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Authors	McNulty, David;Buckley, D. Noel;O'Dwyer, Colm
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# Structural and Electrochemical Characterization of Thermally Treated Vanadium Oxide Nanotubes for Li-ion Batteries

D. McNulty<sup>a,b,c</sup>, D. N. Buckley<sup>a,b,c</sup>, and C. O'Dwyer<sup>d</sup>

<sup>a</sup> *Charles Parsons Initiative on Energy and Sustainable Environment,  
University of Limerick, Limerick, Ireland*

<sup>b</sup> *Department of Physics and Energy, University of Limerick, Limerick, Ireland*

<sup>c</sup> *Materials & Surface Science Institute, University of Limerick, Limerick, Ireland*

<sup>d</sup> *Applied Nanoscience Group, Department of Chemistry, and Tyndall National Institute,  
University College Cork, Ireland*

Vanadium oxide nanotubes (VONTs) have been successfully synthesized by hydrothermal treatment of a mixture of vanadium oxide xerogel and nonylamine. Traditionally dodecylamine and hexadecylamine are used as the structure maintaining template. In this study, however, evidence of high quality nanotubes templated with nonylamine is presented. Thermogravimetric analysis was used to determine the temperature at which the amine molecules can be removed from the nanotubes. The removal of amines is desirable as heavy functionalization of VONTs by amine molecules can impede the intercalation of lithium ions. The removal of the amine chains resulted in a change in morphology from pristine nanotubes to polycrystalline vanadium oxide nanorods. High resolution transmission electron microscopy was used to characterize the VONTs before and after annealing to high temperatures. Fourier transform infrared spectroscopy confirmed the removal of the amine template after annealing. Galvanostatic discharge tests were performed to compare the electrochemical behavior of bulk  $V_2O_5$  powder, VONTs and polycrystalline nanorods (poly-NRs). A comparison of their specific capacity values after the first discharge is also presented.

## Introduction

Rechargeable lithium-ion batteries hold great promise for use in powering electric and hybrid electric vehicles (1) and continue to be crucial in medical and handheld portable devices. However, power and energy density, coulometric efficiency and rate performance are important factors that need to be further improved for them to meet demands for powerful portable devices. (2) Vanadium pentoxide has attracted attention due to its structural flexibility and chemical and physical properties which are of interest for catalytic and electrochemical applications. (3) Both vanadium pentoxide crystalline powder and vanadium pentoxide xerogels exhibit a layered structure, and this enables intercalation of a wide variety of inorganic and organic guest species

(4). Vanadium is known to exhibit a wealth of compounds over its range of oxidation states (+2 ... +5), while access to its multiple redox couples at relatively high potential allows for theoretical capacities up to  $\sim 440 \text{ mAh g}^{-1}$  (for a complete 3  $\text{Li}^+$  insertion). While it has a relatively low average cell potential of 2.0-2.5 V, vanadium oxide still serves as a test-bed for intercalation into templated and layered materials, and benefits from good electrical conductivity in a wide variety of its structural polymorphs. These morphological varieties are possible through a series of well-known synthetic approaches such as sol-gel and hydro/solvothermal syntheses. (5-10) In their bulk form however, vanadium oxides are not very useful as a cathode material due to poor cycle life and material pulverisation issues. Many of the problems associated with the bulk material can be overcome by using vanadium oxide nanostructures, which have attracted increasing attention due to their unique geometry, low cost, facile preparation and large specific capacity. (11) Vanadium oxide nanotubes (VONTs) are particularly attractive since they provide several access regions for intercalates such as lithium ions. (12) This large surface area to volume ratio allows a greater area of vanadium oxide to be in direct contact with the electrolyte as compared with bulk vanadium oxide. (13) When coupled with the nano-scale dimensions of the VONTs that facilitates shorter diffusion lengths for Li ions within the  $\text{V}_2\text{O}_5$  crystal lattice, the reversibility of the insertion-removal redox process can be improved compared to bulk materials, provided however, that intercalation sites for cations are not blocked by organic templates. Additionally, the geometry of the VONTs could potentially promote facile strain relaxation during battery operation, where volume expansion and often observed pulverization of the active materials caused by crystal structure or phase changes can be buffered by the scrollable, flexible vanadium oxide in lithium and sodium-ion batteries. (14)

