

Hydrothermal Synthesis of Al/Cr-doped V_6O_{13} as Cathode Material for Lithium-ion Battery

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Abstract. Pure V_6O_{13} and Al/Cr-doped V_6O_{13} were synthesized via a hydrothermal route using $C_2H_2O_4 \cdot 2H_2O$, V_2O_5 , $Al(NO_3)_3 \cdot 9H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ 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 V_6O_{13} , the initial discharge specific capacity of sample 0.02 and 0.06 were 311mAh/g and 337mAh/g larger than pure V_6O_{13} 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 VO_2 , V_6O_{13} , V_3O_7 and V_2O_5 . These compounds had partially filled d-orbitals which mean that a particular electrochemical property [1]. Among them, V_6O_{13} 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 V_6O_{13} 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, V_6O_{13} 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 V_6O_{13} application was how to efficiently improve $Li_xV_6O_{13}$ 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 V_6O_{13} . The V_6O_{13} 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 V_6O_{13} layers to form $Li_xV_6O_{13}$, lithium ion occupied tetragonal pyramid vacancy between dioctahedron and octahedron, so the key of improve $Li_xV_6O_{13}$ cycle performance was reduce the internal resistance from the interface of electrolyt and $Li_xV_6O_{13}$ to $Li_xV_6O_{13}$ 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 V_6O_{13} with initial discharge capacity 370 mAh/g and capacity loss less than 15% after 35 cycles.

In this paper, pure V_6O_{13} and Al/Cr-doped V_6O_{13} were synthesized via a completely aqueous solution based synthesis method. Synthesis of different amounts Al/Cr doped V_6O_{13} were studied. Moreover, electrochemical performance of the pure V_6O_{13} and Al/Cr-doped V_6O_{13} were determined by charge/discharge tests and cyclic voltammetry. Sample designations with doping different amounts of Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Chromium trinitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) as Table 1.

Table 1. Sample designations with doping different amount of Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Chromium trinitrate nonahydrate($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$).

Sample designation	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}(\text{g})$
0.00	0.00/0.00
0.02	0.06/0.02
0.06	0.06/0.06

2 Experimental

2.1 Synthesis

All chemical reagents were analytical grade and used without any further purification. Al/Cr-doped V_6O_{13} were prepared according to the following procedure. 1.25g Oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) and 0.4g Vanadium pentoxide (V_2O_5) was dissolved in 20mL of deionized water. The mixed solution was kept under stirring at 80 °C in a water bath until a blue colored solution formed. The reaction is followed.



Taked it out and the solution was cooled to room temperature naturally. The solution was filtered. Suitable amount of Aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Chromium trinitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 15mL of deionized water, when it completely dissolves, pour it into as-synthesized Vanadyl oxalate ($\text{VOC}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$) solution, then 3ml Hydrogen peroxide 30% (H_2O_2) was added to mixed solution, solution came 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 came up to bubbles. The autoclave was sealed and maintained at 160 °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 °C at 3 °C/min for 1 h in argon.

2.2 Characterization

The morphology of V_6O_{13} were observe by Hitachi S-4800 Field emission scanning electron microscopy (FESEM). The phase of V_6O_{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 V_6O_{13} .

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_6O_{13} and Al/Cr-doped(0.02, 0.06) V_6O_{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_6O_{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_6O_{13} , all the diffraction peaks were also in accordance with the standard diffraction peaks of pure V_6O_{13} , which meant that did of Al/Cr doping did not change the basic structure of V_6O_{13} . Furthermore, Lattice constant may changed by dope because the ionic radius of Al^{3+} (0.535 \AA) and Cr^{3+} (0.755 \AA) are differently the ionic radius of V^{4+} (0.58 \AA) and V^{5+} (0.54 \AA).

