Electrochemical Performance Improvement of Vanadium Oxide Nanotubes as Cathode Materials for Lithium Ion Batteries through Ferric Ion Exchange Technique

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ABSTRACT: Mixed-valence vanadium oxide nanotubes (VO$_x$-NTs) are successfully prepared with dodecylamine as the templates intercalated between VO$_x$ layers. A novel ferric ion exchange technique is carried out to remove the amine templates which have no contribution to electrochemical performance of VO$_x$-NTs. TEM observation, XRD study, and FTIR analysis reveal that a large proportion of the amine templates within VO$_x$-NTs can be exchanged by ferric ions in the reaction process, and the tubular morphology and multiwalled structure are not damaged by this exchange technique. Moreover, XPS results indicate that the ferric ion exchange process is also accompanied by the increase of vanadium valence, which is conducive to the improvement of electrochemical capacity of Fe-VO$_x$-NTs. The final synthesized Fe-VO$_x$-NTs exhibit superior specific capacity (311 mAh g$^{-1}$ at 50 mA g$^{-1}$ discharge current density in the potential range of 1.5−4 V versus Li/Li$^+$) and cycling performance (178 mAh g$^{-1}$ after 50 cycles) compared to congeneric modified materials when used as cathode materials for lithium ion batteries.

1. INTRODUCTION

At present, much attention is being paid to the designing of one-dimensional nanostructures of transition metal oxides.$^{1,2}$ This is due to their important properties from quantum confinement to electrochemical application and catalysis.$^{3–5}$ In recent years, the demand for the high capacity and good cyclic stability of lithium ion batteries has been increasing, which stimulates us to search for higher performance electrode materials, especially cathode materials.$^6$ One-dimensional nanostructured vanadium oxide materials like nanofibers, nanorods, nanobelts, and nanotubes, which can be used as a promising cathode material for lithium ion secondary batteries, have been extensively researched because of their good cyclic stability and higher specific capacity than corresponding traditional cathode materials.$^7$ Among these nanostructured vanadium oxides, the vanadium oxide nanotubes (VO$_x$-NTs), which have open-ended and multiwalled tubular structure, can provide large active surface area and many channels for the fast transport of lithium ions.$^{8,9}$ In general, the synthesis of VO$_x$-NTs was conducted by using lamellar-structured vanadium oxide as precursors and organic long-chain amines as structured-directing templates through hydrothermal reaction.$^{10,11}$ For example, Nordlinder et al.$^{12}$ Li et al.$^{13}$ and Sun et al.$^{14}$ synthesized VO$_x$-NTs that show an initial discharge capacity of nearly 300 mAh g$^{-1}$, but the capacity decay of these VO$_x$-NTs materials was very serious during the cycling. Some researchers introduced metal doping methods$^{15,16}$ and heat treatment process, but these modification methods were not so effective, especially to cyclic performance because of the lower vanadium valence$^{17}$ and the existence of abundant amine templates which have no contribution to the electrochemical performance. To improve the electrochemical performance of VO$_x$-NTs and simultaneously conserve the tubular structure, a new technique, such as cation exchange reaction, was introduced to exchange the organic templates with Na$^+$, Ca$^{2+}$,
or Co$^{2+}$ ions, but the effect of modification on the electrochemical performance is not satisfactory.

In this paper, we successfully synthesize VO$_2$-NTs with dodecylamine as templates through a simple sol–gel process and hydrothermal treatment. The following ferric ion exchange technique was performed to remove the amine templates as much as possible for the improvement of electrochemical performance. This novel ferric ion exchange reaction can effectively remove the protonated amine templates within VO$_2$-NTs, and the reaction process does not damage their tubular morphology and multiwalled structure. Furthermore, the strong oxidizing ferric ions promote the increase of vanadium valence in the samples. Electrochemical measurements are combined with some necessary characterizations to further demonstrate the prepared samples and to discuss the reasons for the improved electrochemical performance as cathode materials.

