Synthesis of V_2O_5 nanoparticles: cathode materials for lithium-ion batteries

G NAGARAJU^{1,*}, T JAYALAKSHMI¹, S ASHOK² and K MANJUNATH³

¹Energy Materials Research Laboratory, Department of Chemistry, Siddaganga Institute of Technology (Affiliated to Visvesvaraya Technological University, Belgaum), Tumakuru 272103, India

²Department of Chemistry, School of Engineering, Dayananda Sagar University, Bangalore 560068, India

³Centre for Nano and Material Sciences, Jain University, Bangalore 562112, India

*Author for correspondence (nagarajugn@rediffmail.com)

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Abstract. Vanadium oxide-based nanomaterials have been showing great promise as cathode materials for lithium-ion batteries (LIBs). Among these, nanostructured V_2O_5 shows a high discharge capacity due to its layer structure and thermodynamically stable form. This work reports the synthesis of V_2O_5 nanoparticles *via* a simple low temperature hydrothermal method using ammonium vanadate and quinol. The reduced size of V_2O_5 has resulted in the blue shift of the absorption spectrum. The material has been examined as a cathode material to study lithium intercalation/deintercalation. It shows an initial discharge capacity of 310 mAh g^{-1} at a current density of 0.1 mA g^{-1} at 1.5–4 V and retains a specific discharge capacity of 184 mAh g^{-1} even after 58 cycles. The present study manifests how the nanostructured size V_2O_5 could be applied as a high-energy cathode material for LIBs.

Keywords. V_2O_5 ; hydrothermal; calcination; nanoparticles; Li-ion battery.

1. Introduction

In recent years vanadium oxide-based materials have received great attention for applications in lithium-ion batteries (LIBs) due to their special structural characteristics. Vanadium oxides usually have different elemental composition, abundant oxidation states and various coordination polyhedral structures which entail the control of structural parameters to further improve their structure-directed properties [1–3]. These vanadium oxides show both p-type and n-type conductivity depending on the substrate and temperature. V_2O_5 is the most stable compound with the highest oxygen concentration among the family of vanadium oxides and it can be built from corner-sharing and edge-sharing VO_6 octahedra. The deformed VO_6 octahedra form wrapped layers, in which oxide anions are shared by the adjacent octahedral. From this structure, it is assumed that weak Van der Waals type of interaction exists between the layers. Thus V_2O_5 exhibits a layer structure and has been used as an electrode material for LIBs due to its high-energy density and low-cost [4,5]. In V_2O_5 , atoms are linked to one another *via* covalent bonds to form two-dimensional layers that are stacked together through the weak Van der Waals interaction. This allows the introduction of the foreign ions or molecules into the interlayer resulting in a good diffusion channel for Li-ions [6].

Many methods are available for the synthesis of V_2O_5 nanorods, nanotubes, nanobelts, nanowires, nanofibres etc.,

for using them as a cathode material for LIBs [7–12]. The literature survey shows that nanostructured V_2O_5 can be easily synthesized through a hydrothermal method [12]. Hydrothermal synthesis is a powerful tool to convert bulk materials into high quality nanostructured materials. The benefits of this method are: (i) takes place at relatively low temperature, (ii) environmentally benign reaction conditions and (iii) controllable morphology and size distribution [13]. In this paper, we reported a cost-effective, template free and low-temperature hydrothermal method to synthesize V_2O_5 nanoparticles using quinol. Previously, we have reported the synthesis of VO_2 nanoparticles from bulk V_2O_5 *via* a hydrothermal method [14] where quinol has been used as a reducing agent to convert V_2O_5 to VO_2 (B) according to the following equation:

In the present study, we have extended the same synthetic protocol [14] for the preparation of V_2O_5 nanoparticles from hydrothermally derived 1-D VO_2 , wherein VO_2 has been subjected to calcination at 500°C for 1 h

Figure 1. (a) PXRD pattern and (b) Rietveld fitted pattern of V_2O_5 nanoparticles obtained by the heat treatment of hydrothermally derived material.

