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# Manganese Vanadium Oxide Nanotubes: Synthesis, Characterization, and Electrochemistry

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Vanadium oxide nanotubes have been formed from the layered vanadium oxide precursor $V_2O_{5+\delta}[C_{12}H_{25}NH_3]$. Both the precursor and tubes have been characterized. The black nanotubes have a relatively low thermal stability in oxygen, being oxidized to $V_2O_5$ below 200 °C. A new manganese vanadium oxide nanotube, $Mn_{0.1}VO_{2.5+\delta}\cdot nH_2O$, has been synthesized by ion exchange. These manganese tubes have a tetragonal layer with $a = 6.157$ (3) Å and an interlayer spacing $c = 10.52$ (3) Å. The nanotubes react with lithium chemically and are also electrochemically active in lithium cells. Two lithium atoms per vanadium can be incorporated chemically from *n*-butyllithium into both the manganese and the alkylammonium nanotubes. The manganese compound electrochemically intercalates 0.5 lithium per vanadium to a 2 V cutoff, giving a capacity of 140 A h/kg.

## Introduction

There has been much interest in mesoporous materials since the discovery of the MCM-41 class of materials,[1,2] and recently this activity has extended to nanostructured materials. Vanadium forms a wide range of layered compounds, exemplified by $V_2O_5$, the double-sheet structures found in $V_6O_{13}$ and $\delta$-$V_2O_5$, tunnel compounds such as the $Na_2V_3O_7$ quantum magnet,[3] and a range of hydrothermally synthesized organic-templated oxides.[4] However, attempts to make vanadium oxide zeolitic materials have not been successful, with cluster compounds being formed instead in the presence of surfactant molecules.[5,6] Recently a major breakthrough occurred when the ETH group[7−10] reported the formation of vanadium oxide nanotubes. Several vanadium oxides are electrochemically active in lithium cells, including $V_2O_5$, $LiV_3O_8$, and $V_6O_{13}$, and recently the $\delta$-oxide $[N(CH_3)_4]_{0.2}Mn_{0.06}V_2O_{5+\delta}$[11] has been found to have a reversible capacity over 200 A h/kg.

The current cathodes in lithium batteries use cobalt compounds, which are expensive and low in natural abundance. Thus, there has been much work to find a replacement, and emphasis has been placed on vanadium and manganese oxides.[12−20] This is in part due to the wide variety of oxide structures of vanadium[4,21] and manganese.[22] Recently the ability to determine the structure formed has increased by using organic amine templates and buffered solutions, which control the polyhedra present. Thus, at low pH values $VO_6$ octahedra are prevalent, whereas in basic solutions $VO_4$ tetrahedra dominate; between one finds $VO_5$ polyhedra.[4,23] We have synthesized a number of vanadium and manganese oxides using structure directing agents.[5,23−26] One of these, $[N(CH_3)_4]_zMn_yV_2O_5\cdot nH_2O$,

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which contains $VO_6$ octahedra performs well as a cathode material in a lithium cell [11] so we are interested in related materials.

By use of the new synthesis technique developed by the ETH group,[8,10] we prepared vanadium oxide nanotubes and report here their characterization, including thermal stability, their ion exchange in manganese solutions, and the electrochemical behavior of the manganese vanadium nanotubes.

## Experimental Section

**Synthesis.** The vanadium oxide dodecylamine nanotubes were created by a solvothermal synthesis based upon the Nesper group technique.[8] In a beaker, 7.58 g (0.0417 mol) of $V_2O_5$ (Alfa) was added together with 7.73 g (0.0417 mol) of dodecylamine (Aldrich). After adding 14 mL of pure ethanol (Pharmco), the beaker was covered and the contents were stirred for 2 h. Then 41 mL of reverse osmosis water were added, and the stirring continued for 30 h. During this latter stirring samples were taken to monitor the progress of the reaction. The first sample was taken after 15 min; then samples were taken hourly for 7 h. The following day, samples were again taken hourly for a 7-h period. Samples were taken from the beaker by dipping a glass rod into the slightly viscous yellow solution, to obtain enough solution for 2–3 drops. These drops were then deposited on the center of a glass microscope slide cover slip and allowed to air-dry to form a flat film suitable for powder X-ray diffraction. After the 30 h of stirring all the reactants, the contents of the beaker were added to a 125-mL-capacity Parr acid digestion vessel and placed in a 180 °C oven for 10 days. The black product was filtered, then rinsed in an ethanol water mixture (50:50 vol) for an hour, and filtered to give a black crystalline solid. The synthesis was repeated and produced the same nanotubes.