2. EXPERIMENTAL SECTION

First, vanadium oxide nanotubes (VO$_2$-NTs) were prepared by the following procedures: (1) 1.02 g of crystalline V$_2$O$_5$ powder was slowly dissolved in a solution of hydrogen peroxide (H$_2$O$_2$, 80 mL, 30%) under magnetic stirring. The strong exothermic reaction took place during the reactive process, which led to the release of oxygen gas and the formation of V$^{5+}$ peroxo complexes. When a clear orange solution was formed after about 30 min, the aqueous solution was aged for 2 days and it gradually changed into a red gel which corresponds to V$_2$O$_5$·nH$_2$O. (2) 1.04 g of dodecylamine (C$_{12}$H$_{25}$NH$_2$) was added to the red V$_2$O$_5$·nH$_2$O gel, and the yellow mixture was stirred vigorously for 24 h. (3) The final composite was moved into a Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 180 °C in a constant temperature oven for 5 days. And finally, the precipitate was filtered, washed with absolute ethanol, and dried at 80 °C under a vacuum for 8 h. The obtained black powder was VO$_2$-NTs.

To synthesize ferric ion exchanged vanadium oxide nanotubes (Fe-VO$_2$-NTs), the cationic exchange technique was carried out as follows: first, 5 g of FeCl$_3$·6H$_2$O was slowly dissolved in 10 mL of deionized water. Then, 0.5 g of VO$_2$-NTs was dispersed in 90 mL of deionized water/absolute ethanol (1/8 volume ratio) mixed solution and kept ultrasonic vibration for 1 h at room temperature. After that, the FeCl$_3$·6H$_2$O solution was slowly injected into the stirred VO$_2$-NTs suspension. Finally, the whole mixture solution was kept at 30 °C and stirred continuously. The ferric ion exchange process was carried out for 12 h with constant magnetic stirring. The resulting precipitate was filtered, rinsed, and dried under a vacuum at 80 °C for 8 h. The final product was Fe-VO$_2$-NTs.

Field emission scanning electron microscopy (FESEM, Philips-XL-30FEG) and transmission electron microscopy (TEM, JEOL-1230) were employed to observe the structure and morphology of the samples. TEM powder samples were prepared by dispersing a drop of sample solution onto a copper wire mesh. Transmission electron microscopy investigations were performed using a 200 kV JEOL-1230 instrument. X-ray powder diffraction (XRD) pattern was obtained by using a RigataD/max-C diffractometer with Cu Kα radiation source (λ = 1.5406 Å). Fourier transform infrared spectroscopy (FTIR) measurements were carried out in the range of 400–4000 cm$^{-1}$ using a Bruker-TENSOR27 FTIR spectrometer. The thermogravimetry (TG) and differential scanning calorimeter (DSC) measurements were carried out on a SDT Q600 in the temperature range of 50–650 °C using a heating rate of 10 °C/min$^{-1}$ under air atmosphere. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin-Elmer) with Mg Kα radiation (hυ = 1253.6 eV). Binding energies were calibrated by using the contamination carbon (C$_{1s}$ = 284.6 eV). The data analysis was carried out by using XPS Peak4.1 software.

The working electrodes (cathode) were prepared by mixing 70 wt% active materials (VO$_2$-NTs or Fe-VO$_2$-NTs) with 20 wt% carbon black as a conducting agent and 10 wt% poly(vinylidene fluoride) (PVDF) as a binder. N-Methylpyrrolidone (NMP) solvent was added to the mixture to form a slurry, which was uniformly pasted on aluminum foils. The coated electrodes were dried in vacuum at 120 °C for 8 h and then pressed. The electrolyte was 1 M LiPF$_6$ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 volume ratio). Lithium metal was used as the counter and reference electrode and a microporous film (Celgard 2500) as the separator. The coin cells were assembled in an argon-filled glovebox. Galvanostatic charge–discharge and cyclic voltammetry (CV) tests were performed by using LAND cell-testing system and CHI660C (Chenghua, Shanghai) electrochemical workstation in the potential range of 1.5–4 V (vs Li/Li$^+$). All tests were carried out at the room temperature.