In this work, we present a convenient and controllable approach to synthesizing vanadium oxide nanotubes and converting them to polycrystalline nanorods (poly-NRs) during template removal, to improve Li-insertion and removal processes when examined as a Li battery half-cell. The VONTs were synthesized by mixing of a lamellar-structured  $\text{V}_2\text{O}_5$  xerogel precursor with primary amines acting as structure-maintaining templates under hydrothermal conditions. The synthesized VONTs are derived from a  $\text{V}_2\text{O}_5$  bulk particle powder and we present a comparative study of the electrochemical discharge characteristics of bulk  $\text{V}_2\text{O}_5$  particles,  $\text{V}_2\text{O}_5$  xerogel and inorganic/organic hybrid VONTs. We highlight the limitations of VONTs which are heavily functionalized with primary amines by comparing as-synthesized VONTs with those that underwent thermal treatment to remove physisorbed and chemisorbed water and amines, which undergo a structural transformation forming solid polycrystalline rods.

## Experimental

Vanadium oxide nanotubes were synthesized by hydrothermal treatment of a vanadium oxide xerogel, following usual procedures. (3) A nonylamine organic template was used in a molar ratio of xerogel to amine of 1:2, with 3 ml of ethanol added per gram of xerogel. Hydrothermal treatment produced a dry fluffy black powder consisting of VONTs. The poly-NRs for electrochemical testing were prepared by thermally treating VONT powder in a quartz glass furnace which was heated from room temperature to  $600 \text{ }^\circ\text{C}$  at  $5 \text{ }^\circ\text{C}/\text{min}$  in a nitrogen atmosphere.

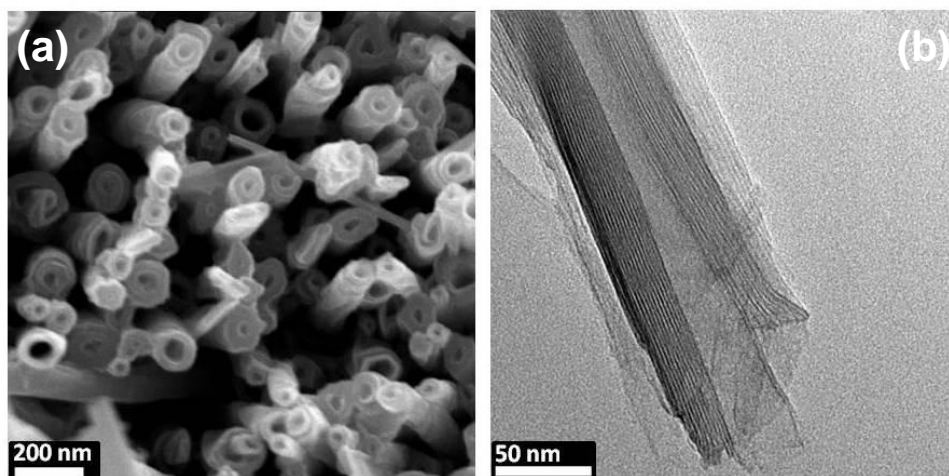
Specimens for transmission electron microscopy (TEM) were prepared by making a suspension of VONTs in ethanol by sonication and dropping 2 ml of the suspension on to a holey carbon grid. The TEM analysis was conducted using a field emission JEOL JEM-2100F microscope operating at an accelerating voltage of 200 kV. Thermogravimetric analysis (TGA)

was carried out using a Perkin Elmer TGA. VONT samples for TGA were placed in an alumina crucible and heated to 600 °C at a series of heating rates ranging from 2-20 °C/min and then cooled, in a nitrogen atmosphere. The FTIR spectra were obtained using a Perkin Elmer series 2000 apparatus in the region of 4000-650  $\text{cm}^{-1}$ .

