



Research Paper

Electrochemical kinetics of Li insertion in nanosized high performance V_2O_5 obtained via fluorine chemistry



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ABSTRACT

The kinetics of the electrochemical lithium insertion reaction in nanosized V_2O_5 prepared from a fluorination synthesis in solution is investigated by AC impedance spectroscopy. The experimental data are obtained vs. x in nano- $Li_xV_2O_5$ over the wide composition range $0 \leq x < 1.8$ and vs. temperature. Kinetic parameters for Li electroinsertion in nanosized V_2O_5 are achieved here for the first time. The charge transfer kinetics is little affected by Li content. A moderate evolution of the chemical diffusion coefficient is related to the peculiar single-phase behavior induced by the nanosize effect combined with shorter Li diffusion pathways. Comparison with experimental data obtained for microsized analogue vs. temperature reveals a much lower activation energy barrier (0.06 eV) for the lithium diffusion process in nanosized V_2O_5 that explains the significant improvement in electrochemical performances and especially a better rate capability. This work illustrates how nanosizing promotes the kinetics of Li insertion reaction, in agreement with the new and specific structural response of nanosized vanadium pentoxide.

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1. Introduction

With an open structure combined with a high capacity (300 mAh g^{-1}) available in the 4 V–2.1 V vs. Li^+/Li potential range, V_2O_5 is still viewed as a model for Li intercalation reactions but also as a superior cathode material for rechargeable Li batteries [1]. Various related forms like xerogel [2,3] and aerogels [4,5] and numerous nanosizing strategies have been considered for enhanced performance. Nanostructuring is an effective approach towards improved properties for cathode materials [6], including a higher electronic conductivity, shorter diffusion pathways for lithium ions, developed electroactive surface area and better accommodation of the structural strain upon lithiation-extraction. Therefore many works have proposed various nano-engineering approaches using efficient synthesis ways including sol-gel processes, precipitation reactions, electrochemical deposition and mainly hydrothermal/solvothermal synthesis [7–16]. A large distribution of particles size and various morphologies are obtained: nanosheets [14], nanorods [13], nanowires [15], nanotubes [16], nanospheres [17], nanoflowers [18] which all

display a clear improvement of their electrochemical performances toward lithium insertion compared to V_2O_5 bulk samples with however a real scattering in terms of cycling stability and rate capability. Furthermore, the two following points are not addressed in these studies:

- (i) First, the understanding of distorted discharge-charge profiles for nanosized V_2O_5 . We recently demonstrated such shape reveals the large impact of the nanostructuring on the lithiation reaction thermodynamics. From XRD and Raman microspectrometry experiments, we provided evidence that electrochemical formation of $Li_xV_2O_5$ from nanosized V_2O_5 proceeds through solid solution behavior over the large Li composition range $0 \leq x < 2$ without domain boundaries [19]. A single-phase mechanism of the ϵ' -type was revealed with reversible and limited structural changes consisting in a linear increase in the interlayer distance and unit cell volume as a function of the lithium content. This finding contrasts with the successive (α/ϵ), (ϵ/δ) and (δ/γ) wide biphasic regions usually observed for micro- $Li_xV_2O_5$ [20–24] and accounts for the significant improvement in electrochemical performances of nano- V_2O_5 .
- (ii) Second, the kinetics of electrochemical lithium insertion in nanosized V_2O_5 is surprisingly not addressed in most papers in spite of its crucial importance.

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In this work, special attention is given toward the kinetics of electrochemical lithium insertion reaction in a high purity nanosized V_2O_5 obtained through an original and facile fluorination reaction of micro- V_2O_5 in aqueous solution. A complete picture of the nanosizing effect is provided through AC impedance spectroscopy measurements carried out as a function of the lithium content x in $Li_xV_2O_5$ ($0 < x < 1.8$), the temperature and the cycle number.

2. Experimental

The synthesis of nanosized V_2O_5 via a fluorination reaction in solution is reported in details in [19]. Micro- V_2O_5 powder is dissolved in an aqueous HF solution. After complete dissolution, the aqueous phase is slowly evaporated at room temperature until a dark red solid precipitates. The obtained product is then heat-treated at 230 °C for 2 h under dynamic vacuum.

The X-Ray Diffraction (XRD) experiments are recorded on a PANalytical X-Pert Pro diffractometer with a X'celerator linear detector, in the 10 to 70° 2θ range, using $Co\ K\alpha$ ($\lambda_{K\alpha} = 0.1789$ nm) source. The data are processed on Eva software to identify peaks and CelRef is used to calculate the lattice parameters. The Raman spectra are 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) is used as the excitation source. The spectra are measured in back-scattering geometry. The resolution is about $0.5\ cm^{-1}$. A 100x objective is used to focus the laser light on sample surface to a spot size of $1\ \mu m^2$. To avoid local heating of the sample, the power of the laser beam is adjusted to 0.2–0.5 mW with neutral filters of various optical densities.