Table 1. Refined structural parameters of V_2O_5 nanoparticles.

Crystal structure		Orthorhombic		
Space group		$Pmmn$		
Lattice parameters (Å)		$a = 3.561(4)$, $b = 11.501(14)$, $c = 4.378(7)$		
$\chi^2 = 1.73$	$R_p = 6.27$	$R_{Bragg} = 5.671$	$R_{WP} = 8.2$	$R_{exp} = 7.44$
Volume of unit cell/formula unit (Å ³)		178.0022		
Atom	x	y	z	B_{iso} occupancy
V ₁	0.25	0.0965(3)	0.3858(7)	1.94(9)1 (4e)
O ₁	0.25	0.558(6)	0.5077(3)	−1.32(8)1 (4e)
O ₂ -	0.25	0.103(4)	0.492(5)	0.987(7)1 (4e)
O ₃	0.25	0.25000	0.4964(4)	0.725(3)1 (2a)

2. Experimental

Commercial V_2O_5 and quinol were procured from Merck, India and used as received. V_2O_5 (181 mg) was dispersed in 40 ml of aqueous quinol solution (1 mmol) by stirring for 2 h. The resulting yellowish suspension was transferred to a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 180°C for 1 day. After the hydrothermal treatment, the autoclave was cooled to room temperature naturally and the resulting solid product was retrieved from the solution by centrifugation and washed with distilled water and ethanol several times and dried in a hot air oven. The dried sample was calcined to 500°C for 1 h.

3. Characterization

Powder X-ray diffraction (PXRD) data were recorded on a Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu-K α (1.5418 Å) radiation. The Fourier

transform infrared (FTIR) spectrum of the sample was collected using a Bruker Alpha-P spectrometer. The absorption spectrum of the sample was measured on a Perkin Elmer Lambda-750 UV–visible spectrophotometer. The morphology of the product was examined by using a JEOL-JSM-6060 scanning electron microscope (SEM).

The electrodes were prepared by mixing V_2O_5 nanoparticles (active material), acetylene black (conducting material) and polyvinylidene fluoride (binder) in a weight ratio of 70:20:10. The slurry was prepared using *N*-methyl-2-pyrrolidone as a solvent. The slurry was coated uniformly on circular aluminium foil of 16 mm diameter as a current collector and finally dried in a vacuum oven at 120°C for 1 day. Lithium metal (16 mm diameter) was used as the counter and reference electrode. 1 M $LiPF_6$ in ethylene carbonate and dimethylene carbonate (1:1 v/v) was used as the electrolyte. Swagelok-type cells were used to assemble the cells in an argon filled glove box (Jacomex). Cyclic voltammogram (CV) measurements were performed using CHI 660C (CH Instrument Electrochemical workstation) between 1.5 and 4 V vs. Li^+/Li at a scan rate of 0.5 mV s^{−1}.

Galvanostatic discharge–charge measurements were performed using an Arbin BT-2000 battery testing unit between 1.5 and 4 V at a current density of 0.1 mA g^{-1} .

4. Results and discussion

Figure 1a shows the PXRD pattern of the product synthesized at 180°C for 1 day followed by calcination at 500°C for 1 h. All the diffraction peaks resemble the orthorhombic phase of V_2O_5 with the space group $Pmmn$. No impurity peaks were detected indicating the purity of the sample. The refinement of the sample was calculated using the Fullprof Rietveld method. The refined pattern and structural parameters are shown in figure 1b and table 1. The obtained lattice parameters, $a = 3.5536 \text{ \AA}$, $b = 11.4698 \text{ \AA}$ and $c = 4.378 \text{ \AA}$, and reliability factors $\chi^2 = 1.73$, $R_p = 6.27$ and $R_{wp} = 8.2$ are consistent with the reported values of orthorhombic V_2O_5 (JCPDS 41-1426).