The electrochemical properties of bulk  $\text{V}_2\text{O}_5$  powder, VONTs and poly-NRs were investigated using a three electrode cell. The cells were assembled in inside a glovebox under an argon atmosphere. A 1 M solution of lithium hexafluorophosphate salts in a 1:1 (v/v) mixture of ethylene carbonate in dimethyl carbonate was used as the electrolyte. The working electrodes were prepared by dropping a sonicated mixture of active material powder and ethanol on a stainless steel mesh substrate and subsequently dried in a vacuum oven at 100 °C for 2 hours to evaporate solvents. No additional conductive additives or binders were added to the various vanadium oxide working electrodes, allowing direct electrochemical examination of the various structures without complications from conductive additives and non-uniform mixtures. The counter and reference electrodes were pure lithium metal. Both working and counter electrodes had a geometric surface area of 1  $\text{cm}^2$ . Galvanostatic discharge/charge tests were performed using a CH Instruments model 605B potentiostat/galvanostat in a potential window of 4.0 V – 1.2 V.

## Results and Discussion

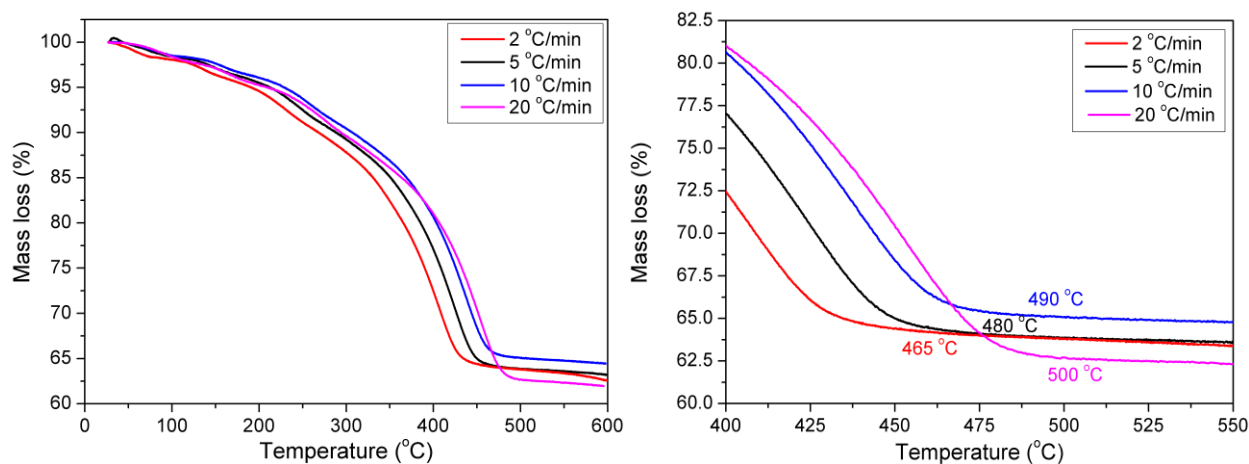
Figure 1 shows SEM and TEM images of VONTs synthesized in a molar ratio of xerogel to amine of 1:2 using nonylamine as the organic structure directing template. Vanadium oxide nanotubes have been synthesized using primarily dodecylamine and hexadecylamine (15) as the primary amine required to facilitate the scrolling of the layers of vanadium oxide during hydrothermal treatment. (16-19) Figure 1 shows evidence of VONTs being successfully synthesized with a shorter nonylamine molecular template, where a hollow core and characteristics flanking layers are found, with an average interlayer spacing of  $\sim 2.17$  nm. Figure 1 (a) shows a top down view of a bunch of VONTs where the tube openings are very well defined.