We used conventional three-electrode cells under argon atmosphere. The cell was filled with 1 M $LiClO_4$ in propylene carbonate (PC). The positive electrode was made of a mixture of active material (V_2O_5 80 wt %), acetylene black (7.5 wt %), graphite (7.5 wt %) and teflon as binder agent (5 wt %) pressed on a stainless steel grid (14 mm diam., 0.35 mm thick) under a pressure of 5 tons per cm^2 . The mass of active material is about 6 mg, leading to a mass loading of $3.9\ mg\ cm^{-2}$. Reference and counter electrodes were made of Li wires in separate compartments filled up with electrolyte. The working electrode compositions were adjusted by coulometric titration using a low current density corresponding to a C/20 rate ($7.4\ mA\ g^{-1}$). Equilibrium was considered to be reached when the open circuit voltage remained stable (potential

variations lower than 0.1 mV per hour). The open circuit voltage (OCV) curve vs. x in $Li_xV_2O_5$ and the discharge-charge curves at very low rate of C/60 superimpose. Impedance measurements were measured in the 10^4 to 2.10^{-3} Hz frequency range with a VMP3 Biologic Multipotentiostat-Galvanostat apparatus. A three-electrode cell with high surface gold wire as counter electrode was used. The excitation signal is 10 mV peak to peak. All the electrochemical measurements were performed in an argon-filled glove box where water and oxygen concentrations are kept less than 1 ppm. Cycling experiments were carried out in two-electrode coin cells (CR 2032) with lithium disk as reference and auxiliary electrodes. The separator consists of three glass Whatman microfiber filters and acts as an electrolyte tank. All the coin cells were assembled in an argon-filled glove box.

3. Results and discussion

The crystallographic structure and crystallinity of the nano- V_2O_5 have been established from X-ray diffraction. Fig. 1 clearly indicates all the diffraction lines can be indexed in the orthorhombic symmetry (JCPDS Card No. 01-077-2418, space group: $Pmmn$) with unit cell parameters $a = 11.501\ \text{Å}$, $b = 3.562\ \text{Å}$, $c = 4.371\ \text{Å}$ very close to those of the micro-sized sample. The broadening of diffraction lines and their low intensity reveal the nanosized character of the sample. The mean crystallite size (L) along the stacking direction is one order of magnitude lower than in bulk oxide (13 nm against 110 nm) and 6-fold lower in the oxide planes (30 nm against 190 nm). The Raman spectrum of the nanosized sample (Fig. 2) confirms the V_2O_5 structure at the level of the chemical bond [19]. A slight increase in the bands width ($10\ cm^{-1}$ instead of $5\ cm^{-1}$ FWHM for micro- V_2O_5) indicates the nanosized character of the powder. The morphology of V_2O_5 nanoparticles was previously characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) [19]. Calisson-like V_2O_5 particles, a few μm long are composed of nanosheets subunits of 100–200 nm long and about 20 nm thick. A high porosity exists in nanosized- V_2O_5 [19] that is responsible for the higher BET surface area of $16\ m^2\ g^{-1}$ instead of $1\ m^2\ g^{-1}$ for the micro-sized oxide.

The typical electrochemical fingerprint of nano- V_2O_5 is represented by the discharge-charge curves obtained at very low current density (C/60 i.e. transfer of 1 mole of electron in 60 hours) reported in Fig. 3. This galvanostatic profile is well superimposed with the OCV curve and describes successive thermodynamic equilibrium states. Three electrochemical lithiation processes appearing as sloping

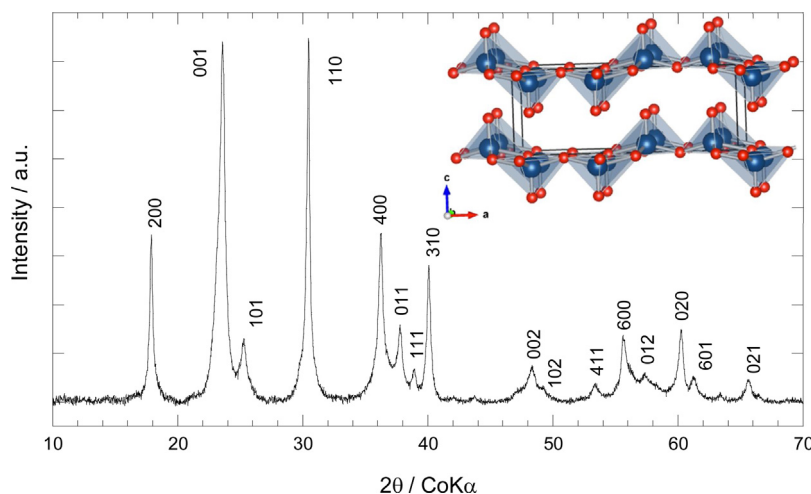


Fig. 1. XRD pattern of nano- V_2O_5 . Miller indices of orthorhombic V_2O_5 in space group $Pmmn$ are indicated. V_2O_5 structure in inset.

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