**Ion Exchange.** The alkylammonium nanotubes were exchanged by manganese in an aqueous–alcohol solution. $MnCl_2 \cdot 4H_2O$ (Baker) was used in a molar ratio from 4 to 300 with 1 $V_2O_5$/amine for ion exchange. $MnCl_2 \cdot 4H_2O$ was placed in a beaker with reverse osmosis water and ethanol in a 1:4 ratio by volume. After the salt dissolved, the ground up vanadium oxide dodecylamine nanotubes were put into the solution with a ratio of 1 g of product per 1 mL of solution. The solution was mixed for 2–3 h and then filtered. Then the solid black ion exchange product was rinsed with ethanol (Pharmco) and hexanes (Aldrich) and allowed to air-dry.

**Lithium Reduction Electrochemistry.** Butyllithium was used to determine the amount of lithium that can be inserted into the nanotubes; 1.6 M butyllithium solution in hexane (Aldrich) was used following standard procedure.[27,28] Electrochemistry was performed in a Swagelok cell setup. The oxide was mixed with polyvinylidene fluoride (Aldrich) and carbon black (Cities Service Co.) after adding 20 drops of cyclopentanone (Aldrich). The resultant slurry was applied onto a nickel disk (1 cm$^2$) and it was left to dry. Upon drying, the coating was dehydrated by heating at 150 °C for about 7 h. The lithium anode was supported on a nickel disk. A 1 M solution of $LiAsF_6$ in dimethyl carbonate (DMC), ethyl carbonate (EC), and ethyl methyl carbonate (EMC) (EM industries) was used as the electrolyte. The applied current density was 0.1 mA/cm$^2$ and the potential varied between 2.0 and 4.0 V. The cell was run using the Mac-Pile system.

**Characterization.** X-ray powder diffraction (XRD) was obtained on a Scintag XDS 2000 powder diffractometer using Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å). Thermogravimetric analysis (TGA), to determine water and organic content as well as overall stability, was done on a Perkin-Elmer TGA 7, typically from 30 to 600 °C at 5 deg/min in oxygen or nitrogen gas. Electron microprobe analyses and scanning electron microscope (SEM) images were obtained with a JEOL 8900 electron microprobe on carbon-coated samples. The Fourier transform infrared (FTIR) instrument used was a Perkin-Elmer Spectrum BX, with all of the samples being pressed into KBr pellets. Transmission electron microscopy (TEM) was done on a Hitachi H-7000 electron microscope at 125 kV with samples mounted on a lacey carbon coated copper grid after suspension in an ethanol–water mixture (50:50 v/v).

