Electrochimica Acta 270 (2018) 224–235

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Lithium insertion in α′-NaV_2O_5: Na-pillaring effect on the structural and electrochemical properties

R. Baddour-Hadjean [a], [*], L.T.N. Huynh [a], [b], N. Emery [a], J.P. Pereira-Ramos [a]

[a] Institut de Chimie et des Matériaux Paris Est, ICMPE/GESMAT, UMR 7182 CNRS-Université Paris Est Créteil, 2 rue Henri Dunant, 94320 Thiais, France
[b] VNU-HCM Key Laboratory, Applied Physical Chemistry Laboratory (APCLAB), Vietnam National University, Ho Chi Minh City, Vietnam

ARTICLE INFO

Article history:
Received 20 February 2018
Received in revised form
9 March 2018
Accepted 13 March 2018
Available online 14 March 2018

Keywords:
Pillar effect
2D NaV_2O_5
Lithium insertion mechanism
Cycling performance
Lithium batteries

ABSTRACT

Electrochemically formed α′-NaV_2O_5 bronze is investigated here as cathode material for rechargeable lithium batteries. We show that the layered structure of this compound, with Na ions located between the V_2O_5 layers, allows the reversible insertion of 1 lithium/mole of bronze at an average voltage of 2.1 V vs. Li^+/Li. The Li insertion-extraction mechanism in α′-$Li_xNaV_2O_5$ is revealed thanks to *ex situ* XRD and Raman spectroscopy investigations. A narrow one-phase region occurs in the $0 < x \leq 0.2$ composition range while a two-phase mechanism prevails for $0.2 < x < 1$. Also, we show that 0.3 additional Li ions can be inserted according to a second solid solution domain, leading to the fully lithiated α′-$Li_{1.3}NaV_2O_5$ material. The structure of the α′-$LiNaV_2O_5$ is isomorphic to the pristine material. It is remarkable that only limited structural changes are found in the $0 < x \leq 1.2$ lithium composition range, consisting mainly in a 7% increase in the interlayer *c* parameter. A high structural reversibility is evidenced, which accounts for the remarkable stable capacities achieved whatever the C rate, near 120 mAh g^{-1} and 60 mAh g^{-1} at C/10 and 1C, respectively after 60 cycles. The lithium chemical diffusion coefficient D_{Li}, in the range $10^{-9} - 10^{-10}$ $cm^2\,s^{-1}$ in the $0.03 \leq x \leq 1.1$ composition domain, is little affected by the Li concentration. The high mobility revealed for lithium ions is also supported by BVEL analysis, while a significant activation energy for Na-ions migration ascertains their immobility in the α′-NaV_2O_5 lattice. These results demonstrate the interest of large interlayer 2D host lattices stabilized by pillaring species such as Na to achieve a stable cycling behavior, a facile guest cation insertion and to promote the ionic diffusion.

1. Introduction

V_2O_5 and its derivatives like mixed oxides and bronzes have received continued interest as host lattice for lithium insertion reactions [1]. Indeed, the strategy of introducing another guest cation in the V_2O_5 structure leads to various two dimensional (2D) or three dimensional (3D) structures depending on the cationic species (Na^+, Ni^{2+}, Cu^{2+}, Co^{2+}, Al^{3+}, Cr^{3+} etc.). Such compounds have been broadly studied as electrode materials for lithium-ion batteries because of their ability to accommodate a large amount of lithium ions, leading to high gravimetric capacity values. This class of electrode materials, including $M_xV_2O_5$ vanadium bronzes and $M_{0.16}/M_{0.11}V_2O_{5.16}$ mixed oxides, is usually prepared by solution techniques [2–5], sol-gel processes [6–13] or hydrothermal and solvothermal methods [14–19]. As far as sodiated phases are concerned, only the 3D $Na_{0.33}V_2O_5$ bronze, characterized by a rigid structure and a complex discharge profile, has been extensively investigated as cathode material for secondary lithium batteries [4,13–16]. Conversely, the sodium-rich compound, i.e. the layered α′-NaV_2O_5 bronze has been little investigated as possible cathodic material [17–19]. It comes out from literature data that only a cursory analysis of the Li insertion properties in α′-NaV_2O_5 has been performed [17–19]. Indeed, the insertion of about 1 Li^+/mole of bronze is reported, but contradictory curves of potential dependence vs. Li uptake are reported. Furthermore, there is no reliable structural investigation to support these data [17,18], which impedes any insight on the lithium insertion mechanism. Cyclic voltammetric curves obtained for α′-NaV_2O_5 thin films show a nice reversible behavior, which suggests promising properties although quantitative data are lacking [19].

