



## Short communication

# Template-assisted formation of porous vanadium oxide as high performance cathode materials for lithium ion batteries



Yanhui Su<sup>a</sup>, Anqiang Pan<sup>a, b, \*</sup>, Yaping Wang<sup>a</sup>, Jiwu Huang<sup>a</sup>, Zhiwei Nie<sup>a</sup>, Xinxin An<sup>a</sup>, Shuquan Liang<sup>a</sup>

<sup>a</sup> School of Materials Science & Engineering, Central South University, Hunan 410083, China

<sup>b</sup> State Key Laboratory of Powder Metallurgy, Central South University, Hunan 410083, China

## HIGHLIGHTS

- V<sub>2</sub>O<sub>3</sub>/KB carbon composite has been fabricated by using porous Ketjen black carbon as templates.
- Porous V<sub>2</sub>O<sub>5</sub> is created after removing the KB carbon in the V<sub>2</sub>O<sub>3</sub>/KB carbon composite.
- The porous V<sub>2</sub>O<sub>5</sub> electrode materials exhibit good electrochemical performance for lithium ion batteries.

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## ABSTRACT

Similar to carbonaceous materials, porous metal oxides have attracted wide attention in energy storage and conversion systems because of their structural advantages, including high activity and electrolyte accessibility. In this work, we report the novel preparation of porous vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) as high performance cathode material for lithium ion batteries. Ketjen black (KB), a porous carbon material, has been employed as hard templates to host precursor species in their porous structures. The porous V<sub>2</sub>O<sub>5</sub> electrode material is prepared after removing the KB carbon framework by calcinating the composites in air. As cathode materials for lithium ion batteries, the porous V<sub>2</sub>O<sub>5</sub> electrodes exhibit high capacity, good cycling stability and rate capability. An initial discharge capacity of 141.1 mA h g<sup>-1</sup> is delivered at a current density of 100 mA g<sup>-1</sup>, very close to the theoretical capacity of 147 mA h g<sup>-1</sup>.

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## 1. Introduction

Rechargeable Li-ion batteries (LIBs) have been widely exploited as energy sources in portable electronic devices over the last two decades, due to their high energy and power density, favorable cycling stability, and long lifespan [1–3]. And they are under serious consideration to power electrical vehicles (EVs) and hybrid electrical vehicles (HEVs) in order to alleviate the pressures caused by the fast depletion of fossil oil and the related environmental issues. The electrochemical properties of LIBs are largely determined by the electrode materials. Therefore, it is of great interest to explore new electrode materials with higher capacity, low cost, good rate capability and safety for the next-generation lithium ion

batteries [4–7].

Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) is regarded as a promising cathode material in rechargeable lithium-ion batteries (LIBs), due to its high capacity, abundant resources storage, and easy fabrication [8–11]. The layer-structured V<sub>2</sub>O<sub>5</sub> undergoes multiple Li<sup>+</sup> insertion/extraction reactions between 4.0 and 1.5 V vs. Li/Li<sup>+</sup>, and possesses a theoretical high specific capacity of 442 mA h g<sup>-1</sup> (3 Li<sup>+</sup> ions intercalation per formula) [12]. However, the practical applications of bulk V<sub>2</sub>O<sub>5</sub> as a cathode material in LIBs are limited by its moderate electronic and sluggish kinetics of Li<sup>+</sup> ion diffusion [13,14]. Thus, much attention has been paid to the construct nanoscaled V<sub>2</sub>O<sub>5</sub> materials to reduce the Li<sup>+</sup> ions diffusion distance and to improve the reversibility of V<sub>2</sub>O<sub>5</sub> based electrodes. To date, various nanostructures such as nanoparticles [12,15,16], nanorods [17,18], nanotubes [19], nanowires [20] and nanobelts [21,22] have been reported, which more or less improves the rate capability of V<sub>2</sub>O<sub>5</sub> electrode materials [14,23]. However, the cycling performance in

\* Corresponding author. School of Materials Science & Engineering, Central South University, Hunan 410083, China.

