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Research Paper

γ'-V_2O_5: A new high voltage cathode material for sodium-ion battery

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ABSTRACT

A new sodium insertion compound, γ'-V_2O_5, is prepared by the chemical oxidation of γ-LiV_2O_5 phase using NO_2BF_4 as oxidizing agent. Nearly one Na^+/γ'-V_2O_5 can be inserted in γ'-V_2O_5 involving the V^{5+}/V^{4+} redox couple at a high working potential of 3.3 V vs. Na^+/Na. With a maximum specific capacity of 145 mAh g^{-1}, γ'-V_2O_5 exhibits a high discharge rate capability with still 135 mAh g^{-1} at C/2 and 120 mAh g^{-1} at C. A strong kinetic limitation is nevertheless evidenced for the first charge process since a 60% efficiency at RT (C/20) is evidenced while a full Na extraction is allowed at 50 °C (C/60). However, an excellent capacity retention is demonstrated whatever the temperature and C rate: At room temperature, a stable capacity of 80 mAh g^{-1} is obtained at C/20 over 40 cycles and still 55 mAh g^{-1} at C/5 over 70 cycles; at 50 °C, a stable discharge capacity of 95 mAh g^{-1} is available at C/10 after 70 cycles. A detailed structural study is reported from X-ray diffraction and Raman spectroscopy measurements. A two phases mechanism involving the γ'-V_2O_5/γ-$Na_{0.7}V_2O_5$ system for $0 \leq x \leq 0.7$ followed by a single phase region for $0.7 < x \leq 0.97$ is evidenced. From the second cycle, sodium insertion-extraction is shown to proceed within the zero strain γ-$Na_xV_2O_5$ structure, which explains the remarkable cycling stability. These results demonstrate that γ'-V_2O_5 forms a new competitive cathode for sodium- ion battery.

1. Introduction

Lithium ion batteries (LIBs) have been the subject of intense research due to their high energy density and good cycling performance [1]. However, considering the low natural occurrence of Li in the upper continental crust (≈ 35 ppm), great concerns have been expressed over whether the available lithium reserves in the earth will be sufficient to meet the ever-growing requirements for LIBs. Therefore, there is a call for batteries based on more earth-abundant alkali metals such as Na-ion batteries (NIBs) which have the second-lightest mass-to-charge ratio in the ranks of alkali metals after lithium [2]. Indeed, Na has much larger natural occurrence (28 300 ppm in the lithosphere and 10 320 ppm in seawater) [3]. Furthermore, Na has similar intercalation chemistry to that of Li with a slightly higher redox potential (-2.71 V vs. SHE for Na^+/Na as compared to −3.02 V for Li^+/Li) that is redeemed by a lower cost, a greater extent of chemical safety and environmental friendliness [2,4,5]. These potential advantages explain the resurgence of research interest in NIBs chemistries in recent years [2,6–13]. 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 [14], $Na_{2/3}(Fe_{1/2}Mn_{1/2})O_2$ [15], $NaMnO_2$ [16], $NaCrO_2$ [17], Na_xVO_2 [18,19], $Na_{1.5+y}VO_3$ [20], $Na_{0.33}V_2O_5$ [21,22]. 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 of gest cationic species from which high discharge-charge rate and minimum structural distortions can be expected. Among them, vanadium pentoxide provides appealing prospects for use as advanced cathodes for secondary batteries. While orthorhombic V_2O_5 was identified very early as a promising cathode material for secondary Li batteries [23–25], studies concerning the use of V_2O_5 for sodium −based energy storage systems are limited. West et al. [26] reported the electrochemical intercalation of sodium into α-V_2O_5 at 80 °C using a polymer electrolyte. Capacities of 200 mAh g^{-1} were reported a low rate of C/25. Pereira-Ramos et al. [27] investigated the electrochemical behavior of α-V_2O_5 at 150 °C in $NaClO_4$ solutions in molten dimethyl sulfone, showing reversible Na insertion without severe structural changes. More recently, our group explored the electrochemical insertion of Na into α-V_2O_5 at

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room temperature (RT) in a 1 M $NaClO_4$/PC electrolyte [28]. 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). Nanostructured bi-layered V_2O_5 compounds prepared from a solvothermal method also exhibit remarkable capacities of 230 mAh g^{-1} available at an average voltage of 2.5 V with satisfactory cycle life [29]. All these promising electrochemical properties motivate the continued development of vanadium pentoxides as high performance cathodes for NIBs.

