Vanadium Oxide Nanotubes: Characterization and Electrochemical Behavior

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Vanadium Oxide Nanotubes: Characterization and Electrochemical Behavior

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ABSTRACT

Vanadium oxide nanotubes (VONT) were formed from vanadium (V) oxide and the dodecylamine templating agent by a sol-gel reaction and subsequent hydrothermal treatment. The nanotubes were characterized by transmission electron microscopy (TEM), electron diffraction, thermogravimetric analysis (TGA), infrared spectroscopy and powder X-ray diffraction (XRD). The nanotubes consist of VO$_2$$_{1.4}$[C$_{12}$H$_{28}$N]$_{0.27}$ and range in diameter from 100 nm to 150 nm. The study further reveals that the compound maintained the tubular morphology when heated at 430°C in an inert atmosphere. However, the tubular morphology is destroyed when the compound is heated at about 130°C in oxygen.

Organic free manganese intercalated vanadium oxide nanotubes (MnVONT) were synthesized by an ion exchange reaction. The previously mentioned techniques were used to characterize MnVONT. Mn$_{0.86}$V$_7$O$_{16+8}$ nH$_2$O layers have 2D tetragonal cell with a=6.157(3) Å, while interlayer spacing is 10.52 (3) Å. VONT, heated VONT and Mn$_{0.86}$V$_7$O$_{16+8}$. nH$_2$O are redox-active and can insert lithium reversibly. This study reveals that the electrochemical performance of VONT is enhanced by removing the organic template by heating in an inert atmosphere or exchanging with Mn$^{2+}$ ions.

INTRODUCTION

In the course of the present efforts towards miniaturization of electronic and mechanical devices, structures with a size in the nanometer region have stimulated intensive research activities as evidenced in increase in volume of publications in recent past. Among such nanostructures are materials with tubular morphology.

Recently transition metal compounds, mainly oxides with two dimensional and three dimensional open structures, have been studied and developed for use as cathode materials in rechargeable secondary lithium battery in our research laboratory [1-3]. Our interest has focused on materials with one-dimensional structures for which the nanotubes are very promising candidates. The tubes attract much scientific interest for electrochemical insertion mainly for two reasons. One, they offer four different contact regions, namely, the inner and outer wall surfaces as well as the tube ends. Secondly, they can provide electrolyte-filled channels for faster transport of the ions to the insertion sites [4]. This study for the first time shows how the electrochemical behavior of the nanotubes can be improved by removing the organic templates by heating under inert atmosphere.

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EXPERIMENTAL DETAILS

The vanadium oxide nanotubes were prepared according to literature method with modifications where necessary [5]. Vanadium (V) oxide and dodecylamine were mixed in the molar ratio 1:1 in ethanol and the mixture stirred for 3 hours in air. The mixture was then hydrolyzed under vigorous stirring followed by aging, which led to the formation of a yellow suspension. Subsequent hydrothermal treatment for 7 days resulted into a black powder. The product was washed with ethanol, diethylether and water to remove excess dodecylamine and any decomposed products. It was then dried under a vacuum at 80°C for 12 hours.

Substitution of the organic template for Mn^{2+} ions was done by stirring a mixture of VONT and MnCl₂ (molar ratio 1:4) for 2 hours in ethanol/water mixture 4:1 (v/v) (200ml/g of VONT). The resulting mixture was centrifuged and washed with water, ethanol and diethyl ether. The product was then dried in the vacuum at 80°C for 12 hours.

The morphology and the structure of the nanotubes were investigated by using XRD and TEM. Thermal stability of the nanotubes was investigated using TGA in oxygen and nitrogen. In an oxygen atmosphere structure collapse at about 130°C. By heating the compound in helium at 430°C for 1 hour the organic portion in the VONT was removed but the tubular morphology was maintained.

The performance of these compounds as positive electrode was tested by galvanostatic cycling in the potential range 1.4-3.9 V vs Li/Li⁺. In all cases the sample was prepared by mixing the nanotubes with equal weight of Teflonized carbon black (25 wt.% polytetrafluoroethylene and 75 wt.% acetylene black). The cathode material was then hot pressed onto a stainless steel Exment™ grid at 110°C to dehydrate the sample. Metallic lithium served as counter and reference electrodes.

DISCUSSION

The product was obtained as black powder suggesting that the vanadium be in mixed oxidation state +4 and +5 because mixed-valent vanadium oxides are generally black e.g. V₆O₁₃. In fact, the compound reduces standard cerium (IV) sulphate. Quantitative analysis indicates that about 46% of the vanadium ions are in oxidation state +4. In the exchange reaction, all of the organic was replaced with metal cations as explained in later sections of this paper. Attempts to replace the organic with lithium ions and other organic molecules are being made.