3. RESULTS AND DISCUSSION

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were employed to characterize the morphology and structure of the synthesized samples. Figures 1 and 2 give the TEM images of VO$_2$-NTs and Fe-VO$_2$-NTs at different magnifications, respectively. It can be seen that both of the two samples have the open-ended multilayered tubular structure with a diameter of about 100 nm. As can be seen from the higher magnification TEM image in Figure 1c, the VO$_2$-NTs are composed of alternately arranged VO$_x$ layers (dark fringes) and dodecylamine templates (broad light fringes). In order to obtain higher specific capacity when used as cathode materials, we must minimize the content of amine templates and simultaneously conserve the multiwalled tubular structure. After the ferric ion exchange process, as shown in Figure 2c, the distance between VO$_x$ layers within Fe-VO$_2$-NTs decreases obviously from ~3 to ~1 nm, but the multilayered tubular structure is almost unaffected by this exchange reaction. For the two-dimensional fringes in the image, one (the dark fringe) represents the VO$_x$ layer, and the other one (the light fringe) stands for residual organic templates (C$_{12}$H$_{25}$NH$_3$$^+$). It is worth noting that a certain degree of deformation will happen to the residual organic templates under the strong electron beam irradiation of TEM, so some fringes look blurry and seem to extend out of the nanotube. We conclude that the dodecylamine templates, which have no contribution to electrochemical performance and impede the fast transport of lithium ion in VO$_2$-NTs cathode materials, are effectively removed by this ferric ion exchange technique without destroying the multiwalled tubular structure. Furthermore, the inner diameter of Fe-VO$_2$-NTs (about 60–90 nm) becomes larger than that of VO$_2$-NTs (about 20–50 nm) by comparing Figure 1b with Figure 2b. A schematic diagram is given in Figure 3 to illustrate this process more clearly. When the long-chain organic templates are removed from the interlayered space, the internal stress inside VO$_x$ layers will drive the neighboring VO$_x$ layers close to each other from the inside out, which makes the inner diameter of Fe-VO$_2$-NTs larger than that of VO$_2$-NTs. Figure 4 shows the...
SEM images of the two samples. It is clear that Fe-VO$_x$-NTs (Figure 4b) exhibit more obviously hollow tubular structure than VO$_x$-NTs (Figure 4a).

The structure of the two samples was examined using powder X-ray diffraction (XRD) measurements. Figure 5 shows two series of diffraction peaks: one is the (00l) set of diffraction peaks (Figure 5a) at the small-angle region (1.5°−15°), which correspond to a well-ordered lamellar structure of the tubular samples, and the other is the (hk0) set of diffraction peaks (Figure 5b) at the large-angle region (15°−50°), which correspond to the two-dimensional structure of VO$_x$ layers. As can be seen from Figure 5a, the (001) peak, which reflects the distance between VO$_x$ layers, has shifted from 3.17° to 7.67° after the ferric ion exchange process. According to Bragg’s
peaks (Figure 5b) remain at the same positions for both of the templates within VO$_2$-dodecylamine, showing the successful intercalation of organic (this value is consistent with the theoretical length of $h k l$) removal of dodecylamine templates. The (this value is consistent with the theoretical length of $h k l$) removal of dodecylamine templates. The ...

Figure 3. Effect of exchange process on the multiwalled tubular morphology of VO$_2$-NTs.

Figure 4. SEM images of VO$_2$-NTs (a) and Fe-VO$_2$-NTs (b).

Figure 5. Small-angle (a) and the wide-angle (b) diffraction patterns of the two samples.

law, the distance between VO$_2$ layers has reduced from 2.79 nm (this value is consistent with the theoretical length of dodecylamine, showing the successful intercalation of organic templates within VO$_2$-NTs) to 1.15 nm, indicating the effective removal of dodecylamine templates. The (hk0) diffraction peaks (Figure 5b) remain at the same positions for both of the samples, showing that the ferric ion exchange reaction does not have impact on the two-dimensional structure of VO$_2$ layers.  

A simplified schematic diagram of the ferric ion exchange process is given in Figure 6. The tube walls (VO$_2$ layers) consist of two sheets of VO$_2$ square pyramids with apexes pointing toward opposite directions and joined by VO$_4$ tetrahedra.  