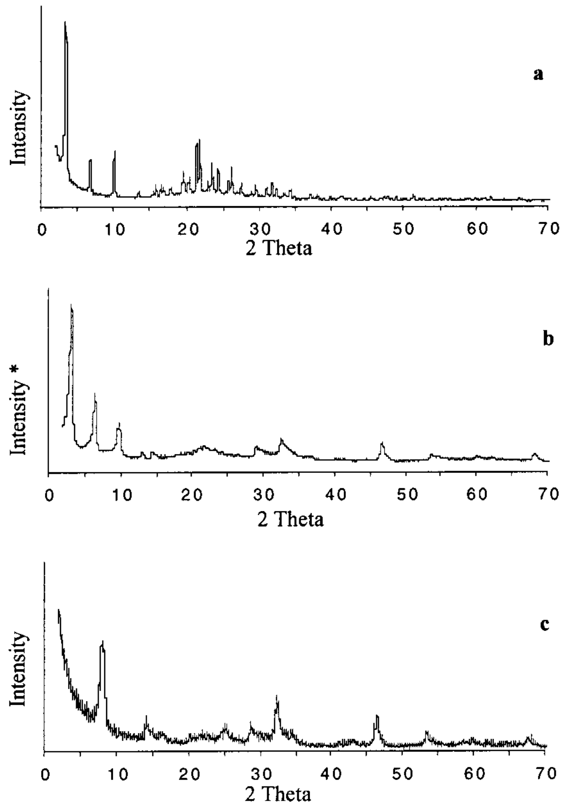

**Figure 1.** XRD patterns of (a) the layered precursor of vanadium pentoxide with dodecylamine, (b) the vanadium oxide nanotubes with dodecylamine with the square root of the intensity, and (c) the vanadium oxide nanotubes with manganese cations.

## Results and Discussion

**Formation of the Layered Compound.** The progress of the reaction between vanadium pentoxide and dodecylamine was followed by frequently sampling the reaction medium. The samples taken over time from the reaction in the beaker showed the development of a layered compound. Even after just 15 min the X-ray diffraction patterns for $V_2O_5$ and dodecylamine were no longer seen, and a broad peak was seen around 3.4° $2\theta$, which is the area where the largest peak appeared for the layered phase. After 5 h sharp peaks were observed at the *d* spacings of the final layered product. At later times the peaks' positions did not change, but they became sharper. The color changed from the initial bright yellow of $V_2O_5$ and white of dodecylamine mixture, to a more uniform moderate yellow color, and then to a yellowish brown product. This final mustard yellow product was the precursor in the hydrothermal reaction for nanotube formation.

The X-ray diffraction pattern of this material is shown in Figure 1a and indicates a layered compound with interlayer spacing of 26.4 Å plus organic residue. The FTIR spectrum, Figure 2a, shows no absorption near

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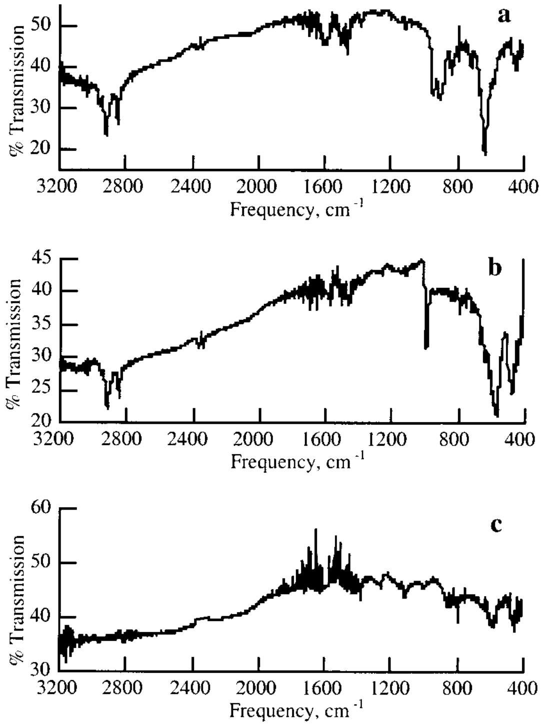

**Figure 2.** FTIR spectra of (a) the layered precursor, (b) the vanadium oxide nanotubes with dodecylamine, and (c) the vanadium oxide nanotubes with manganese cations.

3400 cm$^{-1}$ associated with N−H belonging to a primary amine, but one was found near 3000 cm$^{-1}$ typical of that for N−H stretching in the $NH_3^+$ group that overlapped the C−H stretching bands.[29] Thus the amine is protonated to form $C_{12}H_{25}NH_3^+$. Further evidence for the $NH_3^+$ group is the peak around 1580 cm$^{-1}$, which is the frequency for $NH_3^+$ asymmetric bending.[29] Evidence for the protonated dodecylamine being in the layered product was seen by the C−H vibrations around 2900 and 1465 cm$^{-1}$. The absorptions at 635, 903, and 948 cm$^{-1}$ are assigned to V−O bond vibrations.

