Low Temperature Synthesis and Characterization of $Li_{1.2-y}Na_yV_3O_8$ $(0\!\leqslant\!y\!\leqslant\!1.2)$ from V_2O_5 Gel

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Without overnight heating and stirring, Li_{1.2}V₃O₈ and its analogs Li_{1.2-y}Na_yV₃O₈ ($0 \le y \le 1.2$) were successfully synthesized by adding mixed solution of LiOH and NaVO₃ to V₂O₅ gel and dehydrating the prepared gel in 150—350 °C. The simplicity awards this synthesis process superiority over other low temperature synthesis routes when mass production is concerned. TG-DTA, XRD and TEM experiments were carried out for physical characterization. By galvanostatic charge-discharge and cyclic voltammetry tests, these products showed better electrochemical performance than high temperature products as cathode active materials in secondary lithium batteries. After treatment of Li_{1.2}V₃O₈ at 250 °C, it exhibited a capacity of 350 mAh/g when cycled at current rate of about 60 mA/g over the voltage range of 3.8—1.7 V vs. Li⁺/Li. The influence of partial substitution of Li by Na was also extensively studied.

Keywords low temperature synthesis, V_2O_5 gel, $Li_{1.2-y}Na_yV_3O_8$, cathode material

Introduction

Among the three major groups of vanadium oxides, V_2O_5 , V_6O_{13} and $Li_{1+x}V_3O_8$, which are suited for cathode materials in lithium rechargeable batteries, the third one has attracted much effort for nearly a quarter of one century since Besenhard and Schöllhorn mentioned its application in 1977. For the electrochemical property of Li_{1+x}V₃O₈ depends much on its preparation method, 2 many investigations have focused on performing new synthesis routes of Li_{1+x}V₃O₈ or new treatments on it, including rapid quenching from the melt.³ doping of inert nucleation centers like silica or alumina, 4 sufficient grinding, 5 ultrasonical treatment 6 and intercalation of inorganic molecules such as NH3, H2O and CO2 between layers. Pistoia et al. 8 prepared amorphous Li_{1+x}V₃O₈ using a low-temperature solution method. In virtue of the low temperature process employed in their method, the as-prepared material showed an ability to accommodate up to 4.5 mol of Li+ ions per formula unit, instead of 3 mol for crystalline Li_{1+x}V₃O₈. Furthermore, the absence of a long-range crystallographic order reduces the length of the pathways through which Li⁺ ions diffuse. The favorable morphology endows amorphous $\text{Li}_{1+x}\text{V}_3\text{O}_8$ with a high rate capability. To pursue

the favored benefits brought about by the low-temperature synthesis method, several reformed methods were added to the repertoire. Dai et al. 9 obtained LiV_3O_8 by the reaction of Li_2CO_3 with NH_4VO_3 in the range of 300—350 °C, which were blended in an aqueous solution, and Kawakita et al. 10 prepared Li_{1+x}V_3O_8 by precipitation technique in CH_3OH. The products thus prepared both possess a smaller grain size and better electrochemical performance than the HT (high temp.) samples prepared by conventional high temperature synthesis.

Sodium vanadate, $Na_{1+x}V_3O_8$, has a monoclinic unit cell isostructural with $Li_{1+x}V_3O_8$. The presence of Na^+ ions with larger ionic radii than Li^+ ions expands the gap between the layers, thus awards $Na_{1+x}V_3O_8$ with a higher value of chemical diffusion coefficient of lithium and the excellent cycling performance with a higher charge-discharge efficiency. However, both the discharge voltage and the discharge capacity were lower than those of $Li_{1+x}V_3O_8$. Therefore, it is assumed that partial substitution of Li^+ by Na^+ in $Li_{1+x}V_3O_8$ could compromise the higher diffusion coefficient of lithium and the higher discharge capacity. 12,13

