCTION

Nanostructured vanadium oxides and their derivative compounds have attracted considerable attention as cathode materials for Li-ion battery due to their high capacity, easy synthesis and relatively low cost [1-10]. More interest has been paid to lithium trivanadate (LiV_3O_8) [3,5,6]. However, the cycling stability of LiV_3O_8 is still insufficient for the practical application probably due to its essential structure instability. It is well known that most of vanadates possess the layered structure, the stability of which during the Li ion insertion/extraction process greatly depends on the cycling stability of the electrode. Meantime, the preparation methods often influence its electrochemical performance [6,11-13]. Wang et al found that NaV_3O_8 demonstrates larger layered distance than LiV_3O_8, resulting in better rate capability and cycling stability [14]. With this regard, other cations, such as Na^+ or K^+ was proposed to replace Li^+ to form new cathode materials for Li-ion battery[15,16].

Potassium trivanadate compounds have been synthesized by several preparation methods [16-18]. KV_3O_8 was hydrothermally synthesized at 250 °C from V_2O_5 powder dispersed in KNO_3 solution [16]. West et al. [17] obtained KV_3O_8 with high initial discharge capacity for Li-ion battery by a solution approach. However, no cycling performance was shown in their work. KV_3O_8 with the initial discharge capacity of less than 100 mAh g^{-1} was proposed by Menav et al. [18], which also showed poor cycling performance. Wang et al [19] prepared the $KV_3O_8{\cdot}0.42H_2O$ nanorods by a facile hydrothermal method, with the capacity of 130.1 mAh g^{-1} at 15 mA g^{-1}. Apparently, much more work should be done to further improve the reversible capacity and the cycling performance for this kind of material.

Two-dimensional (2D) nanostructured materials have attracted considerable attention for advanced functional systems owing to their attractive properties [20]. It is noted that 2D nanostructured electrode materials possesses the high surface-to-volume ratio and excellent surface activities, which have stimulated great interest in their development for the next generation of power sources [21,22]. Menav et al. [18] found that the potassium richer compounds showed low recharge efficiency, while the potassium insufficient compounds, like $K_2V_8O_{21}$ and KV_5O_{13}, delivered high capacity and good reversibility. Their work gave us the inspiration. With the aim of getting the high-capacity compound, the potassium-deficient strategy was firstly proposed for KV_3O_8. In this work, potassium-deficient $K_{0.66}V_3O_8$ nanobelts were designed by a facile one-step hydrothermal method. The as-prepared compound exhibited higher reversible capacity in comparison with the stoichiometric one probably due to the potassium-deficiency and the nanobelt morphology.

2. EXPERIMENTAL

2.1 Synthesis and characterization

The starting materials, ammonium metavanadate (NH_4VO_3) and potassium chloride (KCl) were of analytical purity and directly used without any purification. At first, 0.93 g of NH_4VO_3 and 2.386 g of KCl were dissolved in deionized water successively at 70 °C with urgent stirring. Then a proper amount of hydrochloric acid with the concentration of 1.5 mol L^{-1} was added into the solution to adjust the pH value to about 3.0. The mixed solution was then transferred into a 100 ml Teflon lined stainless steel autoclave. The autoclave was sealed and heated at 180 °C for 24 h and then cooled to room temperature naturally. The obtained sponge-like precipitates were filtered, washed with deionized water three times. Finally, the precipitates were dried at 80 °C overnight and then ground by agate mortar.

All X-ray diffraction (XRD) data were given by a Philips X-Pert system (Cu-Kα radiation) with a step of 0.02 °. Morphological studies were conducted using a JSM6430F scanning electron microscopy (SEM). And the energy dispersive spectroscopy (EDS) was also carried out by the JSM6430F SEM. For further confirming the molecular composition, element analysis was performed by an Optima5300DV inductively coupled plasma-atomic emission spectroscopy (ICP-AES) equipment.

