



# Hydrothermal synthesis of high specific capacity Al/Na co-doped $V_6O_{13}$ cathode material for lithium-ion battery



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## ABSTRACT

3D flower-like Al-doped  $V_6O_{13}$  and Al/Na co-doped  $V_6O_{13}$  have been fabricated via a facile hydrothermal method using  $C_2H_2O_4 \cdot 2H_2O$ ,  $V_2O_5$ ,  $Al(NO_3)_3 \cdot 9H_2O$ , and  $NaNO_3$  as raw materials. The microstructure of the samples was characterized by XRD, EDS, XPS, FESEM, and TEM. The results indicated that Al and Na ions co-doping improved the electrochemical performance of  $V_6O_{13}$ , including the specific discharge capacity and cycling stability. When the doped mole ratio of Al to V and Na to V were 0.033 and 0.020, respectively, the sample exhibited the best electrochemical performance with initial discharge specific capacity of 514 mAh/g. After 80 cycles, the capacity retention was 70.3%. The enhanced electrochemical performance originates from its superior structural reversibility, enhanced lithium diffusion coefficient and improved electrical conductivity.

## 1. Introduction

Rechargeable lithium batteries with high energy density and long-term stability are considered as one of the most suitable candidates applied for portable electronics. It is well known that cathode materials are particularly critical in determining the performance of lithium-ion batteries. Among various potential cathode candidates for LIBs, vanadium oxides were widely researched due to their high theoretical specific capacity, high energy density and low cost. Vanadium exists in different valence states (from +2 to +5), including single valence oxides such as  $VO_2$ ,  $V_2O_5$ ,  $V_2O_3$  and mixed valence oxides such as  $V_6O_9$ ,  $V_6O_{13}$ ,  $V_4O_6$ , or  $V_5O_7$ . These compounds have partially filled *d*-orbitals which are responsible for the unique electronic, magnetic, and catalytic properties [1]. Among them,  $V_6O_{13}$  has a high theoretical specific capacity of 420 mAh/g and electrical conductivity, which has been considered as one of the promising candidate LIBs cathode materials [2]. The  $V_6O_{13}$  structure contains only slightly distorted  $VO_6$  octahedra joined by edge sharing into single and double zig-zag chains parallel to [010] and linked together by additional edge sharing into single and double sheets of octahedra parallel to the (100) plane [3].  $V_6O_{13}$  is built up of alternating single and double vanadium oxide layers.  $V^{5+}$  only occupied the double layer sites of V atoms,  $V^{4+}$  occupied the single and double layer sites of the V atoms [4,5]. The alternating single and double layers could provide much more sites for lithium intercalation [6,7]. Theoretically, the maximum lithium uptake was eight  $Li^+$  per formula unit, corresponding to a high theoretical specific capacity and energy of 420 mAh/g [8].

The resistance of  $V_6O_{13}$  closely relates to its crystal lattice structures. After lithium inserting into  $V_6O_{13}$ , the formed  $Li_xV_6O_{13}$  would lead to the volume expansion and unstable structure, which may both interrupt the ionic and electronic contact pathways in the electrodes, leading to a rapid capacity fading [4]. Moreover, the number of conduction electrons in  $V_6O_{13}$  crystal was limited, and therefore its electrical conductivity falls quickly. So, the key for improving  $Li_xV_6O_{13}$  cycle performance was to reduce the internal resistance from the interface of electrolyte and  $Li_xV_6O_{13}$  to  $Li_xV_6O_{13}$  crystal between di-octahedron and octahedron, and meanwhile keep stability of crystal structures in the process of lithium insertion. The previous work demonstrated that doping cations could enhance the electrochemical performance of  $V_6O_{13}$  [9–11]. The ribbon-like Cu doped  $V_6O_{13}$  electrode exhibited good capacity retention with a reversible capacity of over  $313 \text{ mAh} \cdot \text{g}^{-1}$  for up to 50 cycles at  $0.1^\circ \text{C}$ , as well as a high charge capacity of  $306 \text{ mAh} \cdot \text{g}^{-1}$  at a high current rate of  $1^\circ \text{C}$  [9]. Mn-doped  $V_6O_{13}$  was synthesized via a hydrothermal method by He, when the sample doping with 2% Mn, the initial discharge specific capacity was 350.1 mAh/g and the capacity retention was 81% after 50 cycles [10]. Al-doped  $V_6O_{13}$  was synthesized via a hydrothermal method by Zou, and they found that the mole ratio of Al/V was 0.041 exhibited the best electrochemical performance, the initial discharge capacity was 496 mAh/g and the capacity retention was 45.8% after 100 cycles [11].