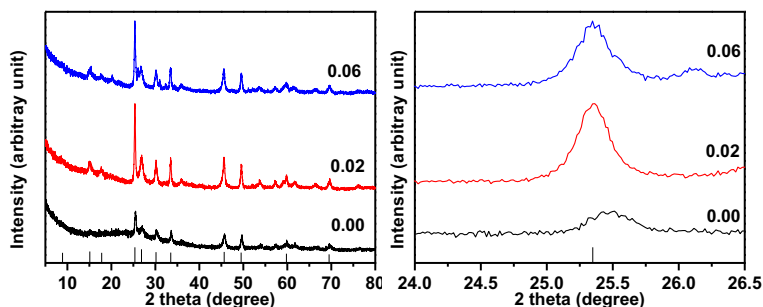


Figure 1. The XRD patterns of both pure V_6O_{13} and Al/Cr-doped(0.02、0.06) V_6O_{13} powders calcined at 350°C .

In order to ascertain actual content in V_6O_{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_6O_{13} . The amount of vanadium were decrease with Al/Cr doping V_6O_{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_6O_{13} .

Figure 2 shown the SEM images of pure V_6O_{13} and Al/Cr-doped V_6O_{13} samples fabricated by hydrothermal method. In the figures, it can be easily seen that the structure units of pure V_6O_{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_6O_{13} agglomeration serious. Al/Cr-doped are adhered together by stacking region in an regular arrangement with every unit. The thickness of pure V_6O_{13} nanosheets was about 500-1000nm larger than Al/Cr-doped V_6O_{13} and the thickness of Al/Cr-doped V_6O_{13} decrease with the increase of doping (0.02 about 400nm, 0.06 about 250nm). Besides, compared with the pure V_6O_{13} , Al/Cr-doped V_6O_{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_6O_{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_6O_{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_6O_{13} . For Al/Cr-doped V_6O_{13} , the oxidation peaks of 0.02 centered at 2.43, 2.81, 2.93 and 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 2.68V, 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.

Sample	V (mass ratio)	O (mass ratio)	Al(mass ratio)	Cr(mass ratio)
0.00	61.66	38.34	0	0
0.02	47.93	50.32	1.23	0.53
0.06	42.00	55.26	1.15	1.64

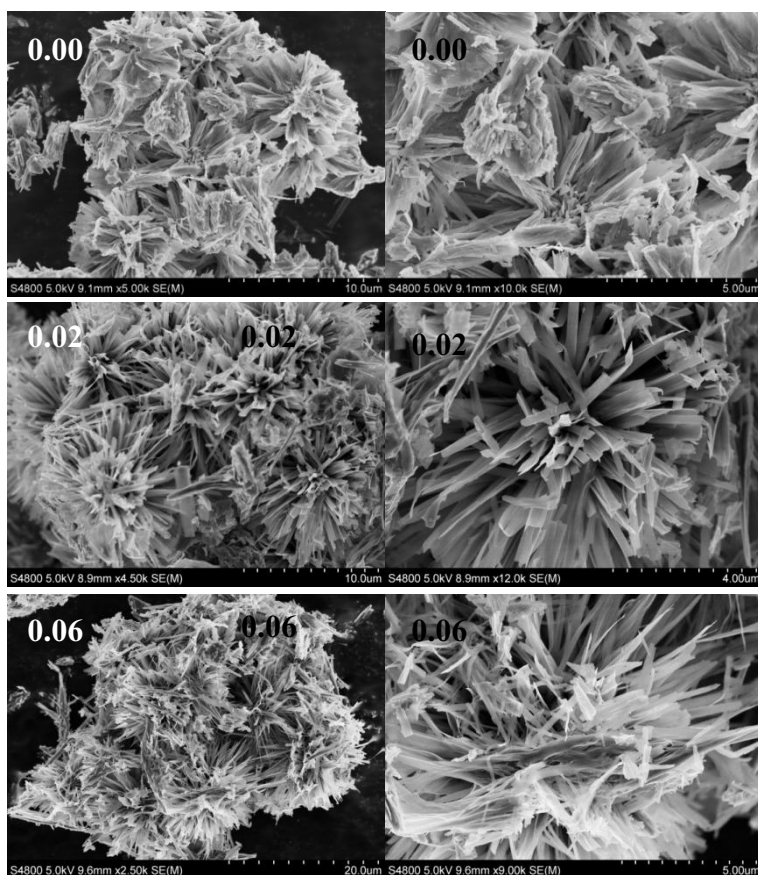


Figure 2. The SEM images of pure V_6O_{13} (0.00) and Al/Cr-doped V_6O_{13} (0.02, 0.06).