2.2 Electrochemical measurements

The electrochemical cells were constructed by mixing the active material, polyvinylidene fluoride (PVDF), and carbon black in the weight ratio of 80:10:10. The N-Methyl Pyrrolidone (NMP) was used as solvent. After enough stirring for 5h, the slurry was cast onto Al foil. After well-drying, the electrodes were assembled into CR2016 coin-type cells with commercial electrolyte (Guangzhou Tinci; 1 M $LiPF_6$ in 1:1 v/v ethylene carbonate/dimethyl carbonate) and a Li metal as counter electrode. The cells were constructed in an Ar-filled MBraun glovebox and cycled galvanostatically between 1.5 and 4.0 V (voltage unit in this paper is versus Li/Li^+) at a desired current density with a Neware battery testing system (CT-3008W) at room temperature. Cyclic voltammetry (CV) test was carried out using the CHI 660d electrochemical station (Shanghai Chenhua, China) with a scan rate of 0.1 mV s^{-1} at room temperature.

3. RESULTS AND DISCUSSION

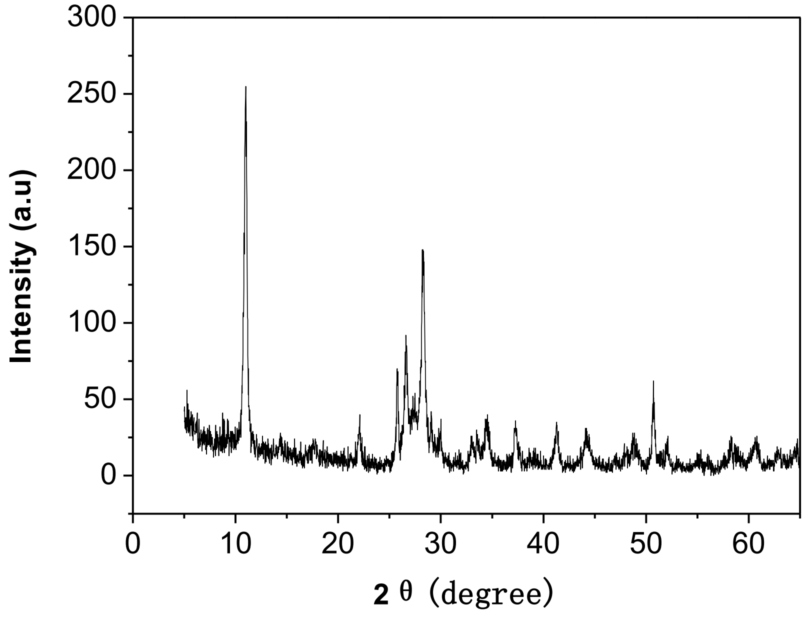
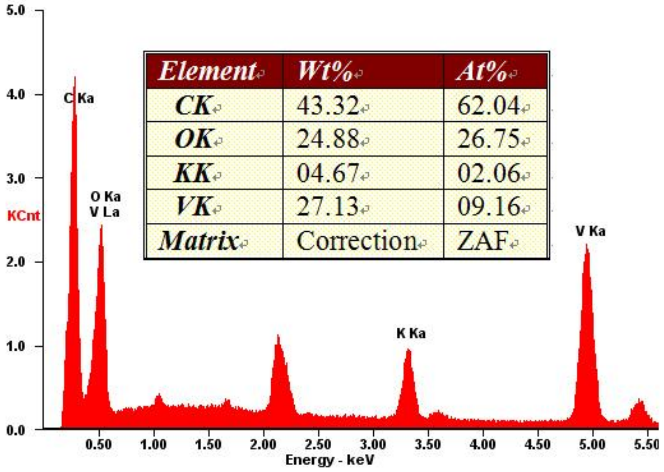


Figure 1. XRD pattern of the as-prepared powder.

XRD pattern of the as-prepared powder is shown in Fig. 1. The diffraction peaks can be indexed into $K_xV_3O_8$ with monoclinic structure and $P2_1/m$ space group[17]. However, it should be noted that some diffraction peaks is a little different from the KV_3O_8 standard PDF card (No.22-1247), which is probably due to the existence of potassium insufficiency. For this reason, the content of potassium in the as-prepared compound was measured by EDS and the ICP-AES results. Fig.2 gives the EDS result for the as-prepared sample. Based on the ratio of K:V, the x in $K_xV_3O_8$ is calculated to be about 0.667. ICP results provide further evidence for the potassium insufficiency. As shown, the ratio of K:V is about 0.219. That is the x in $K_xV_3O_8$ could be about 0.66, which is almost the same with the EDS result. From the results above, it is sure that the as-prepared material could be written as $K_{0.66}V_3O_8$. It is well known that KV_3O_8 crystal consists of V_3O_8 layers and interstitial hydrated K ions. The V_3O_8 layer is composed of corrugated sheets of distorted, edge sharing VO_6 octahedra and the hydrated K ions are located between the layers [17]. In comparison with the LiV_3O_8 and NaV_3O_8, the large K ions could hinder some pathways for lithium ion transferring, resulting in poor electrochemical properties. With this regard, the strategy of potassium deficiency in KV_3O_8 seems to be promising, in which more available accommodation sites for Li ions are expected.