Thermogravimetric analysis, shown in Figure 3a, shows a 51% weight loss from 80 to 450 °C due to loss of the organic portion of the compound, which comes out over a range of temperature. The final product was pure $V_2O_5$, which gives this layer compound the composition: $V_2O_5(C_{12}H_{25}NH_3)_1$.

**Vanadium Oxide Alkylammonium Nanotubes.** Vanadium oxide nanotubes containing dodecylamine were formed during the hydrothermal treatment of the layered vanadium oxide. Excess organic amine was washed away with a 50:50 (vol/vol) ethanol−water mixture; the organic waste contained about 8% inorganic according to residual after TGA.

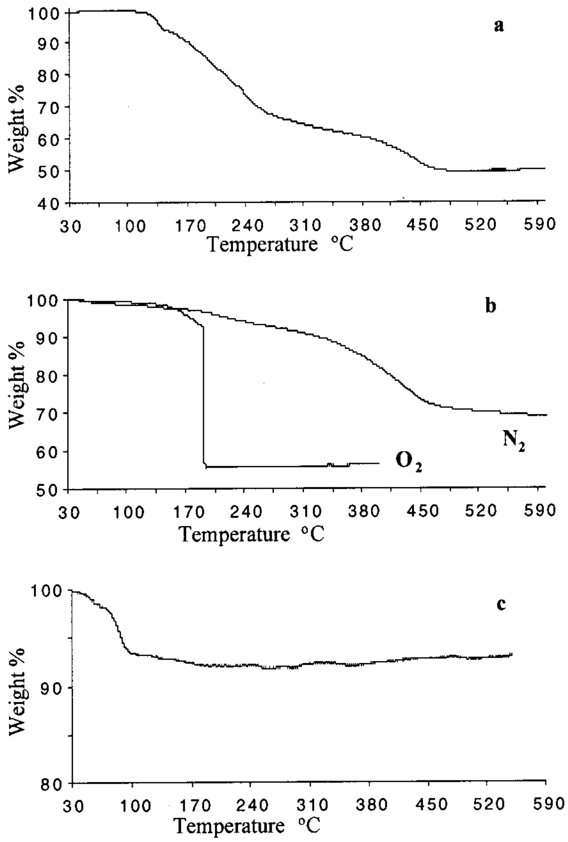

**Figure 3.** TGA graphs of (a) the layered precursor, (b) the vanadium oxide nanotubes with dodecylamine, and (c) the vanadium oxide nanotubes with manganese cations.

The TGA in oxygen, shown in Figure 3b, indicates a 44% weight loss from 30 to 200 °C due to loss of the organic ion, $C_{12}H_{25}NH_3$. Dodecylamine itself, under the same conditions, behaves in a similar manner showing a weight loss beginning around 40 °C. The very abrupt loss in weight of the nanotube, in contrast to the layer phase, suggests a fixed composition for this phase, which is unstable at lower alkylammonium contents. The relatively low thermal stability of the nanotubes in oxygen suggests that the nanotubes are excellent oxidation catalysts; the tubular morphology is totally destroyed before 300 °C. In contrast, when heated in nitrogen the stability is much improved and the tubular morphology is retained until at least 400 °C. The nanotubes have a black color, indicating some V in a 4+ oxidation state; after TGA in oxygen, yellow/orange $V_2O_5$ was formed and confirmed by X-ray analysis. This suggests a chemical composition of $V_2O_{5+\delta}(C_{12}H_{25}NH_3)_{0.74}$ for the nanotube. The nanotubes have around a 25% lower organic content than the precursor layered phase. This organic content, $\approx$0.37 alkyl chains/vanadium, is comparable to the 0.34 reported by Nesper.[9]

The FTIR spectrum shown in Figure 2b indicates the continued presence of the $NH_3^+$ vibrations after the hydrothermal synthesis. Aliphatic C−H bond vibrations were seen around 2900 and 1465 cm$^{-1}$ just as with the layered compound. However, there was a shift in the vanadium−oxygen bands, the vanadyl bond vibration shifted to 993 cm$^{-1}$ and the V−O bond vibration shifted to 576 cm$^{-1}$.