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 structure with various original layers stacking (single, puckered, double layered . . .) combined with a low amount of metallic species, thus optimizing the possible specific capacity. Cocciantelli et al. [30] successfully applied this strategy to obtain the γ'-V_2O_5 polymorph from chemical oxidation of the γ-LiV_2O_5 bronze. The structural [30,31] and vibrational features of γ'-V_2O_5 [31] have been previously reported. The γ'-V_2O_5 polymorph exhibits a lamellar structure composed of infinite ribbons made of VO_5 edges-sharing distorted pyramids with a large interlayer spacing (5.02 Å in γ'-V_2O_5 against 4.37 Å in α-V_2O_5). Moreover, electrochemical lithium insertion in γ'-V_2O_5 was found to occur at a higher voltage (3.6/3.5 V vs. Li^+/Li) than in α-V_2O_5 (3.4/3.2 V vs. Li^+/Li) [32,33]. However, in spite of these favorable structural features and interesting electrochemical properties toward lithium insertion, the γ'-V_2O_5 phase has not yet been investigated as possible sodium insertion material.

In this work, we explore for the first time the electrochemical sodium insertion in the γ'-V_2O_5 polymorph. We demonstrate that γ'-V_2O_5 is a promising cathode material, able to deliver interesting capacities and remarkable cycling stability at high voltage of 3.3 V vs. Na^+/Na. Furthermore, a detailed insight into the Na insertion mechanism is provided through X-ray diffraction (XRD) and Raman investigations during the discharge/charge processes.

2. Experimental section

γ'-V_2O_5 compound is obtained by chemical oxidation of γ-LiV_2O_5 synthesized by the carbothermal reduction method [34]. Deinsertion of Li from γ-LiV_2O_5 is performed in acetonitrile with a solution of NO_2BF_4 (solid Alfa Aesar 96%), molar ratio 1:4. The solution is maintained under stirring at RT for 24 h. After reaction and decantation, the supernatant liquid is removed by pipetting. Powder is washed three times with acetonitrile, and then vacuum dried at 70 °C for 24 h. Powder color changes from black to orange, which confirms the complete lithium deintercalation. Electrochemical titration using galvanostatic oxidation and chemical redox titration confirmed the 5+ oxidation state of vanadium in γ'-V_2O_5.

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 γ'-V_2O_5 positive electrode is prepared by mixing 80 wt % of active material with 7.5 wt % of acetylene black, 7.5 wt % of graphite and 5 wt % of PTFE as binder. About 16 mg/cm^2 of this mix is pressed on a stainless steel grid current collector. The CR2032 coin-cell is assembled in argon-filled glovebox. Galvanostatic experiments were performed at RT and 50 °C at different current densities in the voltage range 1.75 V to 4.00 V, using a VMP3 Biologic apparatus.

In order to investigate the sodium-driven structural changes of the positive electrode, the cells were discharged to the required composition by galvanostatic reduction at C/10 rate. 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

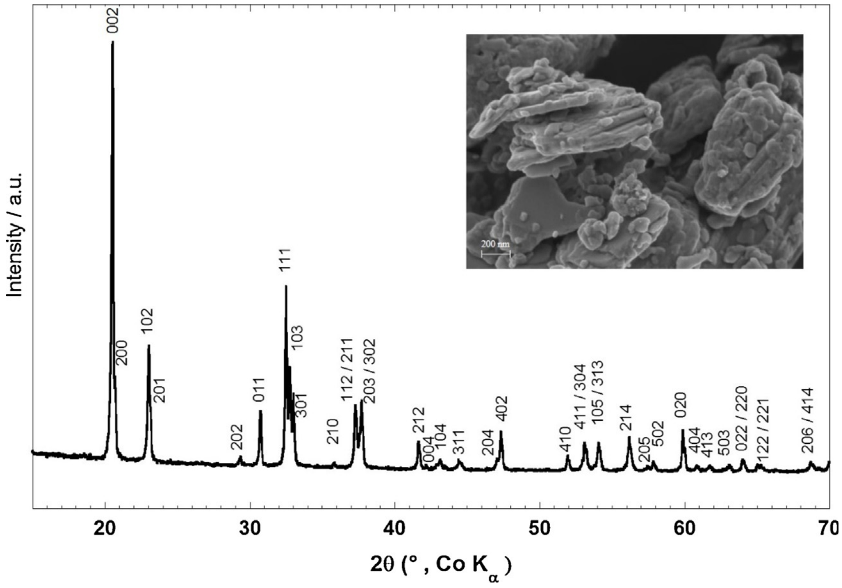

Fig. 1. X-ray diffraction pattern of γ'-V_2O_5. In inset: SEM micrograph of γ'-V_2O_5.