Element	*Wt%*	*At%*
CK	43.32	62.04
OK	24.88	26.75
KK	04.67	02.06
VK	27.13	09.16
Matrix	Correction	ZAF

Figure 2. EDX spectrum of the as-prepared sample.

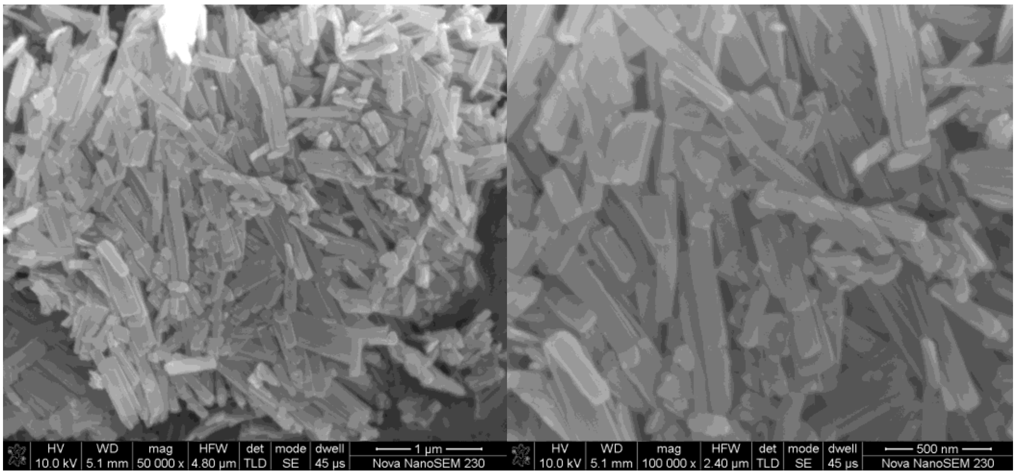


Figure 3. SEM images of the as-prepared sample

Fig. 3 shows the SEM images of the as-prepared sample. As can be seen, the sample demonstrates the nanobelt morphology. The nanobelts are well dispersed and have the average width of about 80 nm. The length of most of nanobelts is less than 1 μm, some of which are only about 100 nm.

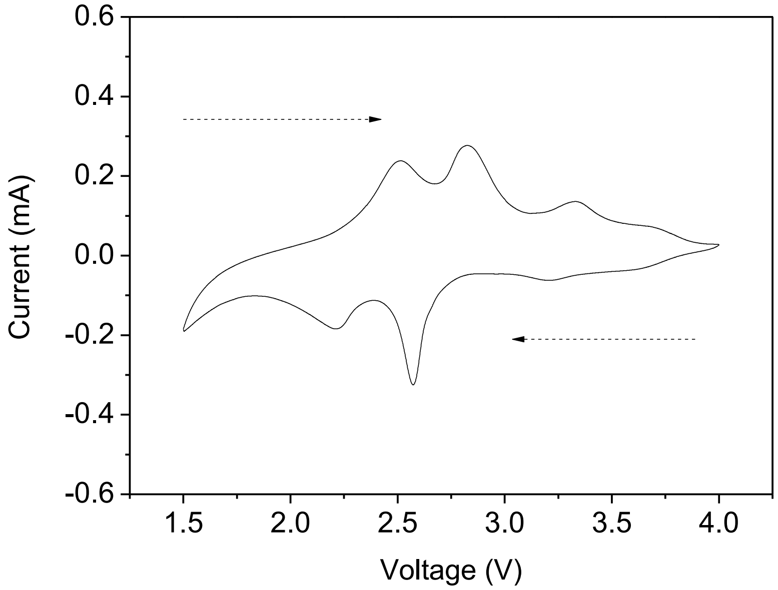


Figure 4. Cyclic voltammetry curves of $K_{0.66}V_3O_8$ nanobelts between 1.5 and 4.0 V at a scan rate of 0.1 mV s^{-1}.