The powder X-ray diffraction pattern of the vanadium oxide nanotube with dodecylamine, shown in Figure 1b, displayed three strong peaks at 27 Å (001), 13.4 Å (002), and 9.0 Å (003). These three peaks are basically the same as for the layered compound, indicating that the *d* spacing in the 00*l* direction is controlled by the dodecylammonium chains. The difference between the two diffraction patterns is due to the basal plane

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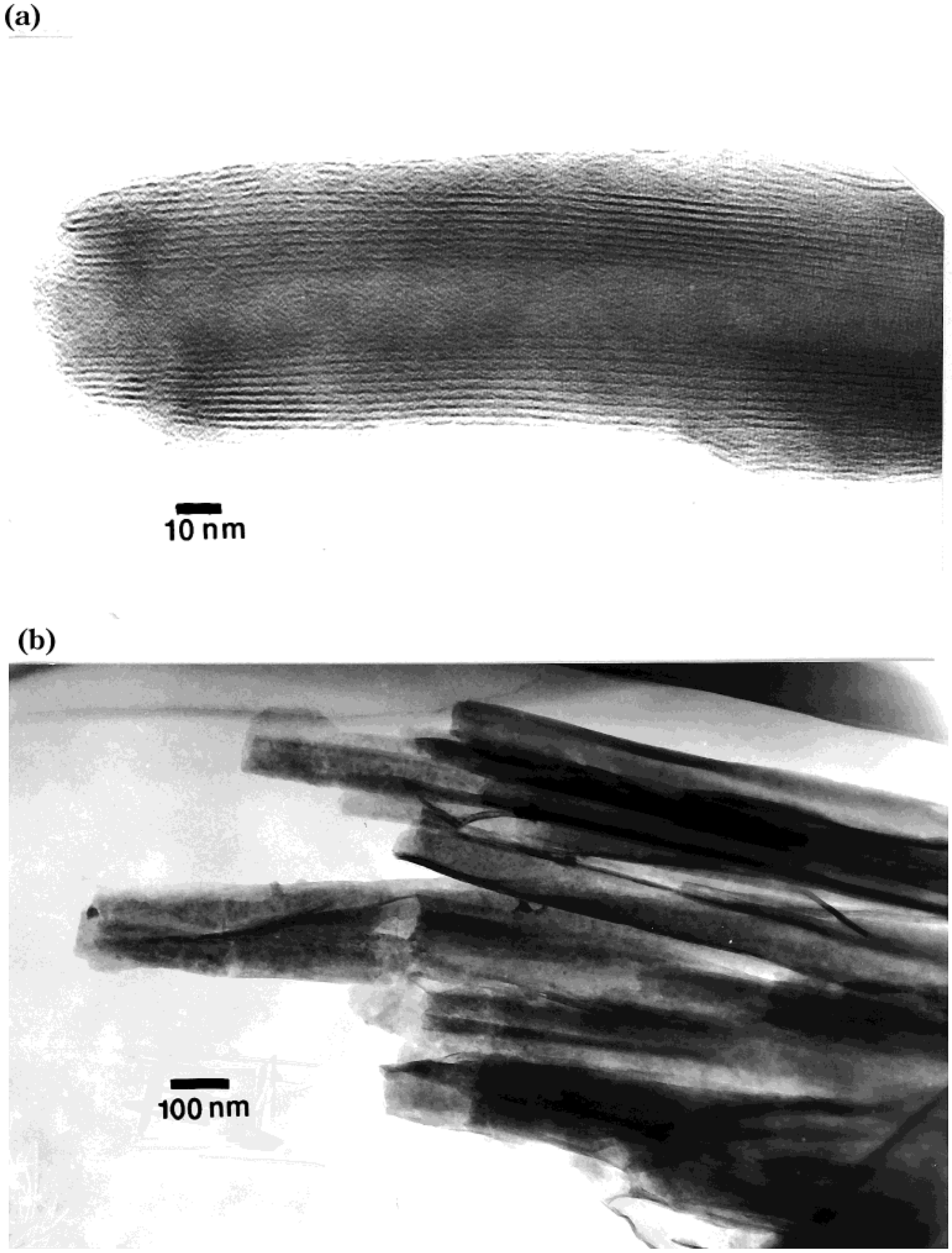