**Figure 1.** SEM and TEM images of VONTs synthesized using nonylamine in a molar ratio of xerogel to amine of 1:2.

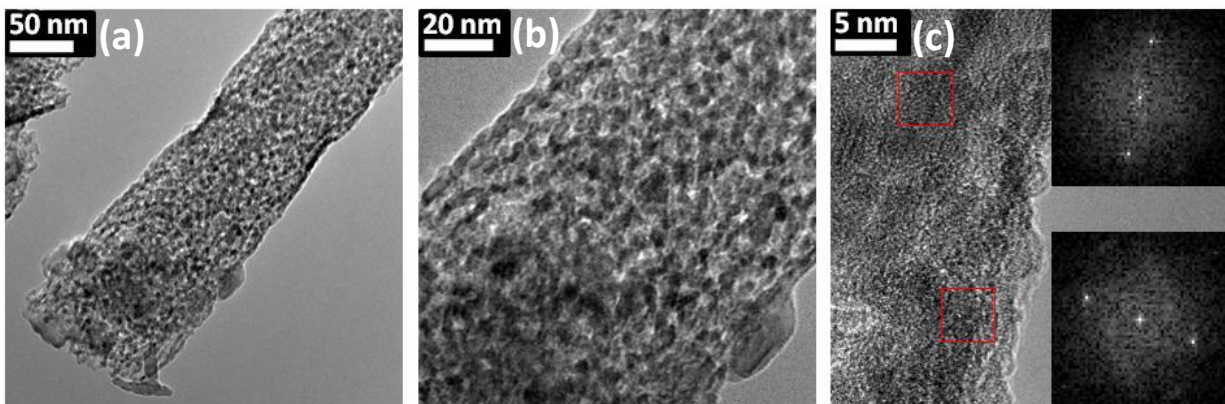
One noticeable difference between a VONT synthesized with nonylamine and the more traditionally used dodecylamine and hexadecylamine templates, is the reduced interlayer spacing of the nanotube walls. The mean interlayer spacing for the VONTs in Fig. 1 was measured to be 2.17 nm, which is smaller than accepted values for dodecylamine (~2.51 nm) and hexadecylamine (~2.98nm). (20) The amines are known to interdigitate as a bilayer between the sheets of vanadium oxide (21, 22), rather than forming a tilted, juxtaposed bilayer. This interlayer ‘velcro’ stabilizes the layered structure of the tubes during scrolling, and since the degree of interdigitation is relatively constant (23) when an excess of amines (and thus maximal functionalization) is used, the interlayer distance scales (in this case reduces) with shorted chained amine templates.

The as-synthesised VONTs are heavily functionalized with primary amines. The presence of nonylamine molecules may impede the intercalation of lithium ions within the VONTs which would have a detrimental effect on their electrochemical performance. Therefore, we investigated the removal of the organic template while still maintaining the advantageous nano-scale dimensions of the VONTs. In order to do this, thermogravimetric analysis of the VONTs was carried out where samples of VONTs were heated at a series of different heating rates (2, 5, 10, and 20 °C/min) in a nitrogen atmosphere.