Fig. 4 shows CV curves of $K_{0.66}V_3O_8$ electrode between 1.5 and 4.0 V at a scan rate of 0.1 mV s^{-1}. It can be seen that Li ions could be well inserted into/extracted from the $K_{0.66}V_3O_8$ electrode.

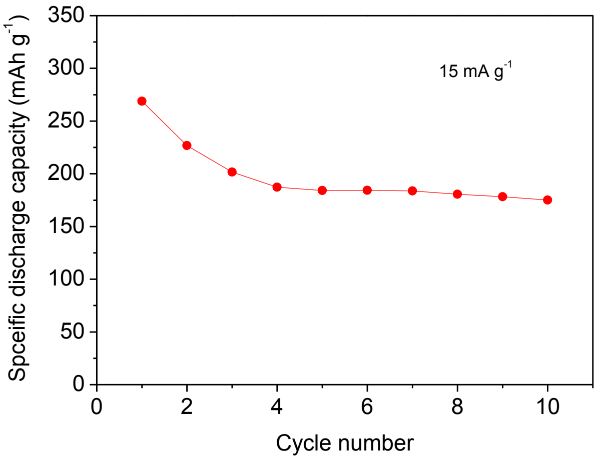
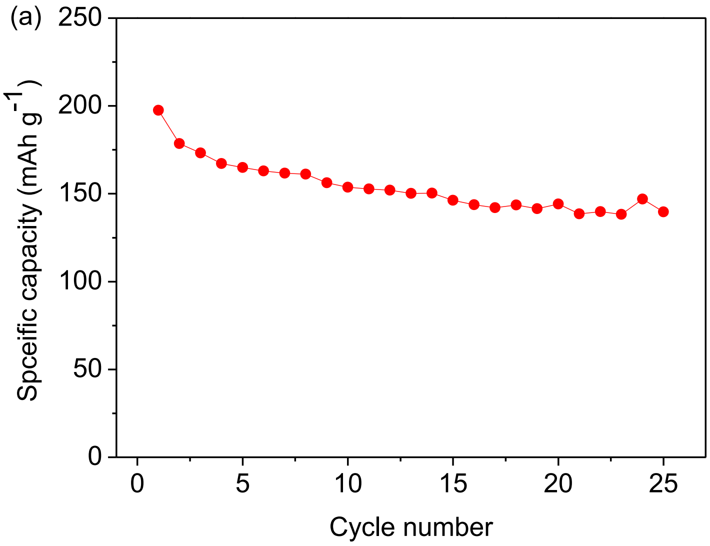


Figure 5. Cycling performance of $K_{0.66}V_3O_8$ nanobelt electrode operated between 1.5 and 4.0 V at a current density of 15 mA g^{-1}.

Three obvious pairs of redox peaks, with the oxidation peaks located at about 2.51 V, 2.84 V, 3.33 V and the corresponding reduction peaks at about 2.21 V, 2.57V, 3.20 V, respectively, are observed. Appearance of redox peaks indicates the reversible Li^+ de-intercalation and intercalation in solid phase [23-25], suggesting the multi-steps electrochemical processes of $K_{0.66}V_3O_8$. Apparently, like other vanadates (LiV_3O_8, NaV_3O_8, $NH_4V_3O_8$), $K_{0.66}V_3O_8$ also possesses complicated Li ion insertion/extraction behavior. The splitting of many redox peaks was because of the different lithium sites with energy difference for holding the lithium ions [26].