In the present work, Al-doped  $V_6O_{13}$  and Al/Na co-doped  $V_6O_{13}$  were synthesized via a facile hydrothermal method. Synthesis of different amounts Al/Na co-doped  $V_6O_{13}$  was studied. Moreover,

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**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 Sodium nitrate ( $\text{NaNO}_3$ ).

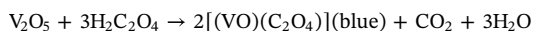
Sample designation	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{NaNO}_3$ (g)
A0	0.06/0.00
A1	0.06/0.01
A2	0.06/0.02
A3	0.06/0.03
A4	0.06/0.04

electrochemical performance of Al-doped and Al/Na co-doped  $\text{V}_6\text{O}_{13}$  were evaluated by charge/discharge tests, EIS, 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 Sodium nitrate ( $\text{NaNO}_3$ ) were listed in Table 1.

## 2. Experimental

### 2.1. Materials preparation

All chemicals were of analytical grade and used without further purification. Oxalic acid dihydrate ( $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 1.25 g) and Vanadium pentoxide ( $\text{V}_2\text{O}_5$ , 0.4 g) was dissolved in 20 mL 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 as follow:



After reaction, the solution was cooled to room temperature naturally. The solution was filtered.

Suitable amount of Aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) (or Aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and Sodium nitrate ( $\text{NaNO}_3$ )) was dissolved in 15 mL of deionized water. When they completely dissolve, the formed mixed solution was poured into the as-synthesized Vanadyl oxalate ( $\text{VOC}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ ) solution, and then 2.9 mL Hydrogen peroxide 30% ( $\text{H}_2\text{O}_2$ ) was added to the above mixed solution, to form a red solution. The red mixed solution was transferred to a 100 mL stainless steel autoclave. The autoclave was sealed and held at 160 °C for 24 h and then allowed to cool to room temperature. Discard the supernatant and add the appropriate amount of deionized water to centrifuge for 5 min (4000 rpm for 5 min). This process was repeated twice more after additional rinsing. The Sample was dried by freeze-drying process for 24 h. After the dried sample was ground into powder,

the collected powder was calcined at 350 °C at 3 °C/min for 1 h in argon.