**Figure 4.** TEM images of (a) the vanadium oxide nanotubes with the amine and (b) the manganese intercalated vanadium oxide nanotubes.

structure of the vanadium oxide quasi-layers. We call them "quasi-layers" since the actual $VO_y$ layers must be bent to form the larger nanotube morphology. The X-ray pattern could be indexed with a tetragonal basal plane with $a = 6.144$ (2) Å and an interlayer spacing of $c = 26.6$ (2) Å. This size $a$ parameter and the square basal plane lattice must come about from a double sheet of vanadium atoms, containing vanadium in mostly distorted octahedral coordination. The $a$ parameter is similar to that, $a = 6.160$ Å and $c = 21.522$ Å, of $BaV_7O_{16}{\cdot}nH_2O$,[30] synthesized hydrothermally, where six of the vanadium atoms are in octahedral coordination and the seventh is in a tetrahedrally coordinated site. We recently have studied[31] the structure of another double-sheet vanadium oxide synthesized hydrothermally: $[N(CH_3)_4]_4[Zn_4V_{21}O_{58}]$. This compound is closely related to $BaV_7O_{16}{\cdot}nH_2O$ but with zinc ions in the tetrahedral sites in the vanadium oxide sheet and a larger in-plane lattice, $a = 16.348$ Å, $c = 11.487$ Å, and space group $P4/n$. We believe that these hydrothermally synthesized nanotubes have a similar structure.

The TEM images at low magnification showed clusters of long needlelike crystals. Magnification at 200 000x showed the crystals to be tubes with a quasi-layered structure, as shown in Figure 4a. Most nanotubes had open ends, while some of them had closed ends with the side of the tube wrapped around the end to close it off. Some of the tubes appeared to be wrapping, or unwrap-

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ping, as some of the outer layers were peeling off. The external diameter of the tubes were similar, typically just under 100 nm.

**Manganese Intercalated Nanotubes.** Manganese very readily ion-exchanged for the organic cations, with all the organic being removed from the lattice. The only weight loss observed, Figure 3c, on thermal analysis in oxygen was below 150 °C and the 7.6% weight loss can be associated with waters of hydration. Above 150 °C there was less than a 1% weight gain, which can be associated with complete oxidation as the color changed from black to a dark yellow. X-ray analysis of the oxidation product indicated $V_2O_5$ and $MnV_2O_6$, consistent with a Mn:V ratio of less than 0.5. This very small weight gain suggests that the vanadium is almost all in the +5 oxidation state.

The electron microprobe was used to determine the ratio of vanadium to manganese and to look for contaminants. No other elements were found, and the ratio of vanadium to manganese was $1-0.12 \pm 0.04$ from scans over a few micrometers that covered several nanoubes. SEM images showed long needlelike crystals clumped together. These images were similar to those observed in the transmission electron microscope, Figure 4b. The nanotubes were up to 100 nm in diameter and 1300 nm in length. However, the manganese nanotubes were rougher in appearance, showing distorted sides with a slight waviness to the side of the tube, and some appeared to have split open probably due to the high stress upon ion exchange. The FTIR spectra on the manganese intercalated nanotubes was relatively poor with only a few peaks, as is fairly typical of manganese oxides. The results, shown in Figure 2c, are consistent with the TGA data, showing no evidence of N−H or C−H vibrations, indicating the complete removal of the amines. Small peaks for the metal oxygen vibrations were seen at 1001 and 593 $cm^{-1}$.