**Figure 2.** Mass loss curves for VONTs heated at a series of different heating rates.

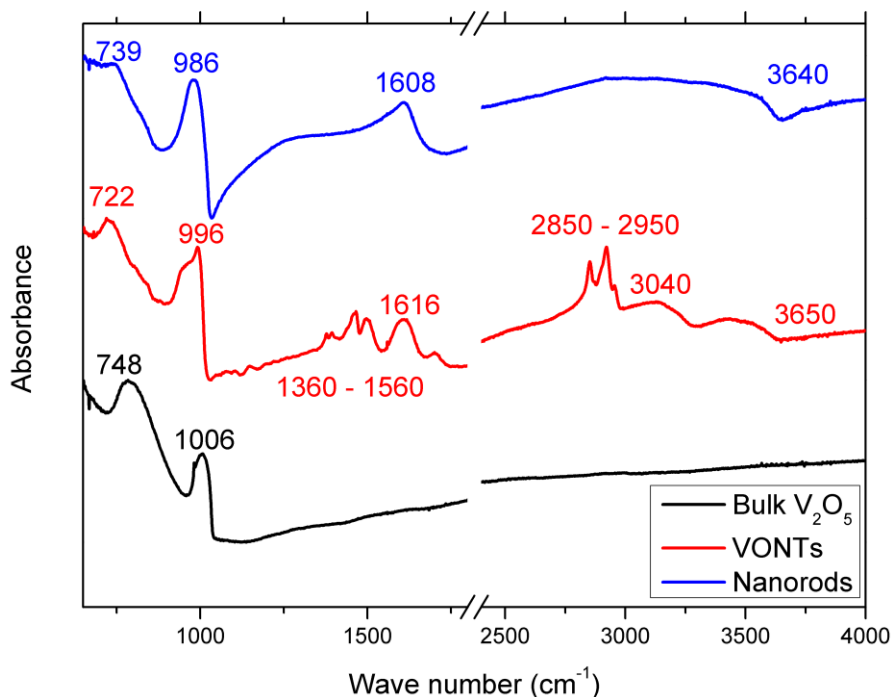
The resulting mass loss curves are shown in Fig. 2. The initial mass losses are due to the removal of physisorbed and chemisorbed water present within and on the outer surfaces of the VONTs. The mass loss curves all level off when approximately 35% of the mass of the VONT powder has been removed. This process is relatively consistent and occurs between 465 °C and 500 °C. At the higher heating rate (20 °C/min), this mass removal process levels off at ~590 °C, which we surmise is due to a time-dependent desorption rate for the amine molecules on the vanadium oxide; lower heating rates require lower upper temperatures for an equivalent organic mass removal. As previously mentioned, amines act as structure-maintaining template. The removal of amine molecules is most likely to affect the structure of the VONTs. Microscopy examination of thermally treated VONTs using TEM, shown in Fig. 3, confirmed the hypothesis that thermal removal of the organic template and heating of the vanadium oxide sheets above the crystallization temperature for amorphous vanadium oxide, results in a drastic change in the morphology of the VONT.



**Figure 3.** (a) and (b) TEM images of nonylamine 2:1 xerogel VONTs after thermal treatment to 600 °C at various magnifications. (c) Reduced area FFTs of poly-NRs.

Figure 3 shows VONTs synthesized with nonylamine with a molar ratio of xerogel to amine of 1:2 which were thermally treated to 600 °C in a nitrogen atmosphere. It is clear that the VONTs have undergone a physical change to their structure. As synthesised VONTs have three main features: the tube openings, the hollow core and the multilayer walls, however after thermal treatment, the order in their structure is lost due to the removal of the nonylamine molecules and recrystallization of the vanadium oxide. The definite tube opening is no longer visible and the multilayer walls have been removed. Imaging using TEM shows the structure in projection, so further work is required to determine whether a central tubular opening remains. After annealing, VONTs become vanadium oxide poly-NRs. The polycrystalline structure of these poly-NRs can be seen in Fig. 3(b), where each of the grains is a nanoscale crystallite of vanadium pentoxide. This is further illustrated in Fig. 3(c) where the individual grain boundaries for each of the crystallites can be seen. The FFT insets in Fig. 3(c) confirm that the nanocrystals are orientated independently of each other. The interplanar spacing of the poly-NRs was measured to be 0.22 nm which corresponds to the  $d$  spacing of (002) plane of bulk  $V_2O_5$  powder. (23, 24) The resulting poly-NRs appear to comprise a granular agglomeration of nanocrystals of vanadium pentoxide, and remarkably, they still maintain similar overall dimensions to the VONTs prior to annealing. This change in physical structure is specifically due to the removal of physisorbed and chemisorbed water and the structure-maintaining amine template, with recrystallization of the layered vanadium oxide into individual nanocrystals. The resulting structure now has nano-scale crystals identical to bulk vanadium oxide powder, within the dimension of the original VONTs.