In the present research, another new low-temperature synthesis route of $\mathrm{Li}_{1.2-y}\mathrm{Na}_{y}\mathrm{V}_{3}\mathrm{O}_{8}$ (including $\mathrm{Li}_{1+x}\mathrm{V}_{3}\mathrm{O}_{8}$) was proposed, in which mixed solution of LiOH and NaVO₃ was added into $\mathrm{V}_{2}\mathrm{O}_{5}$ gel with mild stirring for only several minutes to prepare $\mathrm{Li}_{1.2-y}\mathrm{Na}_{y}\mathrm{V}_{3}\mathrm{O}_{8}$ gel. $\mathrm{Li}_{1.2-y}\mathrm{Na}_{y}\mathrm{V}_{3}\mathrm{O}_{8}$ was obtained by dehydration from this gel in 150—350 °C in air. As-prepared products could be used directly as cathode active materials without further treatments.

Experimental

Preparation of LT-Li_{1.2-y}Na_yV₃O₈

The V_2O_5 gel used in this method was prepared by polycondensation of vanadic acid. ¹⁴ The vanadic acid without any foreign cations was obtained by passing a metavanadate solution through a bed of a proton exchanging resin. Aqueous $\text{Li}_{1.2-y}\text{Na}_yV_3O_8$ gels were formed by adding mixed solutions

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of LiOH and NaVO₃ with varied concentration ratios to V₂O₅ gels under mild stirring. Compounds of nominal composition Li_{1.2-y}Na_yV₃O₈ were obtained by vacuum-drying the gels at 50 °C followed by heating them in the range of 150—350 °C in air. After mild manual grindings in an agate mortar, the products could be used as cathode active materials. For comparison, crystalline Li_{1.2}V₃O₈ was also prepared by the conventional high temperature synthesis. ¹⁵

Characterization of LT- Li_{1.2-y}Na_yV₃O₈ structure

The xerogel vacuum-dried from Li_{1.2} V₃O₈ gel at 50 °C was used in TG and DTA experiments, and the thermal analysis was conducted on a WCT-1A instrument (Beijing Optical Instruments) in air. X-Ray diffraction (XRD) experiments were carried out using a SHIMADZU XRD-6000 X-Ray Diffractometer with Cu K α line. To check the composition of Li_{1.2-y}Na_yV₃O₈, the lithium and sodium contents of the samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis on Thermo-Jarell Ash Autoscan-2000, and the total vanadium content was determined by chemical analysis. For TEM examination, a JEM-100 (XII) microscope was used.

Electrochemical property of LT-Li_{1.2-v}Na_vV₃O₈

The composite cathode electrode consisted of 80% active material, 15% acetylene black and 5% polytetrafluoroethylene (PTFE) binder. The current collector was a mesh of stainless steel. Lithium disks worked as both counter and reference electrodes, and the separator was Celgard-2400. Three-electrode and two-electrode cells were used in cyclic voltammetry (CV) and galvanostatic charge-discharge tests respectively. Unless specified, the charge and discharge current rate was about 60 mA/g. The electrolyte was 1 mol/L LiClO₄ in blended ethylene carbonate (EC) and dimethyl carbonate (DMC) solution with volumetric ratio of 1:1. The CV tests were carried out on a CHI 660A workstation and the galvanostatic charge-discharge tests on ARBIN BT-2000. All cells were assembled in a glove box (MECAFLEX, MECABOX 80-1 "s") filled with purified argon gas, and tested at 25 °C.

Results and discussion

Structural characterization of LT-Li_{1.2}V₃O₈

The results of elemental analysis accorded fairly well with the nominal composition of $\text{Li}_{1.2-y}\text{Na}_y\text{V}_3\text{O}_8$, and also confirmed the advantage of this low temperature synthesis route over the high temperature synthesis route by exempting the volatilization of light elements.