α′-NaV_2O_5 is the highest member of the α′-$Na_xV_2O_5$ ($0.7 \leq x \leq 1$) sodium vanadium bronzes family [20–22]. It exhibits a layered structure with *Pmmn* symmetry and was prepared for the first time according to a flux method from solid-state reaction of $NaVO_3$ and

---

[*] Corresponding author.
E-mail address: baddour@icmpe.cnrs.fr (R. Baddour-Hadjean).

https://doi.org/10.1016/j.electacta.2018.03.087

VO_2 precursors around 600 °C under argon atmosphere. This compound is now mostly obtained through a hydrothermal process at 180–200 °C for one or several days [17–19,23]. Recently, our group reported the irreversible electrochemical formation of NaV_2O_5, isostructural to the high temperature α'-NaV_2O_5 bronze [24]. This new electrode material was shown to reversibly accommodate 0.8 Na^+/NaV_2O_5 near 1.6 V vs. Na^+/Na at room temperature, delivering thus an attractive specific capacity of 120 mAh g^{-1} at C/10 rate over a few dozen of cycles. This recent finding combined with the lack of reliable data on the electrochemical lithium insertion process in α'-NaV_2O_5 prompted us to investigate in details this material as cathode for rechargeable Li batteries.

Here we report for the first time the lithium insertion properties of electrochemically formed α'-NaV_2O_5 including cycling and kinetic data. In addition, the structural response of the host lattice during the first discharge-charge cycle is studied by X-Ray diffraction (XRD) and Raman spectroscopy. The obtained results provide key insights into the Li insertion reaction mechanism and give evidence for previous inappropriate hastily conclusions [17]. Electrochemically formed α'-NaV_2O_5 exhibits a rechargeable behavior at around 2.1 V with an interesting stable specific capacity of 120 mAh g^{-1} over 60 cycles at C/10.

2. Experimental

α'-NaV_2O_5 was obtained as described in Ref. [24], through electrochemical sodiation of the pristine α-V_2O_5 (Alfa Aesar 99.9%) in a two-electrode coin cell (CR 2032) where sodium disk acts as reference and auxiliary electrodes. The positive electrode was made of the active material (V_2O_5 80 wt %), acetylene black (7.5 wt %), graphite (7.5 wt %) and teflon as binder agent (5 wt %). About 6 mg/cm^2 of the active material is pressed on a stainless steel grid current collector (14 mm diam., 0.35 mm thick) under a pressure of 5 tons cm^{-2}. The separator consists of three glass Whatman microfiber filters. The electrolyte is 1 M $NaClO_4$ in propylene carbonate (PC) containing fluoroethylene carbonate (FEC) additive (2% Vol.). All the coin cells were assembled in an argon-filled glove box where water and oxygen concentrations were kept less than 1 ppm. The electrochemically formed NaV_2O_5 samples were prepared by slow discharge (C/20 rate) according to a single step process near 1.8 V vs. Na^+/Na and using a cut-off voltage of 1.4 V. After 2 h of equilibrium time, the discharged electrodes were removed from the cell in the Ar-filled glove box and rinsed with dimethyl carbonate (DMC). Then, they were further introduced in a two-electrode coin cells (CR 2032) where lithium disk acts as reference and auxiliary electrodes in order to investigate the Li insertion properties of α'-NaV_2O_5. The cell was filled with 1 M $LiClO_4$ in propylene carbonate (PC). Galvanostatic and voltamperometric experiments were made with a VMP3 Biologic apparatus.

