

# ELECTROCHEMICAL LITHIUM INSERTION INTO VANADIA NANOTUBES

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**Abstract:** Vanadium oxide nanotubes are promising as cathode material for lithium-ion batteries, this unique material demonstrated the discharge capacity to be about 260 mAh/g. The decrease of discharge capacity of material with number of cycle was accompanied by degradation of tubular-like micromorphology. Analysis of tubular and planar nanostructures by EXAFS, EELS and electrochemical techniques showed that the nanotubes whose are more active electrochemically degrade quicker than planar structures because of the loss of long-range order.

**Keywords:** vanadium oxide nanotubes, lithium electrochemical insertion

## INTRODUCTION

Vanadium oxides are widely used as catalysts, electrochromic, thermochromic, sensor materials [1]. New one-dimensional nanomaterials attract great attention in view of their future applications. Unfortunately, one-dimensional structures in the V-O system are much less investigated compared to others such as carbon nanotubes despite of their easy preparation in the forms of nanotubes, nanobelts or nanowires. This work discusses the process of lithium insertion and extraction into hydrothermally obtained vanadia nanotubes (VNT) in terms of its influence on VNT microstructure, layered structure and functional properties degradation upon cycling.

Vanadium oxide based materials, such as bronzes, xerogels, hybrid materials etc., were intensively studied as efficient cathode materials of high electrochemical capacity [2]. However, most of these forms showed a uniform decrease of discharge capacity mostly because of irreversible lithium insertion.

Vanadium oxide nanotubes are an outstanding material with a layered structure promising for reversible insertion of cations. Recently it was shown that the discharge capacity of VNT changes significantly upon cycling [3]. Here we analyzed the origin of such loss of capacity and suggest approaches to improve the functional properties of VNT.

## EXPERIMENTAL

Orthorhombic polycrystalline  $V_2O_5$  as an inorganic precursor and hexadecylamine-1 (HDA) with the chain length of 2.15 nm as a structure –

directing template were used to prepare vanadia nanotubes. Both vanadia and HDA were preliminary stirred for two days under ambient conditions to form a layered precursor. The hydrothermal treatment of the precursor was performed at 180°C for 2 - 48 h in a Teflon-lined cell. The final product was repeatedly washed with distilled water and ethanol and then dried at 80°C in air.

The samples were examined by X-ray diffraction (XRD) using Rigaku D/MAX 2500 diffractometer (Japan) with a rotating copper anode ( $CuK\alpha$  in a  $2\theta$  range of 5 - 70° with a step 0.02°).

The microstructure of the samples was studied by a transmission electron microscopy (Leo 912 AB Omega (Leo, Germany),  $LaB_6$  cathode, accelerating voltage 100 kV). Micrographs were taken either in a conventional TEM mode or an elastic brightfield mode filtered at zero-loss energy. Energy loss spectra (EELS) were obtained at 120 V potential with exposure times between 10 and 100 s and 5 integration counts were used for EELS acquisition.

EXAFS spectra of the probes were obtained in a transmission mode near the V K-edge region on SPRing-8 center (Japan) at the National Australian Beamline. BN was used as a matrix. XFIT software was applied for the analysis of the spectra.

The X-ray photoelectron spectra (XPS) were measured by the Riber LAS – 3000 (France) spectrometer (semispherical analyzer OPX – 150 with retarding field,  $AlK\alpha$  irradiation, cathode voltage 12 kV, emission current 20 mA). The calibration of photoelectron peaks was performed against C 1s line with a binding energy of 285 eV. NIST database was applied for peak identification.

In order to analyze VNT electrochemical behavior, they were mixed with acetylene black and a binder and placed onto a conducting Ni mesh. Electrochemical cycling of nanotubes was then performed vs metallic lithium in a polycarbonate nonaqueous electrolyte containing  $\text{LiClO}_4$ .

All electrochemical measurements were carried out in a glove box in argon atmosphere. The final quantity of water in electrolyte was controlled using the Fisher method and did not exceed 50 ppm.

Electrochemical insertion and extraction reactions were performed using three-electrode lithium cells. The working electrode consisted of 80 wt. % active material, 10 wt. % acetylene black, and 10 wt. % polyvinyliden fluoride dissolved in N-methylpyrrolidone. The mixture was pressed onto Ni grids and dried at  $120^\circ\text{C}$  for 8 hrs under vacuum and then moved to a glove box filled with Ar gas. The counter and reference electrodes were Li foils, and the separator was a microporous polypropylene sheet. The electrolyte consisted of 1 M solution of  $\text{LiClO}_4$  mixed with propylene carbonate (PC) and dimethoxyethane (DME) (7:3 by volume). The cells were assembled in an argon-filled dry glove box. Galvanostatic charge-discharge cycles were performed with the current density of 10 mA/g of active material using multichannel potentiostat / galvanostat.

