Charge-Discharge Mechanisms of Ammonium Vanadium Bronze NH₄V₄O₁₀ Nanobelts as Cathode for Lithium-ion Battery

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Abstract—Ammonium vanadium bronze NH₄V₄O₁₀ nanobelts show potential interesting properties for an application as the cathode in lithium-ion batteries with an original discharge capacity of 171.8mAh/g. Charge-discharge mechanisms of the material was investigated by using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analysis. Results show that the discharge process passes through three different steps of lithium ion intercalation into the material, whereas the charge process can be completed via two steps of lithium ion de-intercalation out the material. And that the causes of discharge/charge capacity attenuation can be ascribed to the increase of the charge transfer resistance, and further resulted in decrease in cycle life of the cell.

Keywords: ammonium vanadium bronze; Lithium-ion battery; Electrochemical impedance spectroscopy (EIS); Equivalent circuit

INTRODUCTION

In last few years, vanadium pentoxide-based compounds have become a subject of intensive studies. The particular physical–chemical properties of these materials allow a wide range of practical applications such as optoelectronics devices [1], cathode material for lithium batteries [2], humidity sensors [3] and so on. Vanadium oxides are among the best positive electrode materials for rechargeable lithium-ion batteries, due to their high intercalation voltage, large specific capacity and good cycle ability [4]. A large number of vanadium oxides, such as V₂O₅ [5], Li₁ₓV₃O₈ [6] and Ag₂V₄O₁₁ [7], have been extensively studied in the past.

The structure of V₂O₅ is comprised of VO₅ square pyramids, which share the corners of the base to form a sheet, which in the absence of any vacancies has the composition V₂O₅. This structural particularity permits the synthesis of the bronze phase MₓV₂O₅ (M: Li, Na, K, Cs, Ca, Ag etc) with various metal cations embedded between the layers without a far-reaching restructuring [8]. The interest in the vanadium compounds strongly increased during the last few years, when a phase transition in the sodium vanadium oxide bronze α’-NaV₂O₅ was observed [9]. The vanadium ions in this bronze are in the mixed-valence states V⁵⁺ (3d⁰) and V⁴⁺ (3d¹). This bronze is an inorganic material considered to exhibit the spin-Peierls transition. The last fact excites interest to the charge ordering investigations in vanadium oxide bronzes MₓV₂O₅ (M—alkali, alkaline earth metal). These materials are mixed-valence oxides and their physical–chemical properties depend on the nature of M and its atomic concentration [10]. When the VO₂ square pyramids in V₂O₅ arranges with all the apices up in one sheet and down in the other, double sheets of V₂O₅ were consequently formed [11]. Various cations can also be embedded between sheets.

Recently, much effort has been devoted to developing new approaches to fabricate nano-belt materials because of the promising building-block function for nano-electronics and optoelectronics [12]. We have reported previously the synthesis and electrochemical performances of this material as cathode for Li ion battery [13]. However, the charge-discharge mechanisms of the material is unknown as yet. In this paper, we investigated the charge-discharge mechanisms of NH₄V₄O₁₀ nano-belts by using a series of electrochemical techniques.

EXPERIMENTAL

Synthesis of ammonium vanadium bronze NH₄V₄O₁₀ nanobelts

In the present work, NH₄V₄O₁₀ nanobelts were synthesized under hydrothermal conditions according to the methods described in literature [13]. The sample was obtained in a typical procedure, in which a light yellow solution of NH₄VO₃ and H₂C₂O₄·2H₂O solid powder was directly mixed completely to form a clear black-green solution, and the resultant mixture was then treated hydrothermally at 140 ºC for 48h in a Teflon-lined autoclave with a stainless steel shell. The final black-green precipitate was collected, washed, and dried at 110 ºC for 5h in the argon atmosphere. All of the chemical reagents used in this experiment were analytical grade without other treatments.

