

Synthesis of γ - $\text{LiV}_2\text{O}_5/\text{VO}_2$ mixture by thermal lithiation of vanadium (+4, +5) oxides

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Abstract: γ - $\text{LiV}_2\text{O}_5/\text{VO}_2$ composites were synthesized through thermal lithiation reaction of mixed valence (+4, +5) vanadium oxides by lithium bromide. The phase evolution, morphology and discharge behavior at 500 °C were investigated by thermal gravimeter/differential thermal analysis (TG/DTA), X-ray diffraction(XRD), scanning electron microscopy(SEM) and specific surface analysis(BET). The mixed vanadium oxides are obtained from the pyrolytic decomposition of ammonium metavanadate, with V_6O_{13} as main phase. Results show that the lithiation reaction begins at about 258 °C, with γ - LiV_2O_5 and $\text{VO}_2(\text{B})$ as the product. $\text{VO}_2(\text{B})$ can transit to $\text{VO}_2(\text{R})$ in the range of 400–500 °C, following by grain growth and crystalline development with the increase of temperature and roasting time. The ratio of γ - LiV_2O_5 to VO_2 can be modified by the additive content of lithium bromide. A lattice shearing model about the nucleation and growth of $\text{Li}_x\text{V}_2\text{O}_5$ and $\text{VO}_2(\text{B})$ inside mixed valence (+4, +5) vanadium oxides (e.g. V_6O_{13} , V_3O_7) is speculated, which is relative to oxygen-/vacancy-diffusion and structural evolution inspired by lithium-insertion. The open-circuit voltage of 2.6 V is observed in the single cell of $\text{Li-B}/\text{LiCl-KCl}/(\gamma\text{-LiV}_2\text{O}_5/\text{VO}_2)$ at 500 °C, and the specific capacities of 146 and 167 mA·h/g (cut-off voltage 1.4 V) are measured for the positive material at 100 mA/cm² and 200 mA/cm², respectively.

Key words: thermal cell; γ - $\text{LiV}_2\text{O}_5/\text{VO}_2$ composite material; lithiation

1 Introduction

Transition-metal oxides were investigated as the potential cathode materials of thermally activated molten salts battery. Attention was focused on the oxides based on vanadium, such as V_2O_5 and LiV_3O_8 . These materials are more thermally stable and have higher open-circuit voltages than widely used disulfides (FeS_2 and CoS_2 mainly), but show lower usable capacities and exhibit sloping discharge curves due to frequent structure changes or insertion reactions[1–2]. The resultant product obtained by in situ thermally reacting $\text{V}_6\text{O}_{13+x}$ with LiBr is usually entitled as LVO (lithiated vanadium oxide) that consists of γ - LiV_2O_5 and VO_2 mainly. LVO was introduced as the cathode material of thermal cell with lithium alloys anode firstly in 1986[3]. It has more flat discharge profiles than γ - LiV_2O_5 , VO_2 , their machine-made mixtures and other vanadium oxides, and is compatible with many molten electrolytes such as LiCl-KCl , LiCl-LiBr-LiF . Another material named vanadium-oxide-carbon(VOC), produced by baking the

mixture of V_2O_5 , LiCl-KCl eutectic salt and acetylene black in inert atmosphere, has the same discharge active compounds of γ - LiV_2O_5 and VO_2 that are also from the lithiation and reduction reaction of V_2O_5 [4–5]. Although the effects of the addition of LiBr on thermal stability and electrochemical characteristics of LVO were investigated later[6–7], any detail on the synthesis and physical performances of LVO and VOC has not been reported up to now.

The crystallographic structure of LiV_2O_5 and VO_2 are both variable and temperature-dependent. It's reported that VO_2 has at least six polymorphs. Rutile $\text{VO}_2(\text{R})$ (above 68 °C), monoclinic $\text{VO}_2(\text{M})$ (below 68 °C) and triclinic $\text{VO}_2(\text{T})$ phase are similar in structure and convertible at 52–67 °C[8]. There are other three VO_2 phases designated as tetragonal $\text{VO}_2(\text{A})$ [9], monoclinic $\text{VO}_2(\text{B})$ [10] and layered $\text{VO}_2(\text{C})$ [11], respectively. There are also a series of compounds $\text{Li}_x\text{V}_2\text{O}_5$ based on α - V_2O_5 in the range of $0 \leq x \leq 1$. The one with $0.88 \leq x \leq 1$ is generally recorded as LiV_2O_5 that has at least three polymorphs denoted δ , ε and γ , respectively. γ - LiV_2O_5 is the high temperature phase,

while δ phase appears only at low temperature and can transform spontaneously to another form ε at 110–130 °C [12–13]. But the temperature range relating to the $\varepsilon \rightarrow \gamma$ transition is still not well defined. Several values were observed, such as 175–220 °C [12], above 300 °C [13] or 350 °C [14]. It's not known whether any structural transformations about LiV_2O_5 and VO_2 run in the preparation of LVO.