The crystallite size of V_2O_5 nanoparticles was calculated using Scherrer's formula and found to be 50–60 nm:

$$D = 0.9\lambda / \beta \cos \theta$$

where λ is the wavelength of the X-ray, β is the full-width at half-maximum of the diffraction peak and θ is the angle of diffraction.

Figure 2 shows the FTIR spectrum of V_2O_5 nanoparticles. The absorption bands between 400 and 1050 cm^{-1} can be indexed to various vibrations of V–O type. The peak at 1018 cm^{-1} is a characteristic stretching vibration of the terminal V=O group. The bands located at 586 and 833 cm^{-1} are due to the symmetric and asymmetric vibrational modes of the V–O–V stretching in V_2O_5 respectively [15]. UV–visible

Figure 2. FTIR spectrum of V_2O_5 nanoparticles.

Figure 3. UV–visible absorption spectra of (a) V_2O_5 nanoparticles and (b) standard V_2O_5 .

spectrum (figure 3) shows well-defined absorption band edges at 520 and 470 nm for commercial V_2O_5 and V_2O_5 nanoparticles, respectively. The absorption band at 470 nm corresponds to the $n \rightarrow \pi^*$ transition of V=O group of V_2O_5 . The shifting of maximum absorption peak to lower wavelength similar to commercial V_2O_5 indicates the reduced size which is consistent with the reported literature [16].

Furthermore, the direct band gap (E_g) was also estimated using Wood and Tauc method [17]. The absorption coefficient α , due to inter-band transition near the band-gap is well described as

$$\alpha \hbar \omega = B(\hbar \omega - E_g)^2$$

$\hbar \omega$ is photon energy and E_g is an optical gap. This Tauc plot defines the optical properties in amorphous semiconductors (figure 3). The estimated values of band gap energies of commercial and nanostructured V_2O_5 are found to be ~ 1.87 and $\sim 2.15 \text{ eV}$ which is in good agreement with the reported literature [18]. The hybridization with different orientations of oxygen $2p$ and vanadium $3d$ orbitals in the distorted octahedral symmetric structure, C_{4v} , two broad structures of the pre-edge absorption, separated by about 2.1 eV , are attributable to the t_{2g} -like and e_g -like structures.

The morphology of the prepared V_2O_5 nanoparticles has been analysed using SEM and is shown in figure 4. It is clear from the SEM image that the material exhibits particle like morphology and the size of the V_2O_5 nanoparticles is found to be 50 – 150 nm .

4.1 Electrochemical performance

In order to examine the electrochemical properties of V_2O_5 nanoparticles, CV experiment was carried out. V_2O_5 electrode with two lithium ions has a favourable capacity performance with reversible phase formation, whereas, in the case of three lithium ions insertion, it was found that irreversible formation will lead to its control. For this reason we have applied

Figure 4. SEM images of V_2O_5 nanoparticles obtained by the heat treatment of hydrothermally derived material.

Figure 5. CVs at a scan rate of 0.5 mV s^{-1} in the voltage range of 1.5–4 V.

Figure 6. V_2O_5 cycling stability and Coulombic efficiency over 60 cycles at 0.1 mA g^{-1} .

Figure 7. Galvanostatic discharge/charge profiles of the V_2O_5 electrode at 0.1 mA g^{-1} .

the current for two lithium ions. Figure 5 shows the CV curves of V_2O_5 nanoparticles for lithiation-delithiation in the voltage range of 1.5–4 V at a scan rate of 0.5 mV s^{-1} . Two pairs of well-defined reduction and oxidation peaks were observed, which is very similar to the one reported by Liu and Yang for V_2O_5 [19]. As clearly shown in figure 5, during cathodic scan, two distinct peaks were obtained around 3.2 and 2.1 V, which indicates a multi-step lithiation and the corresponding phase was transformed from $\alpha\text{-}V_2O_5$ to $\delta\text{-Li}V_2O_5$ (3.2 V) and $\gamma\text{-Li}_2V_2O_5$ (2.1 V). In the following anodic scan, two peaks were observed at 2.8 and 3.5 V vs. Li/Li⁺ and are ascribed to the deintercalation of the second and first lithium ions [7]. The insertion/extraction behaviour of lithium ions thus can be tentatively expressed as

Table 2. Comparison of battery performances of nanostructured V_2O_5 prepared by different methods.