The protonated dodecylamine cations (C$_{12}$−NH$_3^+$) bind electrostatically to the VO$_2$ layers, which forms the alternately intercalated structure because the protonated organic template is positively charged and the VO$_2$ layer is negatively charged. However, this binding force is not so strong, and so the Fe$^{3+}$ ions, which are smaller-sized and also positively charged, would embed into the space between VO$_2$ layers easily. At the same time, the corresponding organic templates (C$_{12}H_{25}NH_3^+$), which have the same number of positive charges, are released from their previous positions in order to maintain the electrical neutrality of the system. In addition, the internal stress of VO$_2$ layer with a certain degree of crystallinity will promote this exchange process. Through ferric ion exchange reaction, the C$_{12}$−NH$_3^+$ species as supporting pillar between VO$_2$ layers can be substantially replaced by the positively charged iron layers, resulting in the shrinkage of the interlayer spacing.

The FTIR spectra of the two samples are illustrated in Figure 7. The characteristic peaks of vanadium oxide for VO$_2$-NTs appear at 1002, 785, 575, and 496 cm$^{-1}$ corresponding to the stretching vibration of terminal oxygen bonds (V=O), the vibration of doubly coordinated oxygen (bridge oxygen) bonds, and the asymmetric and symmetric stretching vibrations of triply coordinated oxygen (chain oxygen) bonds, respectively.  

The absorption peaks at 721, 1465, 2850, and 2920 cm$^{-1}$ for VO$_2$-NTs can be attributed respectively to the various bending and stretching modes of the different C–H vibrations in the dodecylamine templates.  

The broad peaks at 3425 and 1620 cm$^{-1}$ for both of the samples are assigned to H–O stretching and H–O–H bending vibration modes.  

Through ferric ion exchange reaction, the vibration peak of bridge oxygen bonds shifts from 785 to 711 cm$^{-1}$, and the two vibration peaks of chain oxygen bonds initially at 575 and 496 cm$^{-1}$ merge into a peak at 533 cm$^{-1}$. These changes may be associated with the lattice distortion and microscopic stress variation within the VO$_2$ layers.  

It is worth noticing that the relative intensity of the peaks related with organic templates at 1465, 2850, and 2920 cm$^{-1}$ for Fe-VO$_2$-NTs significantly weakens, and the peak at 721 cm$^{-1}$ disappears. It reveals that most of the protonated organic templates can be removed and replaced by this ferric ion exchange process. The reaction can be written in detail as the following formula:

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\begin{align*}
[mC_{12}H_{25}NH_3^+]_{-}VO_2\text{-}NTs + nFeCl_3 & \rightarrow [nFe^{3+} + (m - 3n)C_{12}H_{25}NH_3^+] - VO_2\text{-}NTs \\
& + 3n[C_{12}H_{25}NH_3^+]_\text{Cl}^-
\end{align*}
\]

C$_{12}H_{25}NH_3^+$ represents the protonated dodecylamine template which binds electrostatically to the negatively charged VOx layer. On the condition that the system of VO$_2$-NTs or Fe-VO$_2$-NTs always keeps electrically neutral, one trivalent Fe$^{3+}$ ion would substitute three positively charged C$_{12}H_{25}NH_3^+$ groups. However, this exchange reaction is not 100%—a part of organic templates still exists between VO$_2$ layers.

The thermogravimetry (TG) and differential scanning calorimeter (DSC) measurements were conducted to determine the content of organic templates in the samples. As seen...
from Figure 8, the evaporation and oxidative decomposition of organic templates for VO\textsubscript{x}-NTs and Fe-VO\textsubscript{x}-NTs are completed at 411 and 397 °C, respectively. The two exothermic peaks between 200 and 450 °C are due to the decomposition of organic templates and the crystallization of vanadium oxide.\textsuperscript{30} A weight loss of 39.2% and 19.7%, reflecting the content of templates, is observed for VO\textsubscript{x}-NTs (Figure 8a) and Fe-VO\textsubscript{x}-NTs (Figure 8b), respectively. It indicates that a large proportion of organic templates are removed by this ferric ion exchange reaction. The weight loss processes for VO\textsubscript{x}-NTs and Fe-VO\textsubscript{x}-NTs between 50 and 200 °C are different: the weight of VO\textsubscript{x}-NTs keeps almost constant, but Fe-VO\textsubscript{x}-NTs show continuous weight loss and obvious endothermic peak with the increase of the temperature. This is because, after the ferric ion exchange process, the cohesion between amine templates and VO\textsubscript{x} layers becomes weaker in Fe-VO\textsubscript{x}-NTs than in VO\textsubscript{x}-NTs, which is conducive to the thermal volatilization of amine templates.