In order to compare bulk vanadium pentoxide composition and inorganic-organic interactions, with those of the synthesized VONTs and the poly-NRs, FTIR spectra were acquired; IR spectra were acquired for VONTs synthesized using nonylamine before and after annealing to 600 °C. The FTIR spectra, shown in Fig. 4, show the vibrational contribution of the intercalated amines (N-H and C-H frequencies) and their interaction with the vanadium oxide layers, and the vibrational characteristics of the vanadium oxide crystal structure.



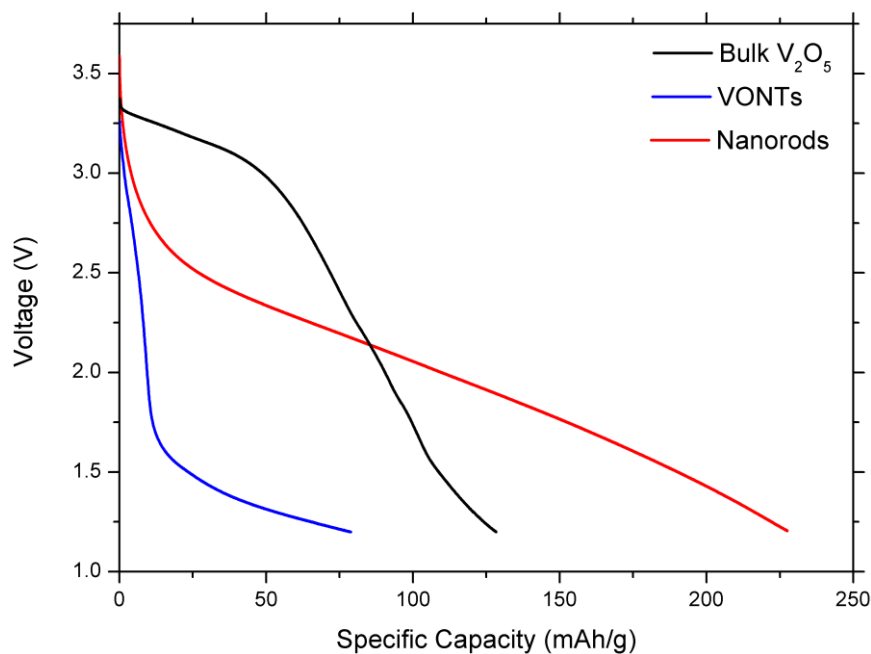
**Figure 4.** FTIR spectra for bulk V<sub>2</sub>O<sub>5</sub> powder, VONTs and poly-NRs.

The absorption occurring at the first peak, 720 – 750 cm<sup>-1</sup>, is attributed to lattice vibration of vanadium oxide. The peaks observed between 2850-2930 cm<sup>-1</sup> and 1360-1560 cm<sup>-1</sup> are due to C-H stretching and bending vibrations respectively. (25) These peaks can only be seen for the VONT sample, and from comparison of as-received vanadium oxide and the poly-NRs, the absence of C-H and the majority of N-H vibrations confirms successful removal of the amine template. The elimination of these peaks in the poly-NRs spectra is indicative of the removal of nonylamine molecules. The broad band beginning at 3040 cm<sup>-1</sup> is assigned to ammonium ions implying that the NH<sub>2</sub> head group of the amine molecules are present in the vanadium oxide layers as NH<sub>3</sub><sup>+</sup> groups. Another broad band from 3300 cm<sup>-1</sup> to 3650 cm<sup>-1</sup> is attributed to the stretching and bending modes of O-H vibrations. Both of these bands are not found, as expected, in the spectra from bulk vanadium oxide powder, but are quite clear in the IR absorbance from the VONTs due to the presence of amine molecules and water (in the form OH groups and crystal water).