No.	Material	Reaction conditions	First specific capacity	Specific capacity after n th cycle	Ref.
1	Hierarchical sisal-like V_2O_5	Hydrothermal method at 180°C for 20 h	255 mAh g ⁻¹	180 mAh g ⁻¹ after 400 cycles	[10]
2	V_2O_5 nanowires	Via hydrothermal method at 230°C for 12 h	200 Ah cm ⁻²	80 Ah cm ⁻² after 1000 cycles	[11]
3	V_2O_5 nanoparticles	Rice husk carbon mediated calcinations	250 mAh g ⁻¹	230 mAh g ⁻¹ after 50 cycles	[20]
4	V_2O_5 hollow structures	Solvothermal treatment	273 mAh g ⁻¹	189 mAh g ⁻¹ after 50 cycles	[21]
5	V_2O_5 nanorod assemblies	Microwave-assisted hydrothermal synthesis	275 mAh g ⁻¹	175 mAh g ⁻¹ after 50 cycles	[22]
6	V_2O_5 sheets	Organics-assisted pyrolysis method	310 mAh g ⁻¹	230 mAh g ⁻¹ after 50 cycles	[23]
7	V_2O_5 nanobelts	180°C for 2 days	288 mAh g ⁻¹	191 mAh g ⁻¹ after 6th cycle	[24]
8	V_2O_5 nanobelts	180°C for 7 days	390 mAh g ⁻¹	300 mAh g ⁻¹ after 8th cycle	[25]
9	V_2O_5 nanowires	200°C for 5 days	280 mAh g ⁻¹	22 mAh g ⁻¹ after 40 cycles	[19]
10	V_2O_5 nanobelts	180°C for 1 day	280 mAh g ⁻¹	235 mAh g ⁻¹ after 14 cycles	[26]
11	V_2O_5 nanowires	205°C for 4 days	130 mAh g ⁻¹	90 mAh g ⁻¹ after 50 cycles	[27]
12	V_2O_5 nanoparticles	180°C for 1 day	310 mAh g ⁻¹	184 mAh g ⁻¹ after 58 cycles	Present work

Figures 6 and 7 depict the discharge–charge curves, cycle performance and discharge–charge profile for an electrode composed of V_2O_5 nanoparticles at 1.5–4 V. The initial discharge capacity was found to be 310 mAh g⁻¹ and it is higher than the theoretical capacity. It still retained a specific discharge capacity of 184 mAh g⁻¹ even at 58 cycles. The electrochemical performance of V_2O_5 nanoparticles depends on various parameters including synthesis conditions, morphology, current rate etc. For instance, Naiteng *et al* [10] have synthesized hierarchical sisal-like V_2O_5 via hydrothermal method at 180°C for 20 h using polyoxyethylene-20-cetyl-ether as the surfactant to examine electrochemical performances. They found that it shows an initial discharge capacity of 255 mAh g⁻¹ and retains its discharge capacity of 180 mAh g⁻¹ after 400 cycles. Yue *et al* [11] have synthesized V_2O_5 nanowires via a hydrothermal method at 230°C for 12 h. It shows initial areal capacity of 200 Ah cm⁻² and retains 80 Ah cm⁻² even after 1000 cycles. Kai *et al* [20] have reported the synthesis of V_2O_5 nanoparticles using rice husk carbon as templates by calcinating bulk V_2O_5 at 600°C for 45 min. They observed that it shows initial discharge capacity of 250 mAh g⁻¹ and retains its discharge capacity of 230 mAh g⁻¹ even after 50 cycles at a current density of 300 mA g⁻¹. Xingyuan and his group [21] prepared V_2O_5 hollow structures via solvothermal treatment followed by thermal annealing shows an initial discharge capacity of 273 mAh g⁻¹ and continues to 189 mAh g⁻¹ after 50 cycles at 0.2 C rate. Jing and co-workers [22] have synthesized V_2O_5 nanorod assemblies by microwave-assisted hydrothermal synthesis, combined with annealing treatment which exhibits an initial discharge capacity of 275 mAh g⁻¹ and retains 275 mAh g⁻¹ after 50 cycles at a current density of 100 mA g⁻¹. Haoyang [23] synthesized V_2O_5 sheets

