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Enhanced electrochemical performance of W incorporated VO_2 nanocomposite cathode material for lithium battery application

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ABSTRACT

We report the synthesis, characterization, and performance evaluation of tungsten (W) incorporated vanadium oxide (VO_2) nanocomposite cathode material for improved lithium storage performance. VO_2 nanorods, 100–200 nm in diameter and 1–3 μm in length are synthesized using a hydrothermal method. W incorporation at different weight percent results in the VO_2 morphology shifting from rods to a sheet type structure. The lithium storage performance of VO_2 has improved remarkably by increasing the loading of W to an optimal level, which influence the intercalation/ deintercalation of lithium ions into the expanded lattices of VO_2. The maximum specific capacity observed for the optimal VO_2/W_4 composite was 381 mAh/g at a current density of 0.1 C. Cyclic voltammetry measurements showed the presence of an electroactive V^{3+}/V^{4+} redox couple, leading to lower peak separation and voltage polarization differences. Superior charge storage performance was observed with the VO_2/W_4 composite as compared to the VO_2 based devices.

1. Introduction

Lithium-ion batteries (LIBs) are attractive because of their high energy density, good cycle life, and environmental friendliness [1,2]. The overall charge storage properties of LIBs depend on the materials used for the cathode, anode, and electrolyte. To improve the properties of the electrode material many approaches have been employed, including surface modification, stabilization of lattice structure by mixed metal composites, and the use of nanoparticles to increase surface area [3].

Metal oxides are interesting materials because of their high stability in electrochemical storage performance and unique charge transport properties [4]. Among the transition metal oxides, vanadium based oxides have received much attention due to their diverse chemical structure and high specific charge capacity [5]. Vanadium metal centre exists in different oxidation state [6] within the oxide lattice from V^{+2} to V^{+5} with many metastable forms such as VO_2 (A), VO_2 (B), $V_3O_7{\cdot}H_2O$, along with other stable structures [7–9] such as V_6O_{13} and V_2O_5. Even though, all such materials showed good lithium storage capacities (200 mAh/g), they suffer from irreversible structural changes and poor electrical conductivities which reduce the rate of charge/discharge and cycling performance of the devices over time.

The performance of metal oxide based materials is usually improved by incorporating suitable cations into the lattice. For example, incorporation of a small amount of metal ions such as [10–13] Ti^{4+}, Zn^{2+}, Cr^{2+} and Mg^{2+} into the VO_2 lattice led to significant changes in the crystal structure and improved thermochromic properties [14]. Similarly, when W is incorporated into VO_2 lattice undergoes significant expansion (ionic radii of $V^{4+} = 0.58$ Å, ionic radii of $W^{6+} = 0.60$ Å) with increased conductivity. Such lattice changes alter the optical and electrical properties of VO_2. In

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particular, the enhanced lattice plane spacing is useful for the insertion/extraction of smaller ions such as lithium [15,16].

In this study, different loading percentage of W was used to obtain the optimum storage properties of VO_2/Wx composites. Pristine VO_2 and VO_2/Wx composites were prepared with different morphologies and the lithium storage performances were evaluated. The optimum percentage of W incorporated inside the VO_2 lattice showed the best lithium storage performance compared to the reported data (Table S1) in the literature for VO_2.

2. Experimental section

2.1. Synthesis of VO_2 (B)

Vanadium pentoxide (0.2 g, 1.1 mmol) powder was dispersed in water (50 mL) and sonicated for 30 min followed by the addition of citric acid monohydrate (0.3 g, 1.4 mmol). The mixture was heated for an hour at 75 °C which led to the formation of a dark green solution. The solution was transferred to a 100 mL Teflon lined stainless steel autoclave, sealed, heated at 200 °C for 12 h and cooled to room temperature. The dark green solid obtained after centrifugation was washed with copious amounts of water (3 × 100 mL), followed by methanol (2 × 100 mL) and dried at 60 °C overnight.

2.2. Synthesis of W incorporated VO_2 (B) (VO_2/Wx)

To synthesize W incorporated vanadium composites (VO_2/Wx), the required amount of ammonium paratungstate $(NH_4)_{10}(H_2W_{12}O_{42}\cdot 4H_2O)$ (11.4 mg, 0.0036 mmol) was mixed with V_2O_5 (0.2 g, 1.1 mmol) in water (50 mL) and sonicated for 30 min. Citric acid monohydrate (0.3 g, 1.4 mmol) was added to the above mixture and heated at 75 °C to form a dark green solution. After one hour, the mixture was transferred to 100 mL Teflon lined stainless steel autoclave, sealed, heated at 200 °C for 12 h and cooled to room temperature. The black solid obtained after centrifugation was washed with copious amounts of water (3 × 100 mL), followed by methanol (2 × 100 mL) and dried at 60 °C overnight. Elemental analysis and energy-dispersive X-ray (EDX) spectroscopic studies showed the presence of vanadium, tungsten and oxygen in the black solid.

2.3. Electrochemical characterization

Two electrode coin cells were employed to study the electrochemical lithium storage performances of VO_2/Wx. Pure VO_2 (B) sample was used for comparison. A slurry of 75 wt% VO_2/Wx or VO_2 (B), 15 wt% acetylene black, and 10 wt% polyvinylidenedifluoride (PVDF) binder in N-methylpyrrolidone (NMP) solvent were mixed and applied onto the copper current collector as a working electrode. A solution of $LiPF_6$ (1 M) dissolved in a mixture (1:1 v/v) of ethyl carbonate (EC) and diethylcarbonate (DEC) was used as an electrolyte and Li metal was used as both the reference and counter electrodes. The active material loading for all electrodes was between 1.2 and 1.5 mg/cm^2. The cells were assembled inside a glove box filled with argon gas and the galvanostatic discharging/charging measurements were performed by means of constant current mode cycling over a potential range of 3.3–1.0 V vs Li^+/Li. The observed capacities were normalized to VO_2 (B) content and reproducibility of the data was tested.

2.4. Material characterization

The sample morphologies were characterized by a field emission scanning electron microscope (FESEM, Zeiss Merlin) operating at a variable voltage of 1–10 kV with energy-dispersive X-ray spectroscopy (EDX, Bruker XFlash 6). Information about the crystallinity of the samples was obtained using a powder X-ray diffractometer (XRD, Bruker D2 PHASER) using Cu Kα radiation at 40 kV and 30 mA from a 2θ angle of 10–60°. FT-IR measurements were done by a Bruker ALPHA FT-IR spectrophotometer with 4 cm^{-1} resolution in the spectral range of 500–4000 cm^{-1} using KBr as the matrix. Transmission electron microscopy (TEM) images were recorded using a JEOL 2010 microscope operated at 200 keV. X-ray photoelectron spectroscopy (XPS) measurements were done using an Omicron EA125 electron energy analyzer. The positions of the peaks were referenced to the surface C–C or C–H bond at 284.5 eV at a base pressure around 2×10^{-10} mbar. Raman spectra were taken on a Horiba Jobin Yvon Raman spectrophotometer. Metal ion concentrations in the sample were measured quantitatively using a Dual-view Optima 5300 DV Inductively coupled plasma-optical emission spectroscopy (ICP-OES) system. Cyclic voltammetry (CV) was conducted with a Bio-logic SA, Model VMP3. Sorption isotherms (BET) were recorded using Nova 2200e surface area and pore analyzer (Quantachrome, USA), where prior to the experiment, the samples were degassed at 120 °C overnight.

3. Results and discussion

3.1. Morphological and structural characterization

VO_2/Wx composites incorporated with 4, 8, 10, 13, 17 and 21 wt% of W (referred as VO_2/W1, VO_2/W2, VO_2/W3, VO_2/W4, VO_2/W5 and VO_2/W6, respectively), were synthesized using hydrothermal treatment. The morphology of as prepared samples were examined using high resolution FESEM and TEM microscopy experiment, the results of which are shown in Fig. 1. Pure crystals of VO_2 appeared as nanorods of 1–3 μm in length with a mean diameter of 100–200 nm (Fig. 1A). Upon incorporation of 4 wt% (VO_2/W1) and 8 wt% of W (VO_2/W2), the morphology changed from nanorods to plate-type heterogeneous structures (Fig. S1). The dimensions of the plates were not uniform and exhibited characteristic lengths of a few hundred nm and width of 10–15 nm. Predominantly sheet type structure was observed in samples (Fig. S1C) for loading of W close to 10 wt % (VO_2/W3). At higher W weight percent (i.e. 13%), thinner sheet-type morphology was observed for VO_2/W4 composites (Fig. 1B) [17]. No significant changes were observed for the morphology when the amount of W was further increased to 17 and 21 wt% (i.e. VO_2/W5 and VO_2/W6, Fig. S1).

Quantitative analyses of wt % of elemental W in all composites were done using both energy-dispersive X-ray (EDX) spectroscopy and ICP-OES spectroscopy method. The results from both the techniques has indicated the presence of V, W, and O to be at the expected quantities (Fig. S2). The values obtained from EDX matched well with the values obtained using ICP-OES methods (Table 1).

The observed morphologies were further confirmed using TEM analysis and was compared to monitor changes in the morphology and crystallinity of composites with and without W incorporation into the VO_2 lattice (Fig. 2).

From the TEM image, the dimension of VO_2 nanorods shows width of ~100 nm and length ~1–2 μm (Fig. 2A). In VO_2/W4, majority of the particles exists as distorted nanorods or extended flakes (Fig. S3). The TEM micrographs also indicated that addition of W induces subtle changes in the morphology of VO_2 crystals. No specific changes in shape or morphology were observed after increasing the percentage of W to 10 wt% (Figs. S3–S5). To confirm the crystallinity and lattice structure of VO_2, HRTEM (Fig. 2C and D) micrographs and selected area electron diffraction pattern (SAED) were studied (Inset: Fig. 2E, F). Elemental mapping was conducted