For open circuit voltage (OCV) experiments, equilibrium was considered reached when the OCV remained stable (<0.2 mV for 1 h). AC impedance measurements were performed in the frequency range 10^5 to 3 10^{-3} Hz with a VMP3 Biologic Multipotentiostat-Galvanostat apparatus. The excitation signal was 10 mV peak to peak.

In order to investigate the lithium-driven structural changes of $Li_xNaV_2O_5$ electrodes, the cells were discharged to the required composition by galvanostatic reduction at slow C/20 rate. After reaching equilibrium, the cell was opened in the glovebox and the positive electrode was removed, rinsed with DMC and placed in specifically designated airtight sample holders to be further analyzed by *ex-situ* X-ray diffraction and Raman spectroscopy.

The X-Ray diffraction (XRD) experiments were carried out using a PANalytical X-Pert Pro diffractometer equipped with a X'celerator linear detector and Co Kα radiation (wavelength $\lambda = 1.7889$ Å). The data are processed on Eva software to identify peaks, then with CelRef to calculate the lattice parameters. The as collected pattern of α'-NaV_2O_5 has been analyzed using Rietveld refinement method with GSAS ExpGUI package [25,26]. Two diffraction peaks due to the stainless steel grid appear at 51° and 90°, then the zones 50.6°–51.6° and 88–91.1° were excluded.

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 2 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 filters of various optical densities. For each electrode, 10 different spots have been recorded to check the homogeneity.

The Bond Valence Energy Landscapes (BVEL) analysis has been performed with the BondStr program implemented in the FullProf Suite [27,28], using the soft bond valence parameters defined by S. Adams [29]. The BVEL method derives from the Bond Valence Sum method [30], which is based on the analysis of the bond lengths extracted from the crystal structure. This approach usually gives coarse but reliable results compared to ab-initio calculations on activation energies estimation for ionic conductors and energy storage materials [31]. It is recognized as a quick and simple tool to analyze the possible shape and dimensionality of diffusion paths for a given mobile ion and has been already applied to estimate the Li and Na conduction paths in several cathode materials [32–34]

3. Results and discussion

The XRD pattern of electroformed α'-NaV_2O_5 (Fig. 1) can be indexed using an orthorhombic symmetry in the same *Pmmn* space group than V_2O_5. Results of Rietveld refinement using only one crystallographic vanadium in mixed valence state positioned in *4f* site [35] lead to the following unit cell parameters $a = 11.332(1)$ Å; $b = 3.606(1)$ Å; $c = 4.793(1)$ Å, in good agreement with previous structural data reported for the chemically synthesized material [20–22,35,36]. Wyckoff positions, fractional atomic coordinates and isotropic displacement parameters are gathered in Table 1. The vanadium-oxygen and sodium-oxygen bond lengths are summarized in Table 2.

Compared to electrochemical Li insertion in V_2O_5 ($a = 11.51$ Å; $b = 3.56$ Å; $c = 4.37$ Å), which leads to the δ-LiV_2O_5 phase with lattice parameters $a = 11.20$ Å; $b = 3.56$ Å; $c/2 = 4.95$ Å [37], Na insertion in V_2O_5 surprisingly produces smoother structural distortions. Indeed, the comparison of the lattice parameters for α'-NaV_2O_5 and δ-LiV_2O_5 points to a lesser shrinkage along the *a* direction and lower expansion along the *c* interlayer direction. As illustrated in Fig. 2, the crystal structure of α'-NaV_2O_5 consists of double chains of edge-sharing distorted VO_5 pyramids alternatively up and down running along the *b* axis and linked together by a common corner oxygen to form sheets stacked along the *c* direction.

A cyclic voltammogram (CV) of α'-NaV_2O_5 obtained in the 4 -1 V potential range at very low sweeping rate (4 $\mu V s^{-1}$) is displayed in Fig. 3. One single and well-defined cathodic peak is observed at 2.05 V while the corresponding anodic peak for the Li extraction process is located at 2.3 V. Additional Li ions are extracted at c.a. 3.25 V.

The typical discharge-charge at low rate of C/60 in the 4 - 1 V potential window as well as the equilibrium curve E = f(x) (Fig. 4) confirm the one-step insertion process centered at 2.1 V. A Li