by a facile one-pot organic-assisted pyrolysis method. It exhibits an initial discharge capacity of 310 mAh g⁻¹ and retains 230 mAh g⁻¹ after 50 cycles at a current density of 0.1 C. Li *et al* [24] reported a hydrothermal route to prepare V_2O_5 nanobelts and found the initial discharge capacity of 288 mAh g⁻¹ but reaches 225 mAh g⁻¹ after the 6th cycle in the voltage range of 1.5–4 V. Reddy *et al* [25] reported the synthesis of V_2O_5 nanobelts at 180°C for 7 days. It shows the initial discharge capacity of 390 mAh g⁻¹, and reaches 300 mAh g⁻¹ after the 8th cycle. Liu *et al* [19] synthesized V_2O_5 nanowires by a hydrothermal method at 200°C for 5 days which showed an initial discharge capacity of 280 mAh g⁻¹ and reaches 22 mAh g⁻¹ after 40 cycles. Li and group [26] synthesized V_2O_5 nanobelts through a hydrothermal method at 180°C for 1 day in acidic medium which showed an initial discharge capacity of 280 mAh g⁻¹ and reaches 235 mAh g⁻¹ after 14 cycles. Nagaraju *et al* [27] synthesized ultra-long V_2O_5 nanowires by a hydrothermal method at 205°C for 4 days which showed an initial discharge capacity of 130 mAh g⁻¹ and reaches 90 mAh g⁻¹ after 50 cycles. A comparison of LIB performance of V_2O_5 nanostructured materials prepared by different methods is shown in table 2. It clearly shows that the performance of V_2O_5 nanostructured material depends on the method of synthesis, experimental condition, applied current density, etc.

The high specific discharge capacity indicates a high utilization rate of V_2O_5 nanoparticles, which is derived from a high interfacial contact area between electrode-electrolyte and a shortened lithium ion diffusion and electron transportation distance [28]. The interlayer space renders the possibility for guest ion intercalation and lithium ion intercalates into V_2O_5 . The multi-step transformation may destroy the

partial fracture of their shapes partially and structural degradation takes place after redox cycles resulting in increased cell resistance. This could be one of the reasons for the gradual reduction of capacity by cycle repetition. This has been observed during the charge–discharge process of other V_2O_5 nanostructures [10]. Practically the electrochemical performance of V_2O_5 in LIBs still greatly suffers from limited cycling ability, due to vanadium dissolution and the kinetic limitations for deep discharge that arises from the irreversible phase transition [5]. High degree of crystallinity could indeed improve electrode performance by providing pathways for ionic diffusion, releasing strain during the diffusion process. Small crystallites have poor strain tolerance and could offer high barriers to intercalation of Li^+ , reducing material utilization despite the short diffusion lengths.

5. Conclusions

V_2O_5 nanoparticles have been prepared by a simple low temperature hydrothermal technique. The obtained V_2O_5 has an orthorhombic phase. FTIR studies show the characteristic bands at 586 and 833 cm^{-1} due to the symmetric and asymmetric vibrational modes of V–O–V stretching. Electrochemical properties of V_2O_5 show the specific discharge capacity of 184 mAh g^{-1} even after 58 cycles at 1.5–4 V. The present study shows V_2O_5 nanoparticles could be used as one of the better cathode materials for LIBs.

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