In this study, $\gamma\text{-LiV}_2\text{O}_5/\text{VO}_2$ composites were in situ synthesized via thermal reaction of $\text{LiBr}\cdot\text{H}_2\text{O}$ and vanadium oxides obtained by heating NH_4VO_3 in argon atmosphere. Attention was focused on the effect of synthesis condition on phase composition and resultant morphology in order to show the lithiation process. The positive discharge performances of the resultant at 500 °C were also investigated.

2 Experimental

2.1 Synthesis of $\gamma\text{-LiV}_2\text{O}_5/\text{VO}_2$ mixed oxides

The mixed valence (+4, +5) vanadium oxides were firstly produced by calcining NH_4VO_3 (A.R) in argon atmosphere at 450 °C for 4 h. It was then ball-milled with appropriate $\text{LiBr}\cdot\text{H}_2\text{O}$ (A.R) in an anhydrous ethanol using a resin bottle and ttpolytetrafluoroethylene balls. After dried at 120 °C, the mixtures were heated in vacuum at 320–600 °C for several hours to produce lithiated vanadium oxide.

2.2 Product characterizations

The phase compositions were evidenced by X-ray powder diffraction using a Rigaku D/max2550VB⁺ diffractometer with CuK_α radiation (40 kV, 300 mA, $\lambda = 0.154\ 06\ \text{nm}$, $10^\circ \leq 2\theta \leq 80^\circ$ or $5^\circ \leq 2\theta \leq 85^\circ$). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed in a TAS100 analyzer. Morphology of the powders was observed with a JSM-5600LV scanning electron microscope. The specific surface area of BET was measured using an ASAP2010 type instrument.

2.3 Electrochemical test of $\gamma\text{-LiV}_2\text{O}_5/\text{VO}_2$ composite at 500 °C

The discharge process of $\text{Li-B/LiCl-KCl}/(\gamma\text{-LiV}_2\text{O}_5/\text{VO}_2)$ pellet single cell was simulated at 500 °C, and curves of voltage (vs time) were monitored by an x-y function recorder. The Li-B alloy negative with 67% Li (mass fraction, the same below) is a composite material with Li_7B_6 and pure Li (self-made, thickness of 0.6–0.65 mm). The electrolyte separator (mass of 0.4 g) is the powder pressed pellet of LiCl-KCl eutectic salt (with 45% LiCl , melting point 352 °C) and 30% porous powdered MgO binder. 30% powdered LiCl-KCl was added into $\gamma\text{-LiV}_2\text{O}_5/\text{VO}_2$ powder (obtained at 600 °C

for 4 h, the excess of $\text{LiBr}\cdot\text{H}_2\text{O}$ was 20%), then kept at 450 °C for 1 h to make LiCl-KCl be adsorbed homogeneously. After cooled and crushed, the mixture was pressed as the positive pellet (mass of 0.4 g). The diameter of electrode was 17.5 mm, and two pieces of molybdenum (thickness of 1.0 mm) were used as the collector. The preparation of electrodes and cells was performed in a glove box (relative humidity lower than 2%) to prevent the electrodes from being wetted or oxidized. The cells were loaded at several current densities to cut-off voltage of 1.4 V after being heated between two isothermal metallic tables (at 500 °C) for 1 min.

3 Results and discussion

3.1 Thermal decomposition of NH_4VO_3

X-ray diffraction pattern of the product from thermal decomposition of NH_4VO_3 at 450 °C for 4 h is shown in Fig.1. The product consists of several vanadium oxides. They are V_6O_{13} , V_3O_7 , V_2O_5 and $\text{VO}_2(\text{B})$. Similar result was found in the Ref.[3], in which V_6O_{13} , VO_2 and V_3O_7 still co-existed even further being heated at 550 °C for 2 h. Since the thermal decomposition reaction of NH_4VO_3 is very complex, the decomposition process is usually described by the following two steps[1]:

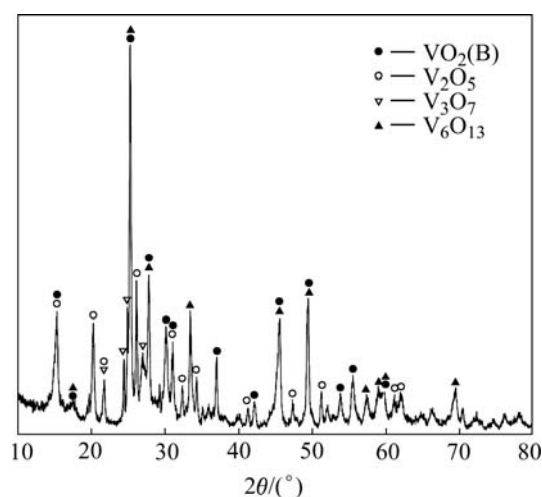
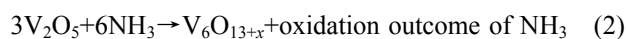
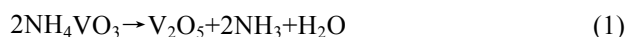


Fig.1 XRD pattern of NH_4VO_3 decomposition

Reactions (1) and (2) represent the decomposition of NH_4VO_3 and the reduction of V_2O_5 , respectively. But the reduction reaction does not end at $\text{V}_6\text{O}_{13+x}$; it can react further with NH_3 and the pyrolytic productions of NH_3 . As a result, a serial of nonstoichiometric vanadium-oxygen compounds are formed unavoidably.

The deoxidization of V_2O_5 to form V_6O_{13} or $\text{VO}_2(\text{B})$

can be described by a model of structure shear[15], in which V_6O_{13} and $VO_2(B)$ structures are obtained from shearing the idealized V_2O_5 lattice by removing every third or every second (020) plane of oxygen atoms and closing the oxygen-lost polyhedra along the shear vector $1/2[110]$, respectively, as shown in Fig.2. V_3O_7 is an intermediate structure between V_6O_{13} and V_2O_5 , whose structure contains both single and double chains of VO_6 octahedra, like V_6O_{13} , as well as some edge-shared zig-zag chains of VO_5 trigonal bipyramids, as those in V_2O_5 . By viewing of the structural intrinsic relationship, the mixture of V_6O_{13} , $VO_2(B)$ and V_3O_7 is produced inevitably if V_2O_5 is deoxidized asymmetrically. To obtain single V_6O_{13} , the molar ratio of vanadium to oxygen is needed to be controlled strictly, and the solid state reaction of stoichiometric V_2O_5 and vanadium is usually chosen[3,15]. Based on the structural relationship of these vanadium oxides, the product obtained at 450 °C is used directly as the vanadium oxide source to get LVO with high specific surface area.

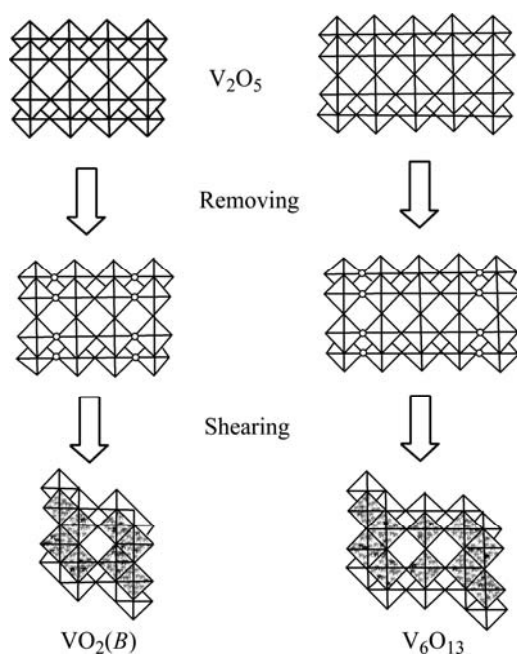


Fig.2 Sketch map of shearing ideal V_2O_5 crystal lattice to form $VO_2(B)$ and V_6O_{13} lattice (Blank circles represent vacancies by removing oxygen atoms)