Electrochemical properties of $K_{0.66}V_3O_8$ nanobelt used as a cathode for Li-ion battery are investigated. The cycling performance at a current density of 15 mA g^{-1} between 1.5 and 4.0 V is displayed in Fig.5. As indicated, the nanobelts deliver a high initial discharge capacity of 268.9 mAh g^{-1} at 15 mA g^{-1}, corresponds with about 3.08 lithium ions insertion into per formula unit, forming the $K_{0.66}Li_{3.08}V_3O_8$. It was reported that KV_3O_8 had lower reversible capacity due to its larger ion radius in comparison with LiV_3O_8 and NaV_3O_8. Menav et al. [18] synthesized the bulk KV_3O_8 by a solid state reaction, the initial discharge capacity of which is less than 100 mAh g^{-1}. $KV_3O_8{\cdot}0.42H_2O$ nanorods prepared by Wang et al. [19] exhibited higher initial discharge capacity, 130.1 mAh g^{-1} at 15 mA g^{-1}, which is still far less than those of LiV_3O_8 and NaV_3O_8 [7,15]. The reversible capacity of $K_{0.66}V_3O_8$ nanobelts here is greatly enhanced probably due to the incorporation of potassium deficiency. After capacity fading in the first several cycles, it maintains the capacity of 180 mAh g^{-1}, which is still much higher than the reported value [18,19]. In ref [19], $KV_3O_8{\cdot}0.42H_2O$ nanorods gave the discharge capacity of 114.3 mAh g^{-1} after 20 cycles, about 87.9% of the initial capacity. The capacity loss in the first several cycles should be attributed to the large polarization of electrode and probable slight structure rearrangement due to lithium ion insertion, as that of $(NH_4)_{0.5}V_2O_5$ [24]. Menav et al. [18] fabricated a series of potassium vanadates with different molecular composition ($K_3V_5O_{14}$, KV_3O_8, $K_2V_8O_{21}$, KV_5O_{13}) and investigated their electrochemical properties for secondary lithium batteries. As demonstrated, the two potassium richer compounds showed low discharge capacity, while a good reversibility and high capacity performance was observed for the two potassium deficiency compounds. Therefore, in this work, the improved electrochemical performance of $K_{0.66}V_3O_8$ could mainly be assigned to the strategies of potassium deficiency and the nanobelt morphology.



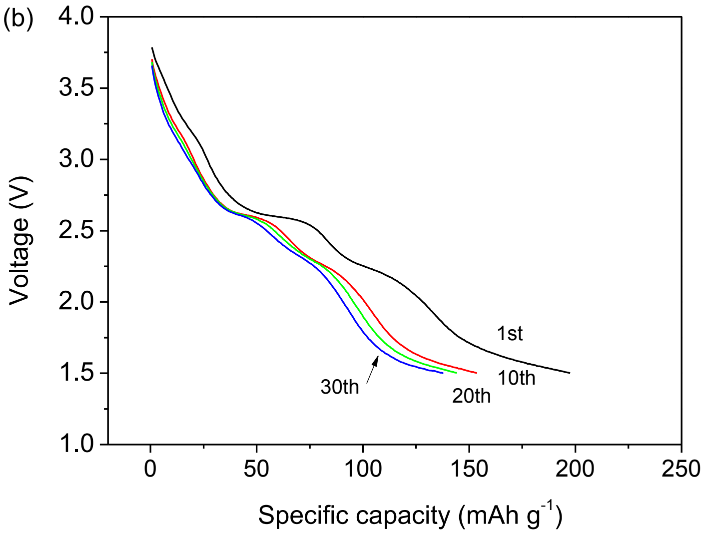


Figure 6. Cycling performance (a) and discharge curves at different cycle of $K_{0.66}V_3O_8$ operated between 1.5 and 4.0 V at a current density of 75 mA g^{-1}.

Electrochemical properties of $K_{0.66}V_3O_8$ nanobelts at a current density of 75 mA g^{-1} are further investigated. Fig. 6 shows the cycling performance and the discharge curves. It can be seen that the nanobelts deliver a reversible capacity of 197.5 mAh g^{-1} with an obvious capacity loss in the first several cycles. After that, the capacity fading is decreased with the capacity retention of 70.8% after 25 cycles. Discharge curves at different cycles in Fig.6 (b) demonstrate several voltage plateaus at 2.62 V, 2.29 V and 1.58 V. There is no obvious change for the curves at 10th and 30th cycles, indicating good capacity retention after several cycles.

4. CONCLUSIONS

In summary, potassium-deficient $K_{0.66}V_3O_8$ nanobelts were synthesized by a facile hydrothermal method as cathode material for Li-ion battery. The nanobelts showed good lithium ion insertion and extraction ability. At a current density of 15 mA g^{-1}, it exhibited an initial discharge capacity of 268.9 mAh g^{-1}. After 20 cycles, the discharge capacity of 180 mAh g^{-1} was maintained. When the current density was increased to 75 mA g^{-1}, the nanobelts still exhibited a high discharge capacity of 197.5 mAh g^{-1} with the capacity retention of 70.8% after 25 cycles.

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