The XRD pattern, shown in Figure 1c, of the manganese-containing vanadium oxide nanotubes had a pattern similar to that of the nanotube with the amine in it. However, there are marked changes below 28° $2\theta$ where the reflections are due to the interlayer spacing. The interlayer spacing changes from 27 Å for dodecylamine to 10.5 Å for the hydrated manganese cation. The peaks above 28° $2\theta$ appear to be unchanged, and they come predominantly from the basal plane of the vanadium oxide. The unit cell of this compound has a tetragonal layer with $a = 6.157(3)$ Å and an interlayer spacing $c = 10.52(3)$ Å. Electron diffraction showed an in-plane lattice distance of 6.2 Å, consistent with the X-ray value. This indicates that the structure of the vanadium oxide sheets is essentially unchanged after ion exchange with just a slight expansion in $a$ from 6.144 to 6.157 Å.

**Lithium Reactivity and Electrochemistry.** Both the alkylammonium and the manganese vanadium oxide nanotubes reacted readily with *n*-butyllithium, 15.3 and 23.9 mol of lithium being consumed per kilogram of solid, respectively, which is just over 2 lithiums per vanadium atom. Thus the vanadium is reduced from +5 to +3, which is consistent with the approximately 1V potential of the reactant versus lithium metal, and is the same as observed for $V_2O_5$ itself.[28]

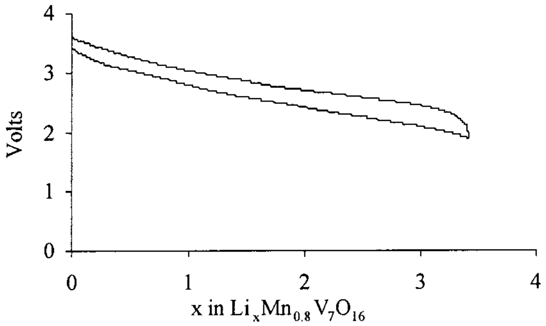

**Figure 5.** First discharge and charge cycle of the manganese vanadium oxide nanotubes in a lithium cell.

The electrochemical intercalation of lithium into the manganese compound is shown in Figure 5. Around 0.5 lithium ions per vanadium atom were intercalated above 2 V, this lithium could be readily removed with little overpotential. The initial cell voltage was 3.5 V, typical of that of other vanadium oxides such as the layered $[N(CH_3)_4]_{0.2}Mn_{0.06}V_2O_{5+\delta}$.[11] The capacity of this cell is 140 A h/kg. This is just two-thirds of the capacity of the layered manganese vanadium oxide, 220 A h/kg,[11] to the same cutoff voltage. Additional capacity can be obtained in the region 2 V down to 1 V, as exemplified by the chemical reaction of two lithium per vanadium with *n*-butyllithium solutions. In addition, there are some other differences. The layered compound has a distinct end of discharge and end of charge points,[11] which has not been attained in these nanotubes where a continuously dropping discharge curve more typical of that of a capacitor is observed; it is also quite similar to that of less crystalline vanadium oxides such as $M_yV_2O_5 \cdot nH_2O$.[32] Cyclic voltammetry of the $[C_{16}H_{33}NH_2]_{0.34}VO_{2.45}$ nanotubes indicated[9] a single reduction peak around 3.3 V. On replacing the amine with sodium ions the reduction peak became broader and dropped to around 2.7 V and a second reduction peak was observed at 1.8 V. The maximum current densities observed in the cyclic voltammograms were around 0.4 $mA/cm^2$.[9]

Further studies will be needed to fully understand the different reduction pathways for the conventional layered vanadium oxides and for these vanadium oxide nanotubes.

## Conclusions

Vanadium oxide nanotubes have been synthesized, characterized and their thermal stability determined. Manganese has been incorporated into the tubes in place of the alkylammonium ions with a contraction of the inter-sheet distance and structure retention. These ion-exchanged tubes react readily with lithium in a reversible manner.

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