## DISCUSSION

Vanadium oxide nanotubes which possess a well-defined layered structure are attractive as a host lattice for electrochemical lithium intercalation. In Fig.1 the microstructure of initial VNT and the electrode slurry (75% of VNT) after 10 electrochemical cycles in a potential window of 3.5 – 1.5 V is shown. The cathode material evolves from the layered compound to a material with an essentially disordered structure. Statistical analysis of TEM micrographs revealed the total degradation of the nanotube structure, i.e. the interlayer distance of about 33-43 Å could hardly be found in this probe. Such the degradation of material could be a result of four factors: irreversible lithium insertion, destructive lithium extraction, formation of solid electrolyte interface (SEI) film and also an interaction of the electrolyte with the surfactant from the structure of VNT [4].

An analysis of XRD data for initial cathode slurry and the cathode material after 10 charge-discharge cycles showed growing stacking disorder in VNT. In particular, the 00l reflections became lower in intensity.

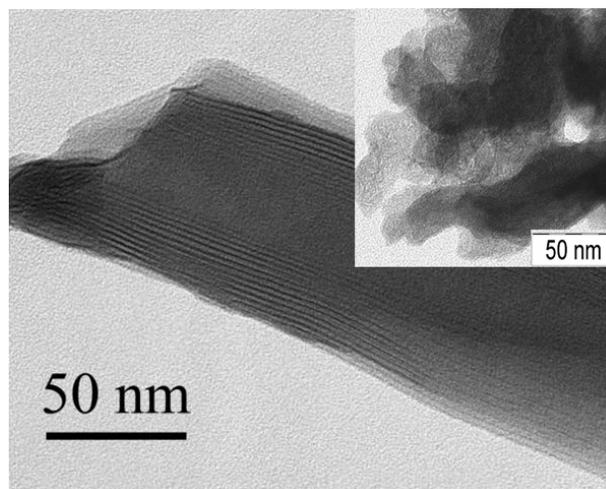


Fig. 1: Micrographs of as-prepared VNT; the inset shows the electrode paste (75% of VNT) after 10 cycles in a 3.5 – 1.5 V potential window.

Electrochemical characteristics of a cathode based on VNT are given in Fig.2. First, the discharge capacity of the cathode increased a little bit and then reduced down to 100 mAh/g of about 15 mAh/g per cycle. In the 1<sup>st</sup> charge-discharge cycle the discharge capacity of the cathode was 220 mAh/g, in the 2<sup>nd</sup> cycle the discharge capacity achieved 260 mAh/g. This behavior is typical for vanadium oxide based cathodes. In the 20<sup>th</sup> cycle the capacity of 64 mAh/g was achieved only. An estimate of theoretical discharge capacity of the materials showed that the molar ratio of intercalated lithium to vanadium should be about 1.5, i.e. the oxidation rates of vanadium in the probe are +4 and +3. In Ref. [3] the presence of  $\text{V}^{5+}$  in discharged VNT based cathode was reported.

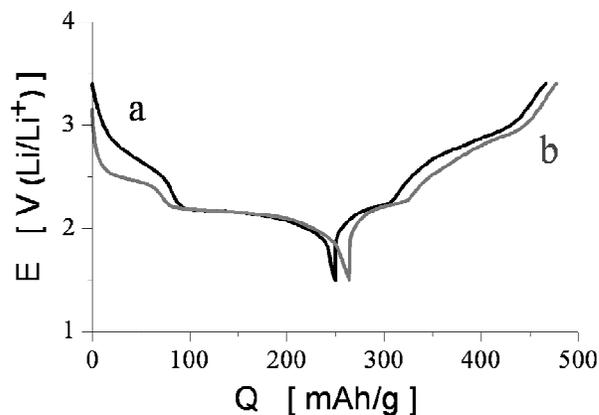


Fig. 2: Charge-discharge curves for a VNT based cathode (75% of VNT) (a) in the 1<sup>st</sup> cycle, and (b) in the second cycle.

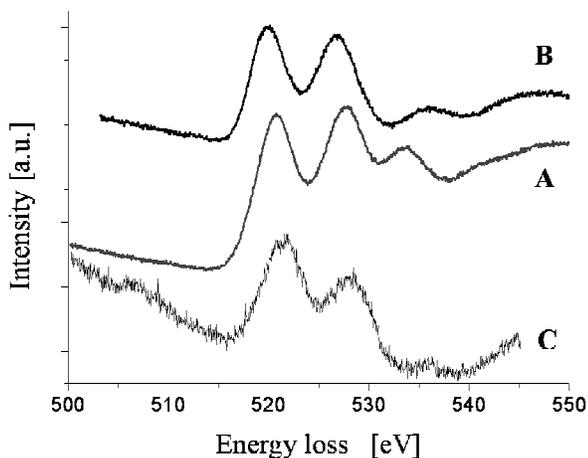


Fig. 3: EELS spectra of (a) VNT, (b) polycrystalline  $\text{NaVO}_3$ , and (c) non-scrolled VNT precursor.