Electrochemical measurements

The electrochemical properties of the NH₄V₄O₁₀ nanobelts were tested using two-electrode system, which consisted metallic lithium negative electrode and the prepared cathode separated by a Celgard 2400 porous polypropylene film. The cathode was made by mixing NH₄V₄O₁₀ active material, acetylene black and poly-vinylidene fluoride (PVDF) in a ratio of 75:15:10 by weight. The mixture was coated onto an aluminum disk (diameter 1cm²), and then dried at 100 ºC for 24h in a vacuum oven before use. The electrolyte was 1M LiPF₆ in the ethylene carbonate (EC) and dimethyl carbonate (DMC) (50:50). All cells were assembled in an argon-filled glove box. Cycle voltammetry measurement was carried out on CHI 660A electrochemical workstation system (CH
RESULTS AND DISCUSSION

3.1. Discharge experiment

Lithium ion cells store charge by intercalating Li\(^+\) from a contacting solution phase, along with an equivalent number of electrons, into the cell’s anode material \[14\]. During discharge the Li\(^+\) must diffuse out of the anode material, through the electrolyte, and intercalate into the cathode material.

Variations of voltage vs. charge/discharge capacity were shown in Fig.1. The initial discharge capacity is 171.8mAh\( \cdot \)g\(^{-1}\). Obviously at constant current drain of 0.1mA (i.e. 12.5mA\( \cdot \)g\(^{-1}\)) for the first cycle, three distinctive flat voltage plateaus at 3.05, 2.8 and 2.5 V in discharge curves and two ones at 2.65 and 3.0 V in the charge curves were presented, implying that there are three steps for lithium intercalating and two steps for lithium de-intercalating into/out the cathode material during charge/discharge process. This multi-step behavior of NH\(_4\)V\(_4\)O\(_10\) indicates that there are probably several different sites for the lithium \[11\]. By theoretical calculation, 201.6mAh\( \cdot \)g\(^{-1}\) of theoretical discharge capacity can be obtained through three electrons process, i.e. through three lithium ions intercalation into NH\(_4\)V\(_4\)O\(_10\) nanobelts and the reduction of vanadium. Meanwhile, in the anodic polarization process, two peaks were observed, corresponding to the de-intercalation of lithium ion out the cathode structure and the oxidation of vanadium. After ten cycles, the cathode peak (IIIc) shifted to higher potential with a decrease of peak intensity and area, while the anodic peak only showed a decrease in peak intensity, revealing that reduction and oxidation proceeds, but with some irreversibility.

3.2. Cyclic voltammogram experiments

In order to ascertain the mechanism of charge/discharge, we explore the cyclic voltammograms for the Li/NH\(_4\)V\(_4\)O\(_10\) cell with scanning rate of 0.1mV\( \cdot \)s\(^{-1}\) between 2.0 and 3.4 V (vs. Li/Li\(^+\)), shown in Fig.2. It can be clearly seen that there are three cathode peaks (marked I\(_c\), II\(_c\), III\(_c\)) during cathode process and two anode peaks (marked I\(_a\), II\(_a\)) during anode process, which means distinct reactions in the scanning process. In the cathode polarization process of the first cycle, three obvious peaks were attributed to lithium ion intercalation into NH\(_4\)V\(_4\)O\(_10\) nanobelts and the reduction of vanadium. Meanwhile, in the anodic polarization process, two peaks were observed, corresponding to the de-intercalation of lithium ion out the cathode structure and the oxidation of vanadium. After ten cycles, the cathode peak (III\(_c\)) shifted to higher potential with a decrease of peak intensity and area, while the anodic peak only showed a decrease in peak intensity, revealing that reduction and oxidation proceeds, but with some irreversibility.
By theoretical calculation, presuming the number of electron for Eq (1.1), Eq (1.2) and Eq (1.3) is 0.5, 0.5 and 2, then the theory discharge capacity of Eq (1.1), Eq (1.2) and Eq (1.3) is 35.1, 34.78 and 138.32mAh g⁻¹, respectively, which are good consistent with the discharge capacities of discharge voltage plateaus (3.05, 2.8 and 2.5V, respectively) in the discharge curves (estimated by cathode material utilization rate of 81.57% in the first discharge), so the range of x, y and z can be considered to be 0<x<0.5, 0<y<0.5 and 1<z<3. The peak voltages of the Eq (1.1~5), are also identical in the discharge plateaus of the charge/discharge curve.