For the poly-NRs we observe a single wide band from 3040 cm<sup>-1</sup> to 3650 cm<sup>-1</sup>, which is found as two individual bands for the VONTs. This band coupled with the absence of peaks associated with C-H stretching and bending vibrations, implies that during annealing the organic component of the nonylamine molecules is indeed being successfully removed from the VONTs. We do find, however, that some of the electrostatically bound, oxidized amino head groups (NH<sub>3</sub><sup>+</sup>) still remain after thermal treatment. There is further evidence for this from the peak between 1610-1620 cm<sup>-1</sup>, associated with an O-H vibration, which can be seen in the spectra for VONTs and poly-NRs but not in the bulk V<sub>2</sub>O<sub>5</sub> spectra. During the initial aging stage in the preparation of the VONTs, the amines are hydrolyzed by water to form ammonium ions and hydroxide ions. The resulting hydroxide ions reduce the V=O bond present in the V<sub>2</sub>O<sub>5</sub> molecule to form (V-OH) and (V-O<sup>-</sup>) bonds and in this manner the vanadium becomes six coordinated while still retaining its pentavalent oxidation state. The presence of peaks and bands associated with remnant V-OH bonds and electrostatic bonds between the oxidized amino head group

( $\text{NH}_3^+$ ) and the reduced vanadyl ( $\text{V-O}^-$ ) bond (most likely due to slight inefficiencies in the removal of every organic template molecule), give evidence that even after annealing to  $600\text{ }^\circ\text{C}$  the vanadium present in the poly-NRs remains six coordinated and thus as  $\text{V}_2\text{O}_5$ .

Galvanostatic discharge tests of bulk  $\text{V}_2\text{O}_5$  powder, VONTs and the poly-NRs were performed to study the effects of altering the morphology and composition of the nanostructures on their electrochemical characteristics and lithium intercalation and removal. Figure 5 shows the first discharge curve for each of these samples as a function of specific discharge capacity. These samples were discharged at a constant current of  $-30\text{ }\mu\text{A}$  to a lower voltage limit of  $1.2\text{ V}$ . As mentioned earlier, none of the active materials contained conductive additive or polymeric binder. The specific capacity of bulk  $\text{V}_2\text{O}_5$  powder after the first discharge was found to be  $\sim 128\text{ mAh/g}$ . After a xerogel has been formed from bulk powder and subsequently mixed and aged with nonylamine, the associated specific capacity value for VONTs is found to decrease to  $\sim 78\text{ mAh/g}$ . This specific capacity degradation is due to the presence of amine molecules, which can occupy sites on the vanadium oxide lattice otherwise amenable to  $\text{Li}^+$  intercalation; most VONTs in fact are covered in a sheath of organic material after hydrothermal synthesis, washing and drying. Consequently the amine molecules are impeding the intercalation of lithium ions, this leads to a reduced specific capacity. By annealing the VONTs to  $600\text{ }^\circ\text{C}$ , the majority of the amine template is removed from the VONTs, while they also change structure to polycrystalline granular nanorods. These poly-NRs however, exhibit a marked increase in specific capacity (even when compared to bulk vanadium oxide with the same crystal structure) and importantly, retain a higher average cell potential than both VONTs and bulk powder. After the first discharge the specific capacity of the poly-NRs is  $\sim 228\text{ mAh/g}$ . This is a significant improvement over the VONTs and bulk powder. We propose that the improved performance is due to reduction in the size of the vanadium oxide crystallites and improved access to the  $\text{V}_2\text{O}_5$  intercalation site for  $\text{Li}^+$  by the removal of the amine template.



**Figure 5.** Specific capacity values after the first discharge for bulk  $\text{V}_2\text{O}_5$ , VONTs and vanadium oxide polycrystalline nanorods.