The XRD profiles in Fig. 1 show that the new synthesis route has really led to the formation of $\text{Li}_{1.2}\text{V}_3\text{O}_8$. The X-ray patterns of the products match the pattern of the high-temperature form fairly well (JCPDS Card, 18-754), and with the

temperature increasing, the crystallinity of these products increases. The product treated at 150 °C is somewhat amorphous, but the main diffraction peaks appear gradually over 200 °C. It should be noted that there is a peak around 12° in the sample at 150 °C or 200 °C, which disappears by heating over 250 °C. For $V_2O_5 \cdot nH_2O$, water molecules are intercalated between the V_2O_5 ribbons and the layer distance decreases with the decrease of the amount of water. A $V_2O_5 \cdot 1.8H_2O$ xerogel with d=1.15 nm was obtained when V_2O_5 gel was dried at room temperature, and a $V_2O_5 \cdot 0.5H_2O$ with d=0.87 nm when treated around 250 °C. ¹⁶ So the peak around 12° (d=0.737 nm) is unlikely to be the (001) peak of V_2O_5 xerogel. This suggests that $Li_{1.2}V_3O_8$ xerogel formed from V_2O_5 gel is somewhat different from V_2O_5 xerogel.

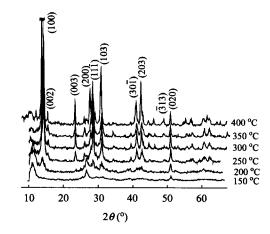


Fig. 1 XRD patterns of Li_{1,2}V₃O₈ with different heating temperature.

Fig. 2 shows the TG-DTA curves of the xerogel obtained by vacuum-drying the $\text{Li}_{1.2}\text{V}_3\text{O}_8$ gel at 50 °C. It can be found that the compound lost weight gradually from 50 °C, and 20.01% weight of it was lost until 350 °C. This means that the $\text{Li}_{1.2}\text{V}_3\text{O}_8$ xerogel vacuum-dried at 50 °C could be termed as $\text{Li}_{1.2}\text{V}_3\text{O}_8 \cdot 4\text{H}_2\text{O}$. The DTA trace shows two endothermic peaks at 72 °C and 174 °C corresponding to the removal of loosely bound water and part of tightly bound water respectively. The exothermic peak at 322 °C should be assigned to the crystallization of $\text{LT-Li}_{1.2}\text{V}_3\text{O}_8$. The TEM images in Fig. 3

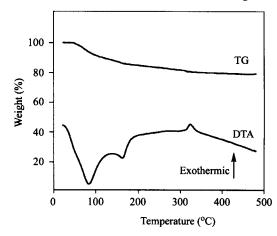
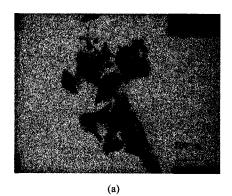
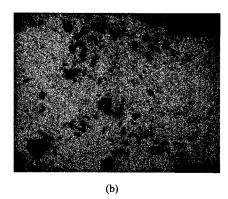
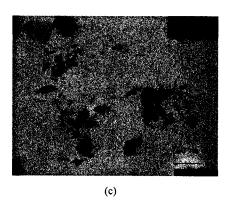


Fig. 2 TG-DTA curves of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ vacuum-dried at 50 °C , 5 °C/s in air.

also confirm it. Fig. 3a shows an aggregation of $\text{Li}_{1.2}\,V_3O_8$ particles. With the increasing of treating temperature, the aggregation collapses into little ones, as seen in Fig. 3b, and then the crystallization occurs with the particle size growing bigger (Fig. 3c, Fig. 3d).







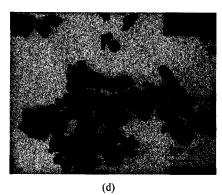


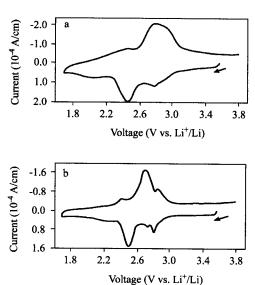
Fig. 3 Transmission electron micrographs of Li_{1.2}V₃O₈ dehydrated at different temperature: (a) heated to 250 °C; (b) heated to 300 °C; (c) heated to 350 °C; (d) heated to 400 °C.