3.2 In situ lithiation synthesis of γ - LiV_2O_5/VO_2 oxides

TGA and DTA curves of the mixture powder with an excess of 20% $LiBr \cdot H_2O$ under flowing argon atmosphere are shown in Fig.3. There are two temperature ranges, in which the mass loses sharply. The first is from 80 °C to 150 °C, with the mass loss of 1.2 mg (11%), corresponding to two endothermic peaks at 118 °C and 148 °C on the DTA curve. The mass loss may be due to the evaporation of the residual balling medium, free water and bond water. The second is 150–260 °C,

with 9.2% mass loss, corresponding to an exothermic peak at 258 °C. The mass loss and the heat release in this range may result from the reactions between the vanadium oxides and $LiBr$. It is awaited to be further confirmed whether the exothermic peak at 377 °C is related to $VO_2(B) \rightarrow VO_2(R)$ phase transition. This transition was observed at (440 ± 20) °C[15], or began at 320 °C and finishes at 500 °C for nanometer $VO_2(B)$ [16]. But in our experiment the transformation isn't completed even after being kept at 500 °C for 4 h. There is the difference of the synthesis technique and initial morphology of $VO_2(B)$ affecting the $VO_2(B) \rightarrow VO_2(R)$ transition. The great and broad endothermic peak at 630 °C is related to the melting of γ - LiV_2O_5 . Because it is an incongruent melting compound, two melting-related endothermic peaks at 572 and 628 °C are once observed in a DTA study[17].

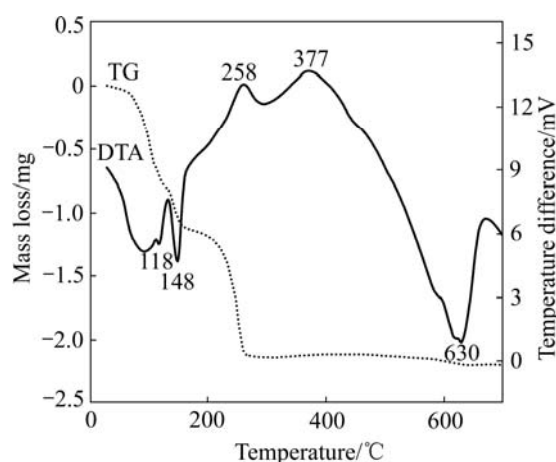


Fig.3 TG/DTA curves for vanadium oxides with $LiBr \cdot H_2O$ (Initial mass of 11.0 mg, 10 °C/min)

The lithium-inserted structures of V_2O_5 , V_6O_{13} and V_3O_7 are changeable at high temperature. $Li_xV_6O_{13}$ is disassembled at 230–265 °C[15]. Lithium-intercalation makes V_3O_7 transit to lithium-rich V_6O_{13+x} even at room temperature[15], also makes V_2O_5 structure transform frequently. Based on their inherent stacking relationship and lithium-insertion properties, in the similar way do V_6O_{13} and V_3O_7 form γ - $LiV_2O_5/VO_2(B)$ as V_2O_5 . Namely, the lithiation reactions of V_3O_7 and V_6O_{13} may contain two steps including the shearing breakup of the matrix resulting from the diffusion of oxygen vacancy or anion, and the nucleation and growth of new structures, as illustrated in Fig.4.

The structural micro-region of α - V_2O_5 in V_6O_{13} and V_3O_7 crystal is more thermodynamically advantageous to lithium-ion insertion (viz. lithiation) than that of $VO_2(B)$, which can be substantiated by the fact that V_2O_5 has higher electrochemical intercalation voltage than $VO_2(B)$ [18]. As lithium ions move into V_2O_5 micro-regions, a new structure is formed. But its frontier keeps the same