E-mail address: [pananqiang@csu.edu.cn](mailto:pananqiang@csu.edu.cn) (A. Pan).

most previous reported works is not quite satisfactory and still needs further improvement. The inferior cycling stability may be attributed to the structural broken into electrolyte during the intercalation and de-intercalation process. Porous electrode materials may improve the cycling performance because of their good capability to accommodate the volume changes and retain the original structural integrity. Recently, Zhang et al. prepared the porous  $V_2O_5$  nanocrystallites, which exhibited superior rate capability and cycling stability [24]. However, it requires high operating temperature (700 °C) and the strict control for vacuum filtration process and calcinations process in air. Thus, it is highly desirable to develop a new simple and reliable synthesis strategy to prepared porous  $V_2O_5$  materials.

Herein, we report the novel synthesis of porous  $V_2O_5$  nanocrystallites by absorbing the liquid precursor solution into mesoporous carbon templates to make the composites, which are converted into porous  $V_2O_5$  after KB carbon template removal. The as-prepared porous  $V_2O_5$  material exhibits good cycling stability and rate capability.

## 2. Experimental section

### 2.1. Materials synthesis

$V_2O_5$  nanosheets were synthesized by two-step calcinations in  $H_2/Ar$  mixed atmosphere and in air, respectively. In a typical procedure, vanadyl oxalate ( $VOx_2O_4$ ) as intermediate vanadium sources was prepared according to the previous reports [25,26].  $V_2O_5$  (1.2 g) and  $H_2C_2O_4 \cdot 2H_2O$  (2.4953 g) were dissolved into 20 mL de-ionized water under magnetically stirring at 80 °C until the obtaining of blue solution. Then, Ketjen black carbon (0.21 g, EC-300J) was dispersed uniformly in the as-prepared solution and stirred for 12 h to allow the vanadium precursor to impregnate the mesopore of the Ketjen black sufficiently. The resulting slurry was dried at 80 °C for 12 h and then baked in 5%  $H_2/95\%$  Ar mixed atmosphere at 600 °C for 1 h at a heating rate of 5 °C  $min^{-1}$  to form  $KB@V_2O_3$ . The porous  $V_2O_5$  nanomaterials were obtained after removing the KB carbon by calcination in air at 400 °C for 1 h using a heating rate of 2 °C  $min^{-1}$ , while the  $V_2O_3$  was oxidized to  $V_2O_5$ .

### 2.2. Structural characterizations

The crystalline structure of  $KB@V_2O_3$  and as-prepared porous  $V_2O_5$  nanomaterials were characterized by X-ray diffraction (XRD, Rigaku D/max 2500 XRD). The morphology of the samples was systematically investigated by scanning electron microscopy (SEM, Quanta FEG 250) and transmission electron microscopy (TEM, Jeol JEM 2010). The calcination process in air was analyzed by thermogravimetric analysis (TGA, NETZSCH STA 449C) from room temperature to 650 °C at a heating rate of 10 °C  $min^{-1}$ .

### 2.3. Electrochemical measurements

The  $V_2O_5$  nanosheets as active material was mixed with acetylene black and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10, and then dropped with an appropriate amount of N-methyl-2-pyrrolidone (NMP) solution to form the slurry, which was then coated on an alumina foil and dried at 100 °C for 20 h in vacuum to obtain the cathode with a diameter of 12 mm. Coin cells were assembled in an ultra-high purity argon-filled glove box (Mbraun, Germany). Li metal foil and polypropylene membrane were used as the counter electrode and separator, respectively, while 1 M  $LiPF_6$  dissolved in ethylene carbonate/dimethyl carbonate/diethyl carbonate (in a volume ratio of EC/DMC/DEC = 1:1) were used as the electrolyte. Land Battery Tester (Land CT 2001A,

Wuhan, China) was applied to record the charge/discharge performance of the cells. The thickness of the cathode materials was about 10  $\mu m$  with the mass loading of 2  $mg\ cm^{-2}$ .