Thermogravimetric analysis

This study showed the presence of the dodecylamine template in VONT is about 33% by weight. Thermoanalysis of Mn₀.₈₁V₇O₁₆·₂·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ₐ·ạn...
Figure 1. XRD patterns of a) VONT and b) MnVONT showing substantial decrease in interlayer spacing (001 reflections shift towards higher angles) while hk0 are at the same positions in both patterns (after [7]).

X-ray diffraction

X-ray diffraction pattern of the vanadium oxide nanotubes (VONT) with dodecylamine displays three strong peaks at 20.720 Å (001), 12.59 Å (002) and 10.23 Å (003). Replacing the organic template with the cations results in drastic reduction of the d-spacing to 9.3 Å [7]. Further evidence for this was shifting of 001 reflections due to interlayer Vanadium oxide sheets to large scattering angle as shown in Figure 1. The hk0 reflections due to the vanadium oxide sheets remain at the same positions showing that the structure of the layers remains the same [8].

Transmission electron microscopy

TEM shows that VONT consists of tubes with outer diameter ranging from 100 nm –130 nm, while their length vary from 500 nm to a maximum of 1500 nm. Closer look at the image shows reveals scroll-like tubes with open ends (Figure 2). Layers or the strides on the walls confirm that vanadium and the organic template molecules distribution occur in distinctly alternating regions in the wall regimes. In contrast, some walls of the Mn²⁺ ions exchanged nanotubes had no distinct alternating regions confirming the incorporations of the metal ions in the layers (Figure 3). Since Vanadium and manganese ions have similar scattering factors, it is difficult to distinguish their sites.

TEM also confirmed that it is possible to remove the organic by heating VONT in helium at 430°C but preserve the tubular morphology. TEM image shows the sites previously occupied by the organic molecules in VONT are empty after heating.
Figure 2. Typical TEM images of VONT (left) showing open ends and MnVONT (right) (product of MnCl₂ treatment). The layered structure inside the VONT walls appears as alternating narrow dark lines and broad bright lines.

X-ray diffraction however shows that the structure of the compound changes after heating. In oxygen, the tubular morphology is destroyed when the material is heated at about 130°C.

Electrochemistry

The cell performance of compounds as it was shown closely depends on the electrolyte salt used. Cells were made in LiClO₄ and LiPF₆ as the electrolyte salt; the solvent used was propylene carbonate (PC). The electrochemistry of MnVONT was investigated in LiAsF₆ (Figure 3). The compound intercalates 0.5 mole Li⁺ ions per one mole of vanadium. Capacity of heated VONT was over 100 mAh/g for at least 40 cycles in the two salts. However, the capacity of VONT drops after the second cycle but remains constant at 46 mAh/g after the eighth cycle (Figure 4). Effect of electrolyte salt on the performance of these compounds has been reported elsewhere [9]. Maximum specific charge in mAh/g for each material is given in the table below.

<table>
<thead>
<tr>
<th>Material</th>
<th>in LiClO₄</th>
<th>in LiPF₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>VONT- VO₂₄[C₁₂H₂₄N]₀.₂₇</td>
<td>60</td>
<td>180</td>
</tr>
<tr>
<td>heated-VONT</td>
<td>120</td>
<td>220</td>
</tr>
<tr>
<td>Mn₀.₈₆V₇O₁₆₊₆·nH₂O</td>
<td>140</td>
<td>240</td>
</tr>
</tbody>
</table>

It appears that heating VONT and replacing part of the organic molecules with metal ions enhance its electrochemical performance as cathode material for lithium battery. We propose that removal of the organic allows for insertion of more lithium ions hence improving its electrochemical behavior.
Figure 3. First electrochemical cycle of MnVONT in LiAsF$_6$ salt. About 3.4 moles of Li$^+$ ions were reversibly intercalated into the compound, after [7].

Figure 4. Capacity of VONT and heated VONT for the first 10 cycles with LiPF$_6$ as salt in propylene carbonate. The electrode material contained 50 wt% teflonized carbon.
CONCLUSIONS

For the first time it was shown that the tubular morphology of vanadium oxide can be preserved if the organic template is removed by heating the material in an inert atmosphere. The present study shows that the performance of the nanotubes as cathode materials can be enhanced by removing the organic template by heating or by substituting it with Mn$^{2+}$ ions.

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References: