Hydrothermal Synthesis of Al/Cr-doped V₆O₁₃ as Cathode Material for Lithium-ion Battery

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Abstract. Pure V₆O₁₃ and Al/Cr-doped V₆O₁₃ were synthesized via a hydrothermal route using C₂H₂O₄·2H₂O, V₂O₅, Al(NO₃)₃·9H₂O and Cr(NO₃)₃·9H₂O as raw materials. The products were characterized by XRD, SEM, EDS. Doping proven to be an effective method to improve the samples discharge specific capacity and cycle performance. Doping samples electrochemical performance were better than pure V₆O₁₃, the initial discharge specific capacity of sample 0.02 and 0.06 were 311mAh/g and 337mAh/g larger than pure V₆O₁₃ sample (241 mAh/g). The capacity retention of samples 0.00, 0.02, 0.06 was 32.0%, 44.69%, 28.78% after 100 cycles, respectively. The increased electrochemical performance originated from the enhanced of electrical conductivity and adhered together by stacking region in an regular arrangement with every unit.

1 Introduction

Cathode materials capacity was the key of the whole specific capacity for lithium ion battery. Vanadium atoms which had various oxidation states (+2, +3, +4, +5), including different kinds of single-valence and mix-valence oxides for example VO₂, V₆O₁₃, V₃O₇ and V₂O₅. These compounds had partially filled d-orbitals which mean that a particular electrochemical property [1]. Among them, V₆O₁₃ become the candidate of high performance cathode materials for lithium ion batteries because it theoretical specific capacity was high (420mAh/g) and electronic Conductivity [2, 3].

The number of conduction electrons in V₆O₁₃ crystal was limited so electrical conductivity fell quickly followed by lithium ion insertion that reduced the utilization coefficient of the active material of cathode materials in high content Li. Moreover, V₆O₁₃ volume changed and poorly stability of crystal structures followed by lithium ion insertion-extraction lead to cycle performance was falling fast[4]. Therefore, the key of influence V₆O₁₃ application was how to efficiently improve LiₓV₆O₁₃ electrical conductivity and cycle performance in high content Li. Practices shown that it without a good effect to add the material with high conductivity directly in V₆O₁₃. The V₆O₁₃ cathode material in the process of lithium insertion and extraction research by J. Barker[5] shown that resistance change correspond to electrode material crystal lattice large change in the process of lithium insertion and extraction. In the process of lithium insertion research based J. O. Thomas [6,7] shown that as lithium ion insertion V₆O₁₃ layers to form LiₓV₆O₁₃, lithium ion occupied tetragonal pyramid vacancy between dioctahedron and octahedron, so the key of improve LiₓV₆O₁₃ cycle performance was reduce the internal resistance from the interface of electrolyt and LiₓV₆O₁₃ to LiₓV₆O₁₃ crystal between dioctahedron and octahedron meanwhile keep stability of crystal structures in

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the process of lithium insertion as possible. J. P. Pereira-Ramos [8, 9] synthesized $\text{Cr}_{0.36}\text{V}_{6}\text{O}_{13.5}$ compounds through chromium ions doped with $\text{V}_6\text{O}_{13}$ with initial discharge capacity 370 mAh/g and capacity loss less than 15% after 35 cycles.

In this paper, pure $\text{V}_6\text{O}_{13}$ and Al/Cr-doped $\text{V}_6\text{O}_{13}$ were synthesized via a completely aqueous solution based synthesis method. Synthesis of different amounts Al/Cr doped $\text{V}_6\text{O}_{13}$ were studied. Moreover, electrochemical performance of the pure $\text{V}_6\text{O}_{13}$ and Al/Cr-doped $\text{V}_6\text{O}_{13}$ were determined by charge/discharge tests and cyclic voltammetry. Sample designations with doping different amounts of Aluminum nitrate nonahydrate ($\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) and Chromium trinitrate nonahydrate ($\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) as Table 1.

**Table 1.** Sample designations with doping different amount of Aluminum nitrate nonahydrate ($\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) and Chromium trinitrate nonahydrate($\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$).

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>$\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}/\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}(g)$</th>
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<tbody>
<tr>
<td>0.00</td>
<td>0.00/0.00</td>
</tr>
<tr>
<td>0.02</td>
<td>0.06/0.02</td>
</tr>
<tr>
<td>0.06</td>
<td>0.06/0.06</td>
</tr>
</tbody>
</table>

### 2 Experimental

#### 2.1 Synthesis

All chemical reagents were analytical grade and used without any further purification. Al/Cr-doped $\text{V}_6\text{O}_{13}$ were prepared according to the following procedure. 1.25g Oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4\cdot2\text{H}_2\text{O}$) and 0.4g Vanadium pentaoxide ($\text{V}_2\text{O}_5$) was dissolved in 20mL of deionized water. The mixed solution was kept under stirring at 80 $^\circ\text{C}$ in a water bath until a blue colored solution formed. The reaction is followed.

$$\text{V}_2\text{O}_5 + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2[\text{VO}](\text{C}_2\text{O}_4)(\text{blue}) + \text{CO}_2 + 3\text{H}_2\text{O}$$

Taked it out and the solution was cooled to room temperature naturally. The solution was filtered. Suitable amount of Aluminum nitrate nonahydrate ($\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) and Chromium trinitrate nonahydrate ($\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$) was dissolved in 15mL of deionized water, when it completely dissolves, pour it into as-synthesized Vanadyl oxalate ($\text{VOC}_2\text{O}_4\cdot5\text{H}_2\text{O}$) solution, then 3ml Hydrogen peroxide 30 $\%$($\text{H}_2\text{O}_2$) was added to mixed solution, solution comed up to lots of bubbles and a red solution was formed. The red mixed solution was transferred into a 100mL stainless steel autoclave after stirring it without comed up to bubbles. The autoclave was sealed and maintained at 160 $^\circ\text{C}$ for 24 h and then cooled to room temperature naturally. The supernatant liquid was discarded, suitable amount of deionized water was added to precipitate and the precipitate was separated by centrifugation (4000 rpm for 5 min). This process was repeated twice more after additional rinsing. Sample drying through freeze-drying process for 24h. After the dried sample was ground into a powder, the collected powder was then calcined at 350 $^\circ\text{C}$ at 3$^\circ\text{C}$/min for 1 h in argon.

#### 2.2 Characterization

The morphology of $\text{V}_6\text{O}_{13}$ were observe by Hitachi S-4800 Field emission scanning electron microscopy (FESEM). The phase of $\text{V}_6\text{O}_{13}$ were obtained by Panalytical X'Pert PRO MRD X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) analysis performed by Thermo Electron Corporation ESCALAB 250Xi. Energy dispersive spectrometer (EDS) by Oxford Instruments INCAIE 350 was used to analyze component of $\text{V}_6\text{O}_{13}$. 

DOI: 10.1051/matecconf/20178801006 

CBNCM 2016
3 Results and discussion

Through X-ray diffraction (XRD) the as-prepared samples were characterized firstly. Figure 1 illustrated the XRD patterns of both pure V$_6$O$_{13}$ and Al/Cr-doped(0.02, 0.06) V$_6$O$_{13}$ powders calcined at 350°C. In the graph, no evidence of impurities for the three samples was detected from the XRD curves according to the standard card No. 71-2235[2]. For pure V$_6$O$_{13}$, there were main characteristic peaks at $2\theta=15.122$, 25.349, 26.842, 30.131, 33.487, 45.619, 49.496, 59.795 and 69.500, corresponding to (200), (110), (003), (-401), (310), (-601), (-603), (-711) and (025) planes, respectively, which can be indexed to JCPDS card No. 71-2235. For the other two Al/Cr-doped V$_6$O$_{13}$, all the diffraction peaks were also in accordance with the standard diffraction peaks of pure V$_6$O$_{13}$, which meant that did of Al/Cr doping did not change the basic structure of V$_6$O$_{13}$. Furthermore, Lattice constant may change by dope because the ionic radius of Al$^{3+}$ (0.535 Å) and Cr$^{3+}$ (0.755Å) are differently the ionic radius of V$^{4+}$ (0.58 Å) and V$^{5+}$ (0.54 Å).

![Figure 1](image-url). The XRD patterns of both pure V$_6$O$_{13}$ and Al/Cr-doped(0.02, 0.06) V$_6$O$_{13}$ powders calcined at 350°C.

In order to ascertain actual content in V$_6$O$_{13}$, samples were tested by X-ray energy dispersive spectroscopy(EDS). Table 1 shown the mass ratio of vanadium, oxide, aluminum, chromium with different quantities Al/Cr-doped V$_6$O$_{13}$. The amount of vanadium were decrease with Al/Cr doping V$_6$O$_{13}$ and the amount of vanadium were continued decrease with the increase of doping. This was because the position of the aluminum and chromium replaced the vanadium in V$_6$O$_{13}$.

Figure 2 shown the SEM images of pure V$_6$O$_{13}$ and Al/Cr-doped V$_6$O$_{13}$ samples fabricated by hydrothermal method. In the figures, it can be easily seen that the structure units of pure V$_6$O$_{13}$ and Al/Cr-doped were nanosheets. The doping amount of Al/Cr was demonstrated to have a effect to the samples final morphologies. Pure V$_6$O$_{13}$ agglomeration serious. Al/Cr-doped are adhered together by stacking region in an regular arrangement with every unit. The thickness of pure V$_6$O$_{13}$ nanosheets was about 500-1000nm larger than Al/Cr-doped V$_6$O$_{13}$ and the thickness of Al/Cr-doped V$_6$O$_{13}$ decrease with the increase of doping (0.02 about 400nm, 0.06 about 250nm). Besides, compared with the pure V$_6$O$_{13}$, Al/Cr-doped V$_6$O$_{13}$ sample have more space this meant that it can accommodate much more lithium-ion(Li$^+$) when charge and discharge.