The fact that Li_{1.2} V₃O₈ gel could be obtained without overnight heating and stirring required in other low temperature methods^{8,9} may be explained by the V₂O₅ gel with an open structure being more reactable with LiOH than crystalline V₂O₅. 17,18 Though the mechanism of the formation of Li_{1.2-y}Na_yV₃O₈ gel is not quite clear yet, we believe that many other vanadium-based compounds, besides Li_{1.2-y}Na_yV₃O₈ could also be synthesized from V₂O₅ gel easily. In fact, we have obtained LT-Ag_{1.2}V₃O₈ using this method, and it will be reported elsewhere.

Electrochemical property of LT-Li_{1.2}V₃O₈

For checking the electrochemical performance of LT- $\rm Li_{1.2}\,V_3O_8$, cyclic voltammetry and galvanostatic charge-discharge tests were carried out.

Fig. 4 shows the typical cyclic voltammograms of LT-Li_{1.2}V₃O₈ and HT-Li_{1.2}V₃O₈ at the scan rate of 0.05 mV/s. For LT-Li_{1.2}V₃O₈ obtained at 250 °C, several broad peaks can be seen in Fig. 4a, instead of sharp peaks of LT-Li_{1.2}V₃O₈ obtained at 350 °C and HT-Li_{1.2}V₃O₈ in Fig. 4b and Fig. 4c respectively. It is tempting to explain this phenomenon by differences of their crystallinity. Fig. 4a represents a typical CV behavior of amorphous material. However, the broad anode peak in Fig. 4c is caused by the polarization



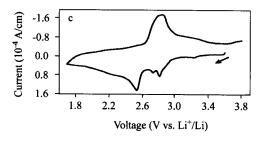


Fig. 4 Typical cyclic voltammograms of Li_{1.2}V₃O₈ at 0.05 mV/s, electrode active mass 5.0 mg; (a) heated to 250 °C; (b) heated to 350 °C; (c) conventional high temperature synthesis at 680 °C.

in the large particles as a consequence of high temperature treatment. The main cathodic peak potentials at 2.8 and 2.5 V are almost identical in each curve.

The third cycle discharge curves of these lithium vanadium oxides are illustrated in Fig. 5. The specific capacity of LT-Li_{1.2}V₃O₈ obtained at 250 °C amounts 345 mAh/g (x = 3.75 of Li_{1.2+x}V₃O₈), which is much higher than 180 mAh/g (x = 1.95 of Li_{1.2+x}V₃O₈) of HT-Li_{1.2}V₃O₈. As also illustrated in Ref. 19 the material with lower crystallinity may have additional sites for lithium intercalation, which increases its specific capacity. Although the LT-Li_{1.2}V₃O₈ prepared at 350 °C has only a specific capacity of 281 mAh/g lower than 345 mAh/g of the material made at 250 °C, this material shows better cyclic performance than 250 °C material. A capacity of 200 mAh/g is still maintained after 40 cycles as exhibited in Fig. 6.

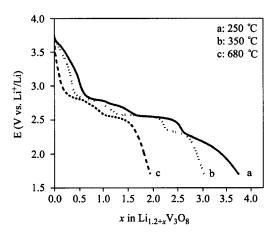


Fig. 5 Discharge curves on the third cycle of $\text{Li}_{1,2}\text{V}_3\text{O}_8$ treated at different temperature (60 mA/g); (a) heated to 250 °C; (b) heated to 350 °C; (c) conventional high temperature synthesis at 680 °C.

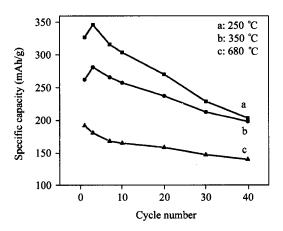


Fig. 6 Changes in discharge capacity as a function of cycle number of $\text{Li}_{1.2}\text{V}_3\text{O}_8$ (60 mA/g); (a) heated to 250 °C; (b) heated to 350 °C; (c) conventional high temperature synthesis at 680 °C.

It is worthwhile to note that water plays an important role in these materials obtained from $\text{Li}_{1.2}\text{V}_3\text{O}_8$ gel. On the one hand, water molecules in LT-Li_{1.2}V₃O₈ enlarge the gap between V₃O₈ layers, ⁷ thus enhancing the mobility of Li⁺ ions

in it. On the other hand, water is one of the hindrances that has to be excluded from the nonaqueous lithium batteries for the sake of cyclability. Unfortunately, the higher temperature required for the complete removal of water would unavoidably bring about some crystallization of the products, which results in a decrease of capacity. Therefore the temperature of 350 $^{\circ}\text{C}$ was chosen for treatments of LT-Li_{1.2-y}Na_yV₃O₈.

Characterization of LT-Li_{1.2-y}Na_yV₃O₈

Li_{1,2-γ}Na_γV₃O₈ was also synthesized easily by the method described above. The X-ray diffraction patterns of LT-Li_{1,2-x}Na_xV₃O₈ with varied y values are illustrated in Fig. 7. Although these materials were all treated at the temperature of 350 °C, they showed different degree of crystallinity. Li_{1.2} V₃O₈ and Na_{1.2} V₃O₈, which have no foreign cations, exhibit higher crystallinity than those which have both Li⁺ and Na⁺ ions in V₃O₈⁻ layers. For Li_{1,2}V₃O₈, Li⁺ ions occupy the octahedral sites in the zigzagged V₃O₈- layers, 20 but for $\mathrm{Na_{1.2}V_{3}O_{8}}$, $\mathrm{Na^{+}}$ ions are situated at octahedral and tetrahedral sites between the layers.21 In the case of Li_{1,2-γ}Na_γV₃O₈, Li⁺ ions function as competitive opponents to Na+ ions relying on their smaller ionic radii and higher mobility by occupying more octahedral sites. This results in some distortion of the regular arrangement of atoms as in Li_{1,2}V₃O₈ or Na_{1,2}V₃O₈, ²¹ and some reduction of the longrange order. The main peak, namely the (100) diffraction peak is the strongest one, which lies between 13° and 14° in each pattern.

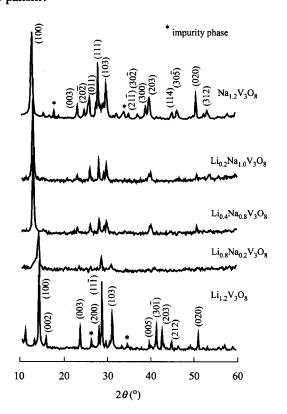


Fig. 7 XRD patterns of $\text{Li}_{1,2-\gamma}\text{Na}_{\gamma}\text{V}_3\text{O}_8$ prepared at 350 °C .

As shown in Table 1, the Li_{1.2-y} Na_yV₃O₈ with higher Na content has larger interlayer distance. The d_{100} increases from 0.6228 to 0.7029 nm as Li/Na ratio dropping from Li_{1.2}V₃O₈ to Na_{1.2}V₃O₈. It is assumed that positively charged Li⁺ or Na⁺ ions act as pillars holding the V₃O₈⁻ layers electrostatically. With the ionic radii of 0.10 nm larger than 0.07 nm of Li⁺, Na⁺ ions set the V₃O₈⁻ layers more apart.