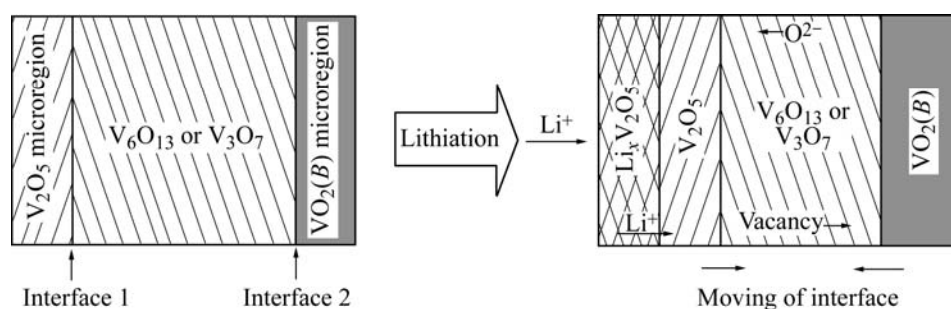


Fig.4 Schematic drawing of lithiation evolution of V_3O_7 and V_6O_{13}

structure as α - V_2O_5 , and shares the plane made up of double octahedral layers as the structural boundary with matrix crystal. The shear-coherence bond raises the lattice distortion near the interface, which is beneficial to breaking the double octahedral sheets. When a (020) oxygen plane in the double layers shears along $1/2[\bar{1}\bar{1}0]$ direction, a stride taking toward V_6O_{13} or V_3O_7 is realized. The shear reaction is the reverse process of the transformation of V_2O_5 to V_6O_{13} shown in Fig.2. The cleavage and bonding on one hand leads to the shift of the interfaces, on the other hand increases the concentration of oxygen vacancy near the interface. High oxygen vacancy concentration induces oxygen anions in V_6O_{13} or V_3O_7 to configurationally transfer to the interfaces (or oxygen vacancies near the interface to the matrix phase), and in turn increases the concentration of oxygen vacancy in the matrix phase. Since a great deal of oxygen vacancy appears at VO_5 micro-region ahead $VO_2(B)$ matrix, it's helpful for the edge-shared zig-zag layers of VO_5 trigonal bipyramids to undergo the shearing along $1/2[110]$, as shown in Fig.2. As a result, the shear drives the interfaces to move along and $VO_2(B)$ structure region spread. Vice versa, the shear that makes $VO_2(B)$ structure region spread is helpful for the extending of V_2O_5 structure. So the lithiation of V_6O_{13} and V_3O_7 is perhaps the phenomenon that the structural decomposition is firstly induced by the diffusion of vacancy or anion, which produces the structure regions of nonstoichiometric V_2O_5 , $Li_xV_2O_5$ and $VO_2(B)$, and that γ - LiV_2O_5 is obtained from further lithiation of $Li_xV_2O_5$.

3.3 Effect of additive content of lithiated reagent

The additive content of $LiBr \cdot H_2O$ is calculated based on the following reaction for the preparation of lithiated vanadium oxides. The XRD patterns of composite materials with $0.8 \leq x \leq 1.3$ in $Li_xV_2O_5$ are shown in Fig.5.

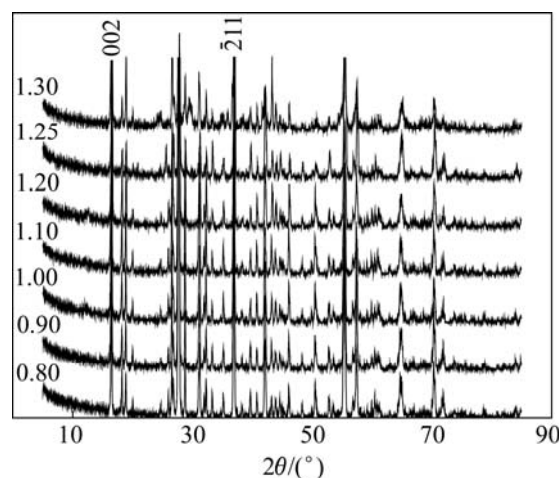
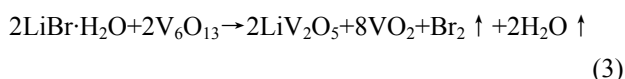


Fig.5 XRD patterns of LVO with different ratios (600 °C, 4 h) of practical mass to calculated value

The ratio of LiV_2O_5 to VO_2 in the resultant products is reported according to the calculated value from Eqn.(3), and the optimum discharge property and the highest thermal stability can not be obtained until the additive content of $LiBr$ is excessive[3,6–7]. To eliminate β - $Li_{0.13}V_2O_5$, α - $Li_{0.04}V_2O_5$ and V_2O_5 phases, 20%–30% excess of $LiBr$ is needed[7]. However, LiV_2O_5/VO_2 composite is gained in this experiment after 600 °C, 4 h treatment with only 80% of $LiBr \cdot H_2O$ calculated value, in which γ - LiV_2O_5 content is just relatively lower and VO_2 content is higher. γ - LiV_2O_5 content rises up and VO_2 drops off with the increase of $LiBr \cdot H_2O$ content from 0.8 to 1.3, as seen in Fig.6. Since the third intensity peak (103) of γ - LiV_2O_5 superposes the highest (011) peak of $VO_2(R)$, the relative contents of both are characterized by the intensity of the highest (002) peak of γ - LiV_2O_5 and the second high (211) peak of $VO_2(R)$, respectively. Based on the fact that γ - LiV_2O_5 and $VO_2(R)$ are both nonstoichiometric[15], it's thought that γ - LiV_2O_5 obtained at low $LiBr \cdot H_2O$ may be a lithium-poor phase and VO_2 a oxygen-rich phase, and that the oxygen-rich VO_2 can be further lithiated to form γ - LiV_2O_5 and oxygen-poor VO_2 phase, as well as

increasing lithium content in γ - LiV_2O_5 . What is more, the lower thermal stability (decomposition temperature) of LVO obtained at low LiBr content[7] perhaps results from the transformations that lithium-poor γ - LiV_2O_5 separates out β' phase and oxide-rich VO_2 separates out V_2O_5 phase.