The cyclic voltammetry curves of sample 0.00, 0.02, 0.06 were shown in Figure 3a. The cyclic voltammetry curves of sample 0.00, 0.02, 0.06 were characterized at scan rate 0.1 mV s$^{-1}$ and the scope of voltage was 1.5-3.5 V. For pure V$_6$O$_{13}$ four oxidation peaks occurred at around 2.35, 2.68, 2.84 and 3.31 V (versus Li$^+$/Li), which represented the intercalation of Li into the non-equivalent sites in the structure of V$_6$O$_{13}$. While the reduction peaks located at around 2.04, 2.44 and 2.71 V (versus Li$^+$/Li) corresponds to the deintercalation of Li from the monoclinic V$_6$O$_{13}$. For Al/Cr-doped V$_6$O$_{13}$, the oxidation peaks of 0.02 centered at 2.43, 2.81, 2.93and 3.28 V while the reduction peaks of 0.02 centered at 1.97, 2.37 and 2.66 V, the oxidation peaks of 0.06 centered at 2.43, 2.81 and 3.35 V while the reduction peaks of 0.06 centered at 1.97, 2.40 and 2.68 V, respectively. After doped with different amounts of Al/Cr, the oxidation peak position and restore its peak there were different change.
indicating that the incorporation of Al/Cr changed vanadium oxide of vanadium ions in the Fermi level.

Table 2. The chemical composition of sample 0.00, 0.02, 0.06.

<table>
<thead>
<tr>
<th>Sample</th>
<th>V (mass ratio)</th>
<th>O (mass ratio)</th>
<th>Al (mass ratio)</th>
<th>Cr (mass ratio)</th>
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<td>55.26</td>
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<td>1.64</td>
</tr>
</tbody>
</table>

Figure 2. The SEM images of pure V₆O₁₃(0.00) and Al/Cr-doped V₆O₁₃(0.02, 0.06).

Figure 3b sample 0.00, 0.02, 0.06 after three cycles of electrochemical impedance spectroscopy. After fitting, pure V₆O₁₃ charge transfer resistance after 3 cycles was 151.6 Ω, and charge transfer resistance of the sample 0.02, 0.06 after 3 cycles are 383 Ω, 493 Ω, respectively. V₆O₁₃ doped with Al/Cr were greater than the charge transfer resistance of pure V₆O₁₃, charge transfer resistance increases with the increase of the amount of doping, which may be V₆O₁₃ spacing of layers increases and partially substituted lithium Al³⁺/Cr³⁺ position, thus preventing insertion of lithium ions, so that impedance increases.
In order to measurement the property of Al-doped V$_6$O$_{13}$ anode material for lithium ion battery, cycle of button cells at room temperature. Figure 4 shown that the relationship between capacity and cycle number. The charge and discharge curves at the current density of 0.1 A g$^{-1}$ in 1.5–4.0 V. All doping samples V$_6$O$_{13}$ discharge performance were better than pure V$_6$O$_{13}$, initial discharge specific capacity sample 0.02 and 0.06 were 311mAh/g and 337mAh/g above pure V$_6$O$_{13}$ sample was 241 mAh/g. The capacity retention of samples 0.00, 0.02, 0.06 after 100 cycles was 32.0%, 44.69%, 28.78%, respectively. The increase in capacity was attributed to introduction of Al/Cr, Al/Cr add to V$_6$O$_{13}$ could increase electrical conductivity, nevertheless a great amount of Al/Cr could destroy V$_6$O$_{13}$ crystal structure cause capacity declined sharply.

Figure 3a. The cyclic voltammetry curves of the third cycle for the pure V$_6$O$_{13}$(0.00) and Al/Cr-doped V$_6$O$_{13}$(0.02, 0.06). Figure 3b. Electrochemical impedance spectroscopy for samples 0.00, 0.02, 0.06 after the 3rd cycle.

4 Conclusion

Pure V$_6$O$_{13}$ and Al/Cr-doped V$_6$O$_{13}$ were synthesized via a completely aqueous solution based synthesis method. Doping proven to be an effective means to improve the cathode material charge and discharge specific capacity. Lattice constant may change by dope because the ionic radius of Al$^{3+}$ and Cr$^{3+}$ are differently the ionic radius of V$^{4+}$ and V$^{5+}$. The doping amount of Al/Cr is demonstrated to have a effect to the samples final morphologies. the thickness of Al/Cr-doped V$_6$O$_{13}$ decrease with the increase of doping. All doping samples V$_6$O$_{13}$ discharge performance are better than pure V$_6$O$_{13}$, initial discharge specific capacity sample 0.02 and 0.06 are 311mAh/g and 337mAh/g above pure
V$_6$O$_{13}$ sample is 241 mAh/g. The capacity retention of samples 0.00, 0.02, 0.06 after 100 cycles is 32.0%, 44.69%, 28.78%, respectively.

References