## 3. Results and discussion

Scheme 1 shows the preparation process of porous  $V_2O_5$  nanosheets by a two-step sintering method, in which Ketjen black (KB) carbon was used as hard templates. The selection of KB carbon as the hard templates was due to their high porosity and easy expansion in aqueous solution. After stirring at room temperature for 12 h, the KB carbon expands and absorbs the liquid solution into the porous structures sufficiently to make the slurry (see step I). After drying and annealing in reducing atmosphere (Step II), the vanadyl oxalate was decomposed into  $V_2O_3$  and located within the porous scaffold of KB carbon to make the  $V_2O_3$ /carbon composite (Step III). After calcination in air, the KB carbon was removed and  $V_2O_3$  was oxidized into  $V_2O_5$  to produce the porous  $V_2O_5$  nanocrystallites (Step IV).

The obtained products after annealing in reducing atmosphere ( $Ar + H_2$ ) were characterized and the results are shown in Fig. 1. Fig. 1a shows the powder X-ray diffraction (XRD) patterns for the  $KB@V_2O_3$  composite. All of the Bragg reflections are unambiguously indexed to Karelite  $V_2O_3$  (JCPDS card 85-1403), without any additional diffraction peaks. No obvious diffraction peak related to the porous carbon was found, which indicates KB carbon was in amorphous state within the composite. Fig. 1b shows the TG and DSC curves of  $KB@V_2O_3$  conducted in ambient atmosphere. The weight of the samples (initially dried at 100 °C for 2 h) we used to perform TG is 12.41 mg. The initial weight loss (1.85%) was attributed to the evaporation of physical or chemical absorbed water and the followed weight increase can be assigned to the oxidation of  $V_2O_3$ . The fast weight loss between 350 and 400 °C was attributed to the burning out of Ketjen black. According to the TG analysis result, the weight percentage of  $V_2O_3$  in the precursor composite was calculated to be 87.2%. Fig. 1c shows the TEM image of the as-synthesized  $KB@V_2O_3$  composite. The  $V_2O_3$  nanoparticles were of a diameter less than 50 nm and distributed homogeneously within the KB carbon substrates. The small particle size and the uniform size distribution are attributed to the existence of KB carbon, which limits the particle growth at high temperature (600 °C). The composite is composed of polycrystalline  $V_2O_3$  and amorphous carbon substrates (see Fig. 1d).

Raman spectrum (Fig. 2) was applied to investigate the amorphous carbon in the as-obtained  $KB@V_2O_3$  composite. Two peaks at about 1352  $cm^{-1}$  and 1595  $cm^{-1}$  are usually associated with the D-band (K-point phonons of  $A_{1g}$  symmetry) and G-band ( $E_{2g}$  phonons of  $sp^2$  carbons). The intensity ratio of the G- and D-bands is  $I_G/I_D = 1.02$  for the as-obtained composite. The intensity of the D-peak is relatively high, which indicates the carbon on the  $KB@V_2O_3$  composite is disordered.

After annealing in air, the vanadium precursor ( $KB@V_2O_3$ ) can be converted into porous  $V_2O_5$  nanomaterials. The phase of vanadium oxide nanosheets was identified by X-ray diffraction (XRD) and the Rietveld refinement. Fig. 3a shows the experimental and refined spectra along with the difference curve. The lattice parameters were calculated as  $a = 11.49383\ \text{\AA}$ ,  $b = 3.56081\ \text{\AA}$ ,  $c = 4.37041\ \text{\AA}$ , (orthorhombic, space group  $Pmmm(59)$ ). Although the peak positions matches quite well, the intensities of different peaks various at different extent. The difference may be attributed to the crystallinity difference prepared by different methods or the preferential crystal growth of  $V_2O_5$ . The morphologies of the  $V_2O_5$  nanosheets are characterized by FESEM and TEM. As shown in Fig. 3b, small voids between the neighboring particles are formed. This is believed to be produced by the burning-out of Ketjen black

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