XPS technique was applied to ascertain the elemental composition of the samples and analyze the valence change of vanadium. The XPS general spectra of VO\textsubscript{x}-NTs and Fe-VO\textsubscript{x}-NTs are shown in Figure 9, a and b, respectively. It can be found that Fe-VO\textsubscript{x}-NTs exhibit weaker C\textsubscript{1s} peak and new Fe\textsubscript{2p} peak, indicating less organic templates and the existence of ferric ions. The weak N\textsubscript{1s} peak at about 400 eV in Figure 9a originates from –C=NH\textsubscript{2} group within the dodecylamine
templates, but this peak disappears in Figure 9b because of the very low content of amine templates on the surface of Fe-VO$_x$-NTs sample. As shown in Figure 9, c and d, V$_{2p}$ region includes V$_{2p3/2}$ and V$_{2p1/2}$ peaks, and the core level binding energy of V$_{2p3/2}$ for Fe-VO$_x$-NTs (517.1 eV) is higher than that for VO$_x$-NTs (516.6 eV), indicating Fe-VO$_x$-NTs have higher vanadium valence. The V$_{2p3/2}$ peaks of the samples can be divided into two peaks at the binding energy of 517.3 and 516.1 eV which are ascribed to V$^{5+}$ and V$^{4+}$.$^{31}$ In order to ascertain the ratios of V$^{5+}$/V$^{4+}$ in the samples, XPS Peak4.1 software was used to fit the experimental data. The fitted results for VO$_x$-NTs and Fe-VO$_x$-NTs are presented in Figure 9, c and d, respectively. Through the calculation based on the ratio of V$^{5+}$ peak area to V$^{4+}$ peak area, the ratio of V$^{5+}$/V$^{4+}$ for VO$_x$-NTs is 0.92, and the ratio for Fe-VO$_x$-NTs is 1.35. It manifests that the exchange of organic templates by ferric ions causes the increase of vanadium valence. During the electrochemical process, the vanadium valence decreases with the insertion of lithium ions when used as cathode materials. That is to say, the higher vanadium valence means the greater potential for lithium ions insertion. To clarify the reason for the increase of vanadium valence, Fe$_{2p}$ region of the element iron at the surface of Fe-VO$_x$-NTs is illustrated in Figure 10. The core level binding energies of Fe$_{2p3/2}$ and Fe$_{2p1/2}$ for the sample are centered at 710.3 and 724.0 eV, respectively. According to the reports of Yamashita et al.$^{32}$ and Roosendaal et al.$^{33}$ the peak positions of Fe$_{2p3/2}$ for ferric ion (Fe$^{3+}$) and ferrous ion (Fe$^{2+}$) are located at 711.0 and 709.0 eV, and the positions of Fe$_{2p1/2}$ for Fe$^{3+}$ and Fe$^{2+}$ are at 724.6 and 722.6 eV, respectively. Through a simple fitting based on the Fe$_{2p3/2}$ peak of Fe-VO$_x$-NTs, it can be easily found that Fe-VO$_x$-NTs contain both Fe$^{3+}$ and Fe$^{2+}$. This is because a part of the strong oxidizing Fe$^{3+}$ ions can oxidize some V$^{4+}$ ions within VO$_x$-NTs into V$^{5+}$ ions, leading to the appearance of Fe$^{2+}$ and the increase of vanadium valence. Galvanostatic charge–discharge and cyclic voltammetry (CV) tests were carried out to demonstrate the electrochemical properties of the samples. The first charge and discharge curves for VO$_x$-NTs and Fe-VO$_x$-NTs at the different current densities of 50, 80, and 100 mA g$^{-1}$ are presented in Figure 11, a and b, respectively. Both of them exhibit smooth charge–discharge curves, reflecting their amorphous features as cathode materials.$^{34}$ The difference between them is that only VO$_x$-NTs show two weak discharge plateaus at about 1.6 and 2.2 V. The first discharge specific capacities of VO$_x$-NTs at 50, 80, and 100 mA g$^{-1}$ are 253, 242, and 225 mAh g$^{-1}$, respectively. In contrast, Fe-VO$_x$-NTs deliver higher specific capacities of 311, 294, and