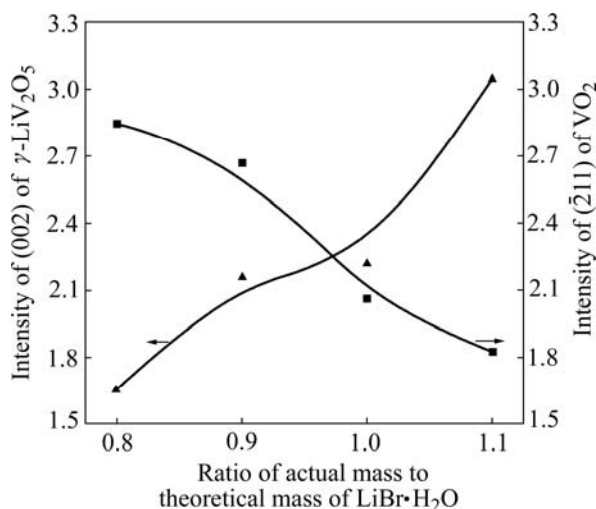


Fig.6 XRD peak intensities of γ - LiV_2O_5 and $\text{VO}_2(\text{R})$ versus $\text{LiBr}\cdot\text{H}_2\text{O}$

3.4 Effects of experimental parameters

XRD patterns of the resultant products obtained at 320–600 °C for 4 h are shown in Fig.7. γ - LiV_2O_5 and $\text{VO}_2(\text{B})$ phase are gained at 320 °C, with two unknown weak peaks at $2\theta=(8-9)^\circ$, which disappear above 400 °C. The resultants consist of γ - LiV_2O_5 , $\text{VO}_2(\text{B})$ and distinguishable $\text{VO}_2(\text{R})$ after being heated at 400 °C and 500 °C, while γ - LiV_2O_5 and $\text{VO}_2(\text{R})$ appear at 550 °C and 600 °C. It's shown that γ - LiV_2O_5 and $\text{VO}_2(\text{B})$ phases are firstly obtained from the lithiation reaction, and the metastable $\text{VO}_2(\text{B})$ will transform gradually to the more stable rutile $\text{VO}_2(\text{R})$ in the range of 400–550 °C.

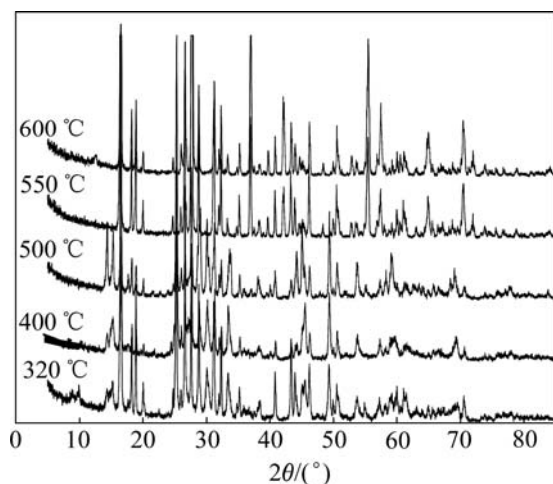


Fig.7 XRD patterns of LVO obtained at different temperatures (for 4 h)

As reported, γ - LiV_2O_5 can be obtained from its low-temperature counterparts, even though the required temperature varies with the lithium content, and varies greatly with measurement methods. For example, for the precursor δ - LiV_2O_5 prepared in an organic solution, the $\varepsilon \rightarrow \gamma$ phase transition begins at 175–220 °C and completely finishes at 235 °C with a heating rate of 0.5 °C/min from the synchrotron X-ray powder diffraction analysis[12]. The ε phase transits quickly at 280 °C from the DSC result[19], or at 300–320 °C or 350–370 °C on the well-accepted presumable phase diagram[12, 14]. It can also be directly gained through chemical reactions, such as, hydrothermal method at 160 °C[20], organic solution processing at 120 °C using vanadium alkoxides and lithium[21], solid-state reaction of $\text{NH}_4\text{V}_3\text{O}_8$ with CH_3COOLi at 285.7–312 °C[22]. This observation is similar to that of the Ref.[22]. The reactions progress quickly at 258 °C and end before 280 °C (shown in Fig.3). Although it's not quite clear whether γ - LiV_2O_5 nucleates and grows directly inside the vanadium oxides or comes from the transformations of its low temperature polymorphs or other low lithium phases (e.g. β phase), it is reasonable that γ - LiV_2O_5 is formed through the structural transition induced by the intercalation of lithium step by step, as presumed in our model.