 Table 1 Changes in d_{100} values as a function of y in $\text{Li}_{1.2-y}\text{Na}_y\text{V}_3\text{O}_8$

 y in $\text{Li}_{1.2-y}\text{Na}_y\text{V}_3\text{O}_8$ 0
 0.4
 0.8
 1.0
 1.2

 d_{100} (10^{-1} nm)
 6.228
 6.328
 6.884
 6.9
 7.029

Electrochemical tests of LT-Li_{1.2-y}Na_yV₃O₈

Fig. 8 depicts the typical discharge curves of LT-Li_{1,2-7}Na₇V₃O₈ obtained at a current rate of 60 mA/g. The amount of inserted lithium decreases with the increase of the content of Na+ in Li_{1,2-r} Na_r V₃O₈. Maybe the electrostatic interaction between Li+ and Na+ ions could account for this. It is assumed that Na+ ions are stabilized in V₃O₈- layers while Li+ ions shuttle in the host of Li_{1.2-γ}Na_γV₃O₈. Consequently there is some repulsion between these two kinds of cations, which results in an obstruction in lithium transportation. As far as the discharge voltages are concerned, the same rule goes. That is to say, Li_{1.2-y}Na_yV₃O₈ with higher Na + content has lower discharge voltage. It is due to the different site energy of intercalated lithium atoms. As seen in Table 1, since the presence of Na+ ions enlarge the interlayer distance between V₃O₈ layers, the tetrahedral sites available for lithium accommodation stand lower site energy.

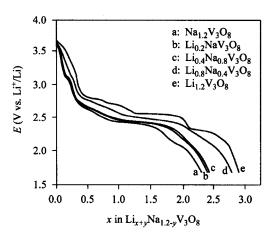


Fig. 8 Typical discharge curves of Li_{1.2-y}Na_yV₃O₈ prepared at 350 ℃ (60 mA/g).

Fig. 9 shows the discharge capacities of LT-Li_{1.2-y}-Na_yV₃O₈ as a function of cycle number. Although Li_{1.2}V₃O₈ has the highest specific capacity, it endures the most rapid capacity fading from 281 mAh/g (x = 2.95 of Li_{1.2-y}-Na_yV₃O₈) dropping to 198 mAh/g (x = 2.0). With the Na⁺ content increasing, Li_{1.2-y}-Na_yV₃O₈ shows better cyclability.

However, too much Li⁺ ions substituted by Na⁺ ions will badly sacrifice its capacity.

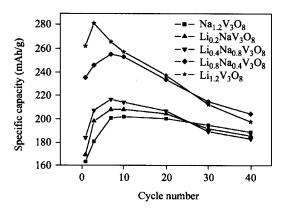


Fig. 9 Changes in discharge capacity as a function of cycle number of Li_{1.2-r}Na_rV₃O₈ (60 mA/g).

A peculiar feature for these low temperature products is also seen in Fig. 9, *i.e.*, the discharge capacity climbs to a climax in the initial cycles before capacity fading. This phenomenon was also observed for other low temperature products. ^{9,22} There is no doubt owing to the structural difference from the high temperature products. During the initial cycles, by shuttling in the chunnels Li⁺ ions probably cause a modification of the host structure so that they diffuse more smoothly. Further study on the detailed mechanism is still in progress in our laboratory.

Conclusion

Li_{1.2} V₃O₈ and its analogs Li_{1.2-y}Na_yV₃O₈ have been successfully synthesized from V₂O₅ gel at relatively low temperature (150—350 °C). The products thus prepared possess smaller particle size, lower crystallinity, and show better electrochemical performances than conventional high temperature (680 °C) products. The new low temperature synthesis route could vigorously enhance the efficiency on production of Li_{1.2-y}Na_yV₃O₈. The electrochemical performance of Li_{1.2}V₃O₈ depends much on its heating temperature required for water removal. Li_{1.2}V₃O₈ treated at 250 °C exhibits the highest discharge capacity of 350 mAh/g, but Li_{1.2}V₃O₈ treated at 350 °C shows better cycle performance than the 250 °C material and higher capacity than the high temperature product.

Partial substitution of Li by Na influences the electrochemical performance of $\text{Li}_{1.2-y}\,\text{Na}_y\,\text{V}_3\text{O}_8$ greatly. With the increase of Na/Li ratio, the cyclability of $\text{Li}_{1.2-y}\,\text{Na}_y\,\text{V}_3\text{O}_8$ is improved indeed, but its discharge potentials and specific capacity are all lowered.

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