259 mAh g\(^{-1}\) at the corresponding current densities. Figure 12a gives the cycling performance of the samples at the different current densities. With the increase of the current density, both of their specific capacities decrease. The capacities of the VO\(_x\)-NTs decrease rapidly to about 33 mAh g\(^{-1}\) during 50 cycles at different current densities, and the corresponding capacity loss ratios are all over 85%. For the Fe-VO\(_x\)-NTs, after 50 cycles at the current densities of 50, 80, and 100 mA g\(^{-1}\), the specific capacities are slowly reduced to 178, 141, and 121 mAh g\(^{-1}\), respectively, and the corresponding capacity loss ratios are 42.8%, 52%, and 53.3%, respectively. Figure 12b shows the initial cyclic voltammetry curves of the samples at the same scan rate. The downward peaks (located at 2.02 and 2.71 V for VO\(_x\)-NTs; 2, 2.4, and 3.04 V for Fe-VO\(_x\)-NTs) are cathodic peaks and the upward peaks (at 3.48 V for VO\(_x\)-NTs; 3 and 3.28 V for Fe-VO\(_x\)-NTs) are anodic peaks, corresponding to the lithium ion insertion and extraction process in the cathode materials, respectively. In order to research the characteristic of lithium-ion insertion/extraction of these amorphous cathode materials in the charge–discharge process, a high scanning rate (500 μV s\(^{-1}\)) is applied in the CV tests. The two weak discharge plateaus exhibited by VOx-NTs in Figure 11a almost can be ignored by comparison with the well-crystallized cathode materials, so there is no corresponding cathodic peak appearing in CV curves, especially in the case of high scanning rate. So, it is difficult to match the redox peaks of CV curves with the weak plateaus. As observed from the curves, Fe-VO\(_x\)-NTs exhibit more pronounced redox peaks and larger peak areas than those of VO\(_x\)-NTs, and the potential positions of redox peaks for Fe-VO\(_x\)-NTs are closer compared with VO\(_x\)-NTs. These results demonstrate that Fe-VO\(_x\)-NTs possess faster kinetics toward lithium ion insertion–extraction and higher capacity than VO\(_x\)-NTs.\(^{35,36}\) It can be found that the higher vanadium valence and the effective removal of organic templates, which do not possess good conductivity and lithium ion insertion–extraction property, can greatly improve the electrochemical performance of VO\(_x\)-NTs.

4. CONCLUSIONS

In this paper, the electrochemical performance of VO\(_x\)-NTs as cathode material for lithium ion batteries has been greatly improved through a ferric ion exchange process. The synthesized Fe-VO\(_x\)-NTs products show higher specific capacity and better cyclic performance than the original VO\(_x\)-NTs and congeneric modified materials. When tested in the potential range of 1.5–4 V at the current density of 50 mA g\(^{-1}\), Fe-VO\(_x\)-NTs have an initial capacity of 311 mAh g\(^{-1}\) and maintain the capacity of 178 mAh g\(^{-1}\) after 50 cycles. The improved electrochemical performance can be attributed to the effective removal of dodecylamine template without destroying the tubular morphology and the multiwalled structure. Furthermore, the ferric ion exchange process leads to the increase in the proportion of pentavalent vanadium, which also has contribution to the improvement of electrochemical capacity. The improved Fe-VO\(_x\)-NTs with higher capacity and better cyclic capability can be used as a new kind of cathode material for lithium ion secondary batteries.
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