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The richness of V_2O_5 polymorphs as superior cathode materials for sodium insertion

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ABSTRACT

In this paper, a special emphasis is given to the newly obtained electrochemical properties at room temperature of the two-dimensional ε'- and γ'-V_2O_5 polymorphs as sodium intercalation compounds. The structural peculiarities and electrochemical properties of each phase are presented. A full electrochemical and structural reversibility is demonstrated for both compounds upon sodium insertion at high voltage of 2.8 V. This noticeable voltage enhancement (+1 V) compared to α-V_2O_5 cathode is ascribed to the specific layers organization consisting of bilayered and puckered sheets in ε'-V_2O_5 and γ'-V_2O_5, respectively. Promising data, with large capacities (from 120 to 200 mAh g^{-1}) and an excellent cycle life allow to identify new high performance V_2O_5- forms as positive electrode materials for sodium-ion batteries.

1. Introduction

Due to the cost and low availability of Li sources, Na-ion batteries (SIBs) are attracting considerable interest as tomorrow's world batteries. Compared to Li-ion batteries (LIBs), the number and performance of electrode materials for SIBs are limited but progress in Na intercalation grows very rapidly [1]. In this respect, one of the most challenging problems involves the identification of suitable cathode materials. Numerous sodiated oxides were studied as potential cathode materials for (NIBs): Na_xCoO_2 [2], $Na_{2/3}(Fe_{1/2}Mn_{1/2})O_2$ [3], $NaMnO_2$ [4], $NaCrO_2$ [5], Na_xVO_2 [6,7], $Na_{1.5+y}VO_3$ [8], $Na_{0.33}V_2O_5$ [9,10]. However, a good compromise between a high stable capacity and a high voltage has not yet been reached.

Layered materials with Van der Waals interlayer spacing constitute ideal frameworks for intercalation reactions of guest cationic species from which high discharge-charge rate and minimum structural distortions can be expected. While orthorhombic V_2O_5 was identified in the 70's as a promising cathode material for secondary Li batteries [11], it is only very recently that Na insertion was addressed in the α-V_2O_5 phase at room temperature [12]. The irreversible formation of α'-NaV_2O_5 was shown with interesting sodium intercalation properties (120 mAh g^{-1} near 1.6 V vs. Na^+/Na at C/10 rate).

An alternative way to identify new attractive stable V_2O_5 polymorphs consists in considering the chemical removal of metallic species from vanadium pentoxide bronzes $M_xV_2O_5$. Such approach allows benefiting from the availability of new types of structures combined with a low amount of metallic species, thus optimizing the possible specific capacity. This strategy has been successfully applied to synthesize the two-dimensional ε'-V_2O_5 [13,14] and γ'-V_2O_5 polymorphs [15]. These polymorphs were obtained from the chemical removal of Cu or Li from the ε-$Cu_{0.9}V_2O_5$ and γ-LiV_2O_5 bronzes respectively by means of strong oxidizing agents. The original structure of the bronze precursors is kept upon the removal of metallic species and as a result, original bilayered stacking was reported by Garcia-Alvarado et *al.* for the ε'-V_2O_5 polymorph [13,14] and puckered layer stacking for γ'-V_2O_5 [15]. Promising performances for both materials were found toward lithium insertion: the ε'-polymorph was reported to reversibly accommodate up to 1.8 Li ions in the 4 V-1 V potential range [13,14] whereas the electrochemical lithium insertion in γ'-V_2O_5 was shown to occur at a higher

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voltage (3.6/3.5 V vs. Li^+/Li) [16,17]. However, in spite these favorable structural features and interesting electrochemical properties, the ε′-V_2O_5 phase has not yet been investigated as possible sodium insertion material. Electrochemical sodium insertion in γ′-V_2O_5 was explored very recently in our group [18]. An easy sodium accommodation was reported at high voltage, i.e. at 3.3 V vs Na/Na^+, in one step involving a maximum specific capacity of 145 mAh g^{-1}. This strongly differs from the properties of α-V_2O_5 phase showing Na insertion more than 1.5 V lower [12]. A strong kinetic limitation was nevertheless evidenced for the first charge process of γ′-V_2O_5, with a 60% efficiency at C/20 at room temperature. Hence, the rechargeable capacity did not exceed 60–80 mAh g^{-1}.

In this work, new data on the electrochemical sodium insertion in the γ′- and ε′-V_2O_5 polymorphs are reported. An appropriate nanosizing approach is applied to optimize the electrochemical properties of γ′-V_2O_5 in order to make the Na extraction process more quantitative to benefit from the high specific capacity of 145 mAh g^{-1}. As a result, the ball milled γ′-V_2O_5 material exhibits a great enhancement of the stabilized capacity of ≈ 120 mAh g^{-1}, i.e. twice that displayed by as prepared γ′-V_2O_5. We demonstrate also in this work that the bilayered ε′-V_2O_5 polymorph is a new high performance sodium insertion material, able to deliver a remarkable stable capacity of 200 mAh g^{-1} at a high average voltage of 2.8 V vs. Na^+/Na.

2. Experimental section

The lithium and copper bronzes precursors γ-LiV_2O_5 and ε-$Cu_{0.9}V_2O_5$ were synthesized in a first step. γ-LiV_2O_5 was prepared by the carbothermal reduction method [19]. ε-$Cu_{0.9}V_2O_5$ was prepared according to [13] by reacting the stoichiometric amount of V_2O_5 (MS company, 99.995%) and Cu powders of high purity (Aldrich 99.99%). The mixture is pelletized under a pressure of 5 tons cm^{-2} for 15 min. The pellet is then heat-treated at 630 °C for 3 h under argon atmosphere. After reaction, the pellet is grounded in an agate mortar in a glovebox to prevent any moisture contamination.

Deinsertion of Li and Cu from the γ-LiV_2O_5 and ε-$Cu_{0.9}V_2O_5$ bronzes, respectively, was performed by reacting 500 mg of the bronze in a solution of NO_2BF_4 (solid Alfa Aesar 96%) in acetonitrile (V_2O_5/NO_2BF_4 molar ratio 1/4) under stirring for 24 h at room temperature. After reaction and decantation, the supernatant liquid is removed by pipetting. Powder is then washed three times with acetonitrile, and then vacuum dried at 120 °C. Electrochemical titration using galvanostatic oxidation and chemical redox titration confirmed the 5+ oxidation state of vanadium in as prepared γ′-V_2O_5 and ε′- V_2O_5 powders. In addition, we observed a color change from brown to orange and black to orange, indicating the loss of the metallic properties for the totally deintercalated ε′- and γ′- phases, respectively.

A nanosizing approach was carried out to investigate the effect on the crystallite size reduction on the electrochemical performance of γ′-V_2O_5. The as prepared γ′-V_2O_5 powder was mechanically ball milled in a Fritsch Pulverisette P7 planetary ball mill at 700 rpm with the sequence 10 min mill, 10 min rest repeated three times to reach 30 min of milling time. Prior to milling, the γ′-V_2O_5 powder and stainless steel balls (1 g weight) with a diameter of 7 mm were loaded in the vial. The ball to powder weight ratio was 39:1. The ball milled sample is labelled γ′-V_2O_5-BM.

Electrochemical experiments were conducted in sodium half-cells consisting into 2032 coin-type cells with a Na foil as the negative electrode, an electrolyte of 1 M $NaClO_4$ in propylene carbonate (PC) containing fluoroethylene carbonate (FEC) additive (2% Vol.) and Whatman glass fiber separator.

The positive electrode is prepared by mixing 80 wt % of active material (γ′-V_2O_5, γ′-V_2O_5-BM or ε′-V_2O_5) with 7.5 wt % of acetylene black, 7.5 wt % of graphite and 5 wt % of PTFE as binder. About 6 mg/cm^2 of the active material is pressed on a stainless steel grid current collector. When indicated, multi-walled carbon nanotubes (CNTs) from Iolitec were also used as conductive agent in the following proportions: 15% CNTs, 80% active material, 5% PTFE. The CR2032 coin-cell is assembled in argon-filled glovebox. Galvanostatic experiments were performed at room temperature at different current densities (147 mA g^{-1} corresponds to 1C), using a VMP3 Biologic apparatus.

The X-ray diffraction and Raman analysis were carried out following this procedure: the electrodes were prepared to the required state by galvanostatic experiment. Equilibrium was considered to be reached when the drift in open-circuit voltage remained less than 0.1 mV h^{-1}. After reaching equilibrium, the cell was opened in the glovebox and the positive electrode was removed, rinsed with dimethyl carbonate (DMC) and placed in specifically designated airtight sample holders to be further analyzed by *ex-situ* X-ray diffraction and Raman spectroscopy. XRD measurements were carried out using a Panalytical X'pert pro diffractometer equipped with an X'celerator detector and a Co Kα radiation (wavelength λ = 1.7889 Å). Data are then processed on Eva software to score peaks then CelRef to calculate the lattice parameters. The Raman spectra were measured with a LaBRAM HR 800 (Jobin-Yvon-Horiba) Raman micro-spectrometer including Edge filters and equipped for signal detection with a back illuminated charge coupled device detector (Spex CCD) cooled by Peltier effect to 200 K. A He:Ne laser (632.8 nm) was used as the excitation source. The spectra were measured in back-scattering geometry. The resolution was about 0.5 cm^{-1}. A long distance 50X LWD objective was used to focus the laser light on sample surface to a spot size of 1 μm^2. To avoid local heating of the sample, the power of the laser beam was adjusted to 0.2–0.5 mW with neutral filter. To check the homogeneity, Raman spectra were recorded on 10 different spots of each electrode.

3. Results and discussion

3.1. Structural and electrochemical study of γ′-V_2O_5

The X-ray diffraction pattern of as prepared γ′-V_2O_5 (Fig. 1a) corresponds to an orthorhombic symmetry (*Pnma* space group; Z = 4) with the following unit cell parameters $a = 9.94$ Å; $b = 3.58$ Å; $c = 10.04$ Å, in agreement with previous reports [15,20]. γ′-V_2O_5 exhibits a layered structure composed of infinite ribbons made of VO_5 edges-sharing distorted pyramids oriented alternatively up and down (see inset in Fig. 1). These ribbons are linked to each other along the *a*-direction by one pyramid corner oxygen, forming puckered layers perpendicular to the *c*-axis, leading to a large interlayer spacing (5.02 Å in γ′-V_2O_5 against 4.37 Å in α-V_2O_5).

As shown in Fig. 1b, the X-ray diffraction pattern of γ′-V_2O_5-BM can be indexed in the same orthorhombic symmetry than the as prepared powder (Fig. 1b). The lattice parameters are very close to those of the as prepared sample: $a = 9.92$ Å, $b = 3.62$ Å; $c = 10.06$ Å. However, a broadening of the diffraction lines for the γ′-V_2O_5-BM powder reveals a decrease in the crystallite size.

The mean crystallite size (L) can be estimated from the Scherrer equation (1) [21] for the *hkl* diffraction peaks, after background correction of the diffraction pattern. K is the Scherrer constant related to crystallite shape, normally taken as 0.9. β is the XRD peak width at half-maximum height (FWHM), θ is the peak position, $\lambda_{K\alpha}$ is the X-ray wavelength.

$$L = \frac{K\,\lambda_{K_\alpha}}{\beta \cos\theta} \qquad (1)$$