The lithiation reactions make the loose agglomerated particles be rock salts. The grain growth and the crystallinity characteristics are reinforced with the increase of calcination temperature and time (shown in Fig.8). The strip crystals with the radial length of less than 1 μm and the longitudinal length of above 10 μm come forth as bundles, and are sintered ultimately to be blocks. This indicates that the calcination, after the complete lithiation reaction, mainly enforces the growth of grain and the increasing of crystallinity except the transformation of $\text{VO}_2(\text{B})$ to $\text{VO}_2(\text{R})$.

The specific surface area analysis results give another evidence for the grain growth (shown in Fig.9). The specific surface area of the vanadium oxides directly from NH_4VO_3 is 11.26 m^2/g . The values of LVO are 5.12 m^2/g and 0.44 m^2/g at 400 °C and 600 °C for 4 h, respectively. It also declines continuously with the prolonging of exposure time.

3.5 Electrochemical test of γ - $\text{LiV}_2\text{O}_5/\text{VO}_2$ composite

The discharge plots of γ - $\text{LiV}_2\text{O}_5/\text{VO}_2$ material (with Li-B alloy anode at 500 °C) are shown in Fig.10. The open-circuit voltage of single thermal cell of Li-B/LiCl-KCl/(γ - $\text{LiV}_2\text{O}_5/\text{VO}_2$) is 2.6 V. The discharge voltage and time drop off with increasing current density. The discharge can last for 650 s till 1.4 V at the current density of 100 mA/cm^2 , and the specific capacity of the

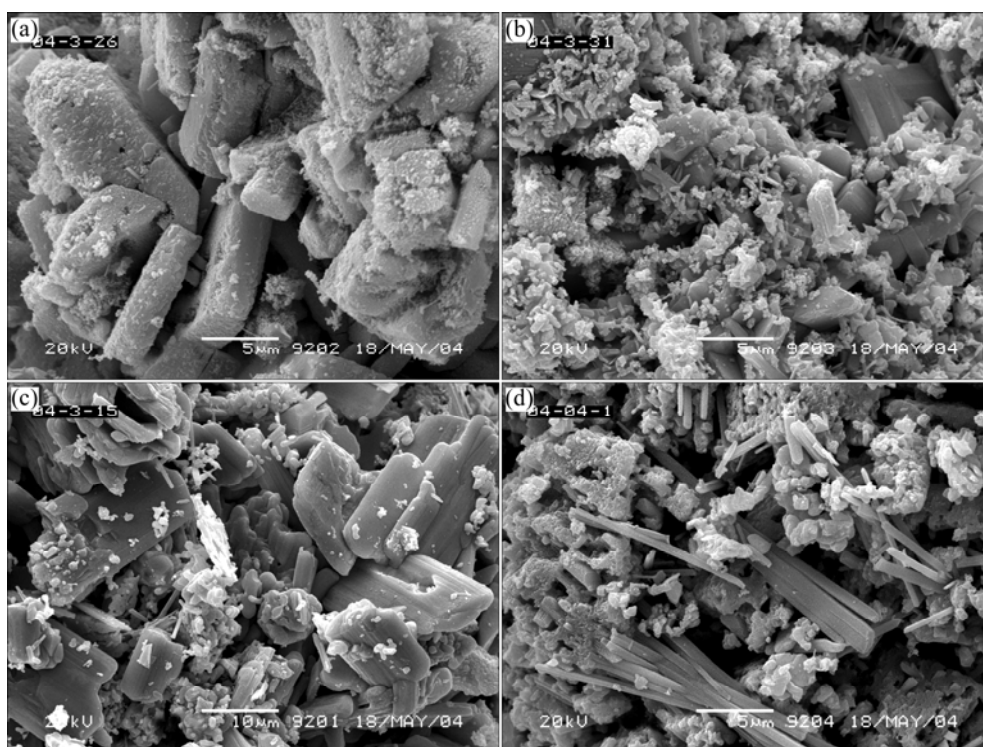


Fig.8 SEM images of products obtained at different calcinated temperatures and time: (a) Vanadium oxides; (b) 500 °C, 4 h; (c) 600 °C, 4 h; (d) 600 °C, 2 h