Figure 3b sample 0.00, 0.02, 0.06 after three cycles of electrochemical impedance spectroscopy. After fitting, pure V_6O_{13} charge transfer resistance after 3 cycles was 151.6Ω , and charge transfer resistance of the sample 0.02, 0.06 after 3 cycles are 383Ω , 493Ω , respectively. V_6O_{13} doped with Al/Cr were greater than the charge transfer resistance of pure V_6O_{13} , charge transfer resistance increases with the increase of the amount of doping, which may be V_6O_{13} spacing of layers increases and partially substituted lithium Al^{3+}/Cr^{3+} position, thus preventing insertion of lithium ions, so that impedance increases.

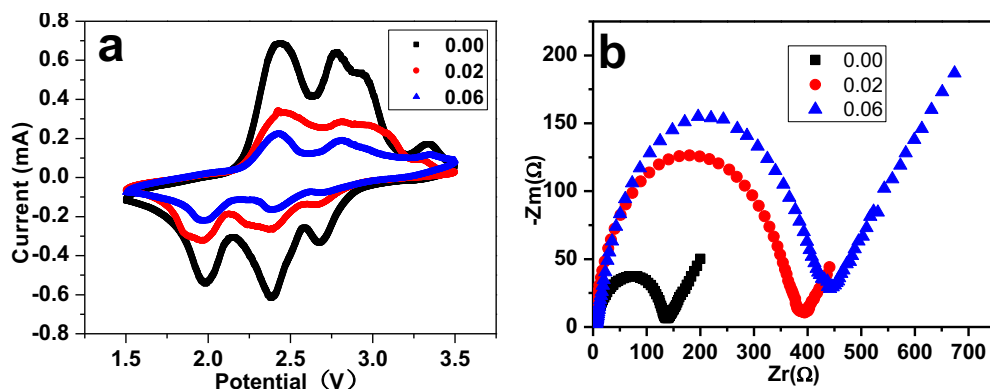


Figure 3a. The cyclic voltammetry curves of the third cycle for the pure V_6O_{13} (0.00) and Al/Cr-doped V_6O_{13} (0.02, 0.06). **Figure 3b.**Electrochemical impedance spectroscopy for samples 0.00, 0.02, 0.06 after the 3rd cycle.

In order to measurement the property of Al-doped V_6O_{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_6O_{13} discharge performance were better than pure V_6O_{13} , initial discharge specific capacity sample 0.02 and 0.06 were 311mAh/g and 337mAh/g above pure V_6O_{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_6O_{13} could increase electrical conductivity, nevertheless a great amount of Al/Cr could destroy V_6O_{13} crystal structure cause capacity declined sharply.

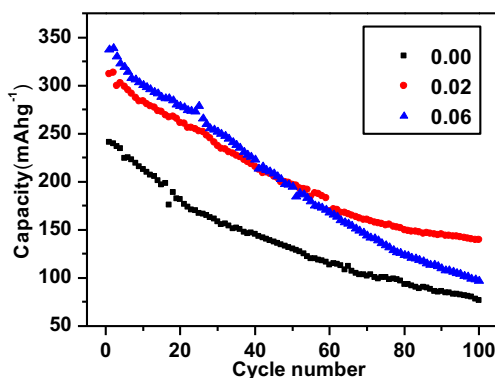


Figure 4. Cyclic performance of the pure V_6O_{13} (0.00) and Al/Cr-doped V_6O_{13} (0.02, 0.06) electrodes at 0.1 C.

4 Conclusion

Pure V_6O_{13} and Al/Cr-doped V_6O_{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_6O_{13} decrease with the increase of doping. All doping samples V_6O_{13} discharge performance are better than pure V_6O_{13} , initial discharge specific capacity sample 0.02 and 0.06 are 311mAh/g and 337mAh/g above pure

V₆O₁₃ 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.

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