The plateaus in the discharge curve for bulk  $V_2O_5$  demonstrate the various phase transitions associated with increasing mole fraction of intercalated lithium ions. Orthorhombic  $V_2O_5$  undergoes a series of structural modifications during  $Li^+$  insertion to form a series of related phases  $Li_xV_2O_5$ . (26) These distinctive plateaus are not seen in discharge curves for VONTs or nanorods. The absence of well defined plateaus indicates the absence of the formation of discrete phases. (27) Limiting the lower cut-off potentials to 2.5 V (where  $x \leq 1.0$ ) during discharging has been shown elsewhere to allow only modest structural changes allowing the material to return to the pristine orthorhombic phase after charging, but this severely limits the specific charge capacities and energy densities. Here, the potential for the VONTs initially decreases rapidly to  $\sim 1.7$  V before decaying more slowly. After the potential of the nanorods has decreased to  $\sim 2.5$  V there is a near-linear potential versus time curve. From Fig. 5 it can be seen that initially the synthesized VONTs, as discussed earlier, do not perform as well as commercially purchased bulk  $V_2O_5$  powder in terms of specific capacity and average cell voltage. These tests were performed without the addition of a conductive additive or a binder and we propose that the functionalization of the VONTs by the amine molecules is impeding the intercalation of lithium ions, resulting in lower specific capacity values. However, when the VONTs are thermally treated there is a significant increase in their specific capacity, cell voltage and energy density, compared to the closest direct equivalent, the  $V_2O_5$  powder. The primary difference is the absence of amines and a reduction in crystal size, which we correlate to the improved performance.

The difference in the structure of the three materials tested also affects their energy and power densities. The specific energy densities after the first discharge for bulk  $V_2O_5$  powder, VONTs and poly-NRs were calculated to be 140, 81 and 2718  $W\ h\ kg^{-1}$  respectively. By forming VONTs from bulk  $V_2O_5$  powder, the associated energy and power densities are reduced. When the amine-templated VONT structure is changed to a polycrystalline nanorod structure, there is a marked increase in the power and energy densities.

## Conclusions

Vanadium oxide nanotubes have been successfully synthesised by a hydrothermal treatment of a mixture of vanadium oxide xerogel and nonylamine. It is well known that VONTs can be produced using dodecylamine and hexadecylamine; however in this report it was shown that VONTs can be produced using a shorter amine chain, while maintaining the key morphological features of VONTs with longer chains. Through thermogravimetric analysis it was determined that the organic amine template can be removed from the VONTs upon heating to 600 °C. TEM imaging after annealing shows that by removing the amine molecules the VONTs physical structure is significantly altered. Initially, VONTs have three main features, the tube openings, multi-layered walls and their hollow core. After thermal treatment the layered walls are no longer visible and the nanotube crystallizes to a polycrystalline vanadium oxide nanorod. This change in the morphology of the VONTs is due to the removal of structure-maintaining amines from the vanadium oxide layers. By removing the organic template the multi-layered order is lost and a polycrystalline structure is formed, comprising nanoscale orthorhombic vanadium pentoxide crystals in a granular, rod morphology. The resulting nanorods still maintain the advantageous nanoscale dimensions of the VONTs.

FTIR analysis of the nanorods confirms the removal of the amine hydrocarbon chains by the absence of peaks associated with various C-H stretching and bending vibrations. Galvanostatic discharge tests were performed on bulk V<sub>2</sub>O<sub>5</sub> powder, VONTs and polycrystalline nanorods. It was shown that initially the as synthesised VONTs did not perform as well as the bulk powder. We propose that this is due to heavily functionalization of the vanadium oxide in VONTs with amine molecules, which impeded the insertion of lithium ions. By annealing the VONTs to form polycrystalline nanorods, significant improvements specific capacity, power and energy densities are found.

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