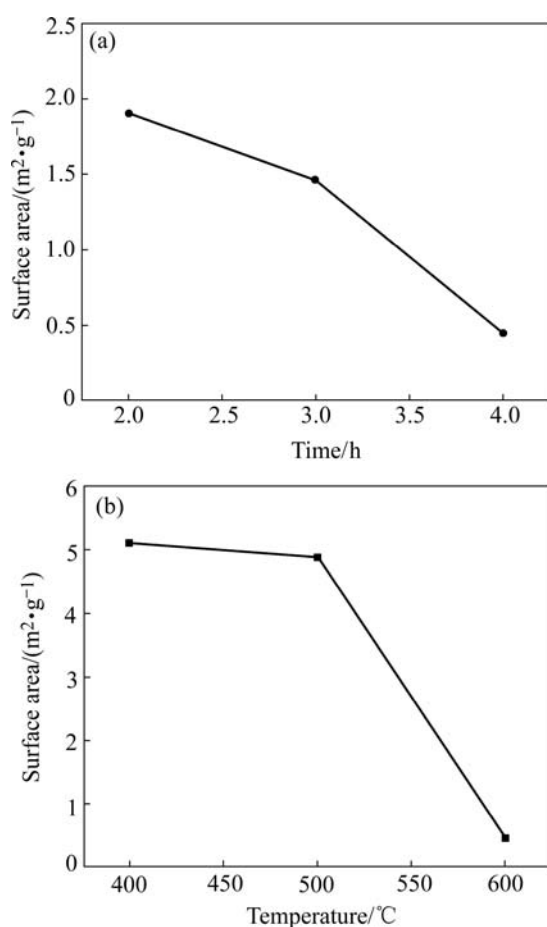


Fig.9 Specific surface area of LVO versus time (at 600 °C) (a) and temperature (for 4 h) (b)

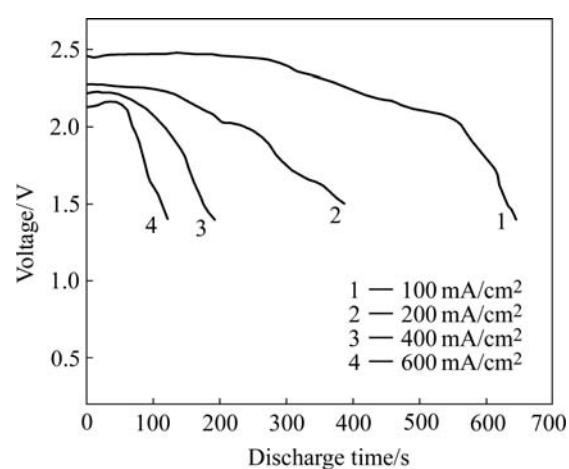


Fig.10 Electrochemical characteristics of γ -LiV₂O₅/VO₂(R) composite

mixed oxides reaches 146 mA·h/g, while 167 mA·h/g at 200 mA/cm². The discharge property is comparable to that previously reported.

4 Conclusions

1) The product from the decomposition of ammonium metavanadate is mainly made up of V₆O₁₃, and contains minor amount of impurities such as VO₂, V₃O₇ and V₂O₅. The multiphase coexistence results from the asymmetric oxygen-loss of V₂O₅, and does not seriously affect the phase composition of lithiated

vanadium oxide.

2) The reactions between the mixed vanadium oxides and lithium bromide take place near 258 °C with γ -LiV₂O₅ and VO₂(B) as-obtained, and VO₂(B) turns to VO₂(R) in the range of 400–550 °C. After the lithiation reaction, the particles grow and the crystalline morphology increases with the increased temperature and the prolonged time till the melting of γ -LiV₂O₅ near 630 °C. The relative content of γ -LiV₂O₅ and VO₂ in LVO can be modified by the additive content of lithium bromide.

3) A nucleation-growth model is speculated to describe the lithiation process of mixed valence (+4, +5) vanadium oxides (e.g. V₆O₁₃, V₃O₇) to form Li_xV₂O₅ and VO₂(B), including deoxidized shearing and oxygen-assembled shearing both inspired by lithium-insertion.

4) The open-circuit voltage of single cell of Li-B/LiCl-KCl/(γ -LiV₂O₅/VO₂) is 2.6 V. The specific capacity of LVO reaches 146 mA·h/g and 167 mA·h/g at 100 mA/cm² and 200 mA/cm² till 1.4 V, respectively.

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