### 2.2. Materials characterization

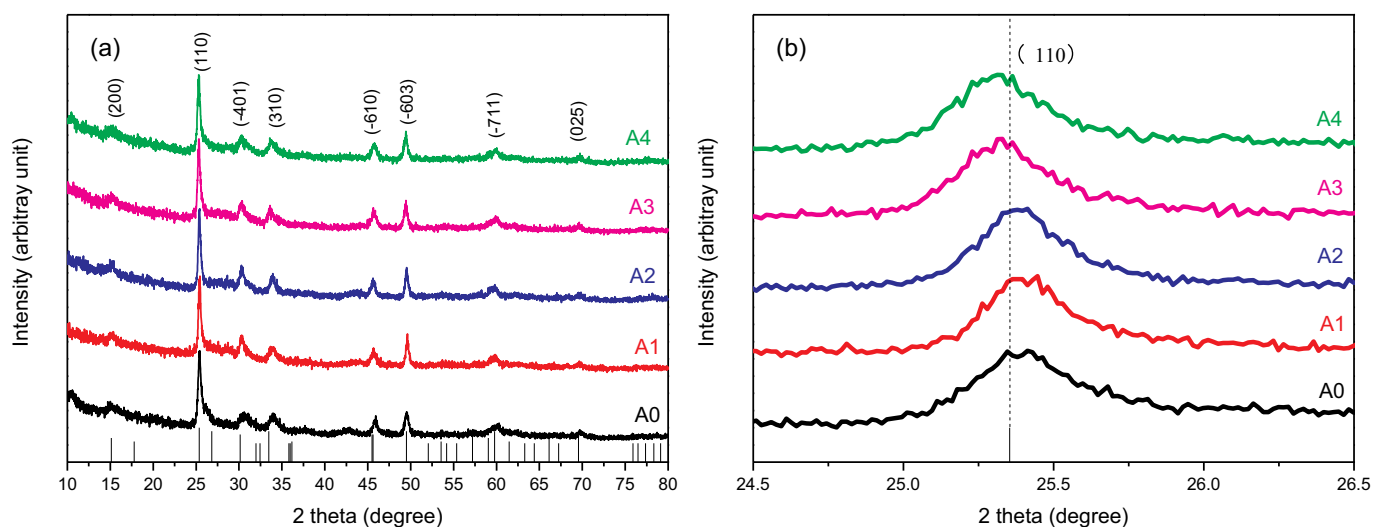
The phase structure of the products was determined by Panalytical X, Pert PRO MRD X-ray diffraction (XRD). The scanning rate was  $8^\circ\text{min}^{-1}$  and diffraction patterns were scanned over the range of  $2\theta$  between 5° and 80°. Energy dispersive spectrometer (EDS) by Oxford Instruments INCAIE 350 was used to analyze component of the product. The oxidation state of key elements (V, Al and Na) was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Electron Corporation ESCALAB 250Xi). The surface morphology of the samples was observed by Hitachi S-4800 Field emission scanning electron microscopy (FESEM). Transmission electron microscopy (TEM) images were gained with a JEOL JEM 2010 high-resolution transmission electron microscope using an accelerating voltage of 200 kV.

### 2.3. Electrochemical test

The electrochemical performances were measured in coin cells. The working electrodes were prepared by mixing polyvinylidene fluoride (PVDF, 10 wt%), acetylene black (20 wt%) and active materials (70 wt %) in *N*-methyl-2 pyrrolidone (NMP) solvent on an aluminum foil (20  $\mu\text{m}$  in thickness) which was used as the current collectors. The coated electrode was dried in vacuum at 90 °C for 12 h. Both the counter and reference electrodes were commercial Li metal and the separator was Celgard 2300 membrane. One molar  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (EC/DMC/DEC = 2: 2: 1 in volume) was used as electrolyte. The cycling performance was tested by NEWARE CT-3008 5 V 10 mA-164 Battery Testing System (BTS). Both the electrochemical impedance spectroscopy (EIS) and the cyclic voltammetry (CV) were tested through a CHI 860D electrochemical workstation, and the CV measurement was performed in the potential range from 1.5 to 4.0 V at a scan rate of  $0.1 \text{ mV s}^{-1}$ .

## 3. Results and discussion

The XRD pattern of the Al- $\text{V}_6\text{O}_{13}$  and Al/Na co-doped  $\text{V}_6\text{O}_{13}$  samples were showed in Fig. 1(a). All the diffraction peaks were indexed to the monoclinic  $\text{V}_6\text{O}_{13}$  phase (JCPDS card No. 71-2235, space group: C2/m) [12]. The diffraction peaks of the samples were quite narrow,



**Fig. 1.** (a) The XRD patterns of the Al-doped  $\text{V}_6\text{O}_{13}$  and Al/Na co-doped (0.01, 0.02, 0.03, 0.04)  $\text{V}_6\text{O}_{13}$  powders calcined at 350 °C. (b) Enlarged peaks at  $2\theta$  ranging from 24.5° to 26.5°.

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