3.3. EIS analysis

Typical AC impedance spectra for the Li/ NH₄V₄O₁₀ cells before discharge and after 1st discharge are shown in Fig.3. The Nyquist impedance spectra appear two different sizes of depressed semicircles between the measuring frequencies. The Nyquist for the before discharge cell seems to appear a diffusion-like line part at low frequency, actually it is the origin of a depressed semicircle, which can be evidenced by the fact that phase angle does not keep constant at low frequency range(10~0.1Hz) in Bode plot(fig.6A'). For the two cells, at a high frequency (10 Hz~100 kHz), the Nyquist plot is composed of a depressed semicircle ((Q₂Rp) circuit), which is attributed to the interface capacitance and resistance between electrolyte and cathode. At the low frequency (0.1 Hz~10Hz), the depressed semicircle ((Q₁Rcont) circuit) is caused by the diffusion and intercalation of Li ion into NH₄V₄O₁₀ structure or the phase boundaries in the structure. The electrolyte resistance is determined by the point of intersection of the high-frequency semicircle with the real axis.

By equivalent circuit fit, the fitted circuit is shown in Fig.4. We can see that the circuit represents the structure of the measured systems and some actually kinetic parameters. According to above analysis, Rs is the electrolyte resistance between anode and cathode, Rₚ represents resistance of the diffusion and intercalation of Li ion into NH₄V₄O₁₀ structure, i.e. charge transfer resistance, here, Q₁ and Q₂ represent double layer capacitance and interface capacitance, respectively, and described with constant phase element, which commonly caused by the cathode and anode surface roughness or by inhomogenous reaction rates on electrode surfaces, the value of constant phase element can be calculated by the formula: \[ Z = 1/Y = 1/Q_0(j\omega)^n \] \[ R_{cont} \] describes interface resistance between electrolyte and cathode. The fitted kinetic parameters for the two cells are given in Table.1. From this table, we can see clearly that the values of electrolyte resistance (Rs) for two cells are nearly equivalent, equal to 6.44 and 6.4 Ω, respectively, whereas values of resistance (R_{cont}) and (Rₚ) are quite different. The difference of values of resistance (R_{cont}) indicates a decrease of interface resistance during the charge/discharge process. While the difference between the values of resistance (Rₚ) can be understood by the fact that the concentrations gradient of Li ions between in the electrode surface region and in the bulk electrolyte were small, and as a result the diffusion and intercalation of Li ions in and out of the surface region and the cathode structure were low for the discharged cell. The increase in charge transfer resistance and impedance at low frequency for the discharged cell, which resulted from the depletion of the solvent and deposition of thin films in the discharged cell [15,16], may contribute to a decrease in cycle life.

![Figure 3. The EIS spectra and fitted (Solid line) plots for the Li/ NH₄V₄O₁₀ cell, Nyquist Plots (A, B), Bode Plots (A', B'); Before discharge (A, A'), After 1st discharge (B, B')](image)

![Figure 4. Equivalent circuit of the Li/ NH₄V₄O₁₀ cell before (A) and after (B) discharge for the ac impedance analysis](image)
## Table 1 Electrode kinetic parameters modified by equivalent simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$R_s$ (Ω)</th>
<th>$R_p$ (Ω)</th>
<th>$Q_1$, n</th>
<th>$Q_2$, n</th>
<th>$R_{cont}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before discharge</td>
<td>6.44</td>
<td>143.5</td>
<td>0.9178e-5, n=0.3676</td>
<td>0.7966e-6, n=0.7311</td>
<td>83.2</td>
</tr>
<tr>
<td>After discharge</td>
<td>6.40</td>
<td>778.7</td>
<td>0.4069e-3, n=0.6859</td>
<td>0.2636e-6, n=0.6067</td>
<td>63.9</td>
</tr>
</tbody>
</table>

## CONCLUSIONS

In conclusion, belt-like ammonium vanadium bronze NH$_4$V$_4$O$_{10}$ nanomaterials can deliver 171.8mAh·g$^{-1}$ capacity. And the mechanism of charge-discharge of the material show that the discharge process passes through three different steps of lithium ion intercalation into the material, whereas the charge process can be completed via two steps of lithium ion de-intercalation out the material. Electrochemical impedance spectroscopy (EIS) analysis and equivalent circuit fit further illustrate that the causes of discharge/charge capacity attenuation can be ascribed to the increase of the charge transfer resistance, and further resulted in decrease in cycle life of the cell. Belt-like NH$_4$V$_4$O$_{10}$ nanomaterials may be a promising cathode material for lithium ion battery if the cycle ability enhanced in the future.

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## REFERENCES