We analyzed EELS spectra of the materials to get some information about positions of inserted lithium cations in the lattice. Fig.3 demonstrates EELS spectra of initial VNT, lithiated cathode and  $\text{NaVO}_3$  as an example of well crystalline vanadium bronze. The V spectrum of sodium metavanadate is shifted to low energies in comparison with VNT spectra. To the contrary, the spectrum of discharged VNT based cathode (included lithium) was shifted to lower energies. The shift of V  $L_{III}$  and V  $L_{II}$  to higher energies usually interprets as a decrease of occupation of 3d shell which usually means an increase of oxidation rate of vanadium. In our case the structural disorder of material might be a reason of such shift of the spectrum. The decrease of 3d shell occupation could also originate from significant distortion of polyhedron, such as an increase of length of vanadyl boundary. Scrolling of V-O layers could also lead to such a distortion.

Table 1: EXAFS data for the vanadium oxide nanotubes and the precursor with planar microstructure.

Coordination spheres	Layers	Nanotubes
V-O(1)	1.52(1)	1.55(1)
V-O(2)	1.98(1)	2.07(1)
V-O(3)	2.33(1)	2.31(1)
V-O(4)	2.65(1)	2.53(1)
V-V(1)	2.93(1)	2.84(1)

In Fig.4 we demonstrated a decrease of discharge capacity of VNT in comparison with data for layered structural precursor of nanotubes, non-scrolled

because of hydrothermal processing with a lower duration. The structure of scrolled V – O layers of nanotube wall is similar to the structure of the precursor, and we suppose only the deficiency increase and small changes of the unit cell as a result of scrolling process lead to so high electrochemical capacity of material. The discharge capacity of VNT decreased from 260 mAh/g to lower values achieving the discharge capacity of the planar structure.

In the second charge-discharge cycle the capacity of planar precursor decreases, such result usually means that some of lithium cations intercalated into the lattice of material at the surface layer irreversibly.

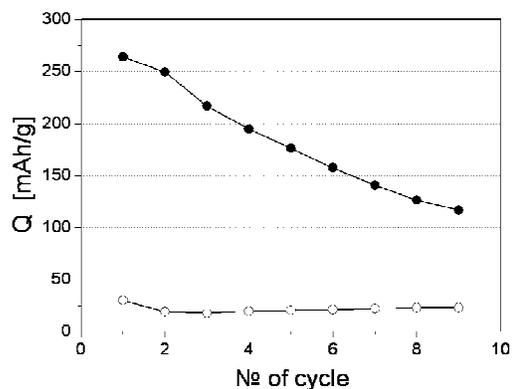


Fig. 4: Decrease of discharge capacity for cathodes based on (a) VNT, and (b) non-scrolled vanadium oxide compound. The electrode slurry contained 75% of active material.

It is known that inserted  $\text{Li}^+$  cations locate oppositely to vanadyl oxygens O(1). We analyzed the structure of VNT and the 2D precursor using EXAFS spectroscopy to reveal a role of the V-site environment in stabilization of inserted  $\text{Li}^+$  cations in the V-O lattice. The FT EXAFS spectra of VNT were rather complex and their interpretation could not be easily given. Some certain peak positions are listed in Table 1. Comparison of two spectra showed compression of coordination spheres as a result of scrolling. The increase of V-O(1) boundary length would mean a smaller mesomeric effect and smaller negative charge at the V-O layer surface.

We analyzed the oxidation rate of vanadium in planar and tubular nanostructures using XPS spectroscopy. It was found that the percent of  $\text{V}^{4+}$  in VNT is higher than in electrochemically inactive precursor. The oxidation rate of vanadium in the analyzed probe of VNT is about +4.25. So this means that the micromorphology and structural peculiarities of vanadium oxide nanotubes are the most important

factors that grant an advantage of the nanotube over planar nanostructures with a similar layer structure in electrochemical cycling.

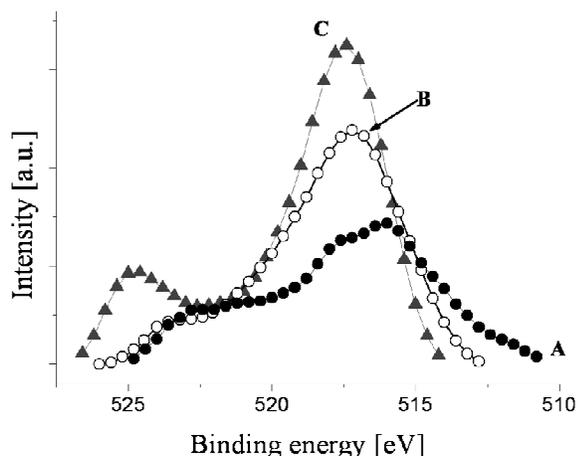


Fig. 5: XPS spectra of V 2p core of (a) VNT, (b) non-scrolled VNT precursor, and (c) orthorhombic  $V_2O_5$  polycrystalline  $NaVO_3$ .

## CONCLUSION

The microstructure of vanadia – based layered nanomaterials permits an efficient lithium intercalation through open ends of nanoscrolls and this possibility makes this microstructure to be preferable for electrochemical lithium-ion cells. However the formation of nanotubes leads also to an increase of deficiency of V-O layers and the long-range ordering is less typical for this material compared to its planar precursor. During the electrochemical cycling insertion and extraction processes lead to structural disordering and, as a result, to degradation of the tubular structure.

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