

Soft-chemical synthesis and high-temperature electrochemical characteristics of VO₂

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Abstract: VO₂ powder was synthesized by a new soft-chemical method using formaldehyde as a reductant. The influences of pyrolysis temperature and time on the phase and morphology of grains were investigated by using thermal gravimeter/differential thermal analysis(TG/DTA), X-ray diffraction(XRD), Fourier transform infrared(FTIR) spectroscopy and scanning electron microscope(SEM). The positive electrode discharge performances of Li-B/LiCl-KCl/VO₂ thermal battery at 500 °C were studied. The results show that the product is mainly non-crystal when the precursor of VO₂ is heated below 300 °C. VO₂(B) appears and transits into VO₂(R) irreversibly as the heating temperature rises. The open-circle voltage of VO₂ is 2.6 V (vs Li-B), and the initial discharge voltage of 100 mA/cm² at 500 °C is 2.52 V. The specific capacities of 100 mA/cm² and 200 mA/cm² at cut-off voltage of 1.4 V are 449 A·s/g and 539 A·s/g, respectively.

Key words: VO₂ powder; synthesis; electrochemical characteristics; thermal battery

1 Introduction

In 1986, LVO (lithiated vanadium oxide) was first presented by FAUL et al[1–3] as positive electrode materials for thermal battery, which is a mixture of γ -LiV₂O₅ and VO₂, but the morphology and crystallography of VO₂ in the mixture were not clear. Up to date it is known that VO₂ has six phases: VO₂(A), VO₂(B), VO₂(C), VO₂(M), VO₂(T) and VO₂(R)[4]. The metastable VO₂(B) phase has a layered structure and shows good performance as a positive host for rechargeable lithium cells with aqueous electrolytes [5]. To our knowledge using VO₂(B)/VO₂(R) (rutile) mixed phases as positive electrode materials for thermal battery has not been reported.

The general methods for VO₂ powder preparation are to heat a mixture of V₂O₃ (or V) and V₂O₅ corresponding to VO₂ composition in an evacuated silica tube at 700 °C for 2 d [6–8], or to reduce V₂O₅ powder in a platinum crucible in a CO₂ atmosphere[6] at 1 227 °C for 3 d, or to melt V₂O₅ in a platinum crucible at 1 350 °C in a nitrogen atmosphere[9]. Some milder methods to prepare VO₂ powder have been developed recently, such as pyrogenation[10–12] and soft chemistry[5, 13–15], or

hydro-thermal methods[4,16,17]. Sol-gel routes[5, 13, 18, 19] and laser-insured vapor-phase aggradation[20] have also been used. But these methods have several disadvantages: long reactive times and high temperature; complexity of experimental equipments and contamination by impurity phases.

In this study, the authors report a novel and very simple method to prepare a fine vanadium dioxide powder by heat-treatment of the black precursor powder, which is prepared by a solution hydrolysis processing by using formaldehyde as a reductant. The influences of the reactive temperature and time on XRD, appearance of the phase and morphology were studied. The positive electrode discharge performances of resultant VO₂(B)/VO₂(R) mixed phase at 500 °C have also been investigated.

2 Experimental

2.1 Synthesis of VO₂ powder

V₂O₅ (analytic reagent) was slowly added into dilute hydrogen chloride solution. In the process of reaction, the solution was agitated continuously by a magnetic stirrer. A transparent yellow VOCl₃ solution was formed after the V₂O₅ had completely dissolved.

Appropriate concentrated formaldehyde was added into the above VOCl_3 solution. After reactions at 80°C for 24 h, a blue VOCl_2 solution was formed. A bulky black gel of high viscosity was obtained after slowly vaporizing the solution at 60°C by hydrolysis of VOCl_2 . During the hydrolysis, the pH of the solution showed acidity. The black precursor, which can easily absorb moisture in the atmosphere and change to a green color, was obtained after the gel had been desiccated in vacuum at 200°C for 2 h. The precursor was then ground and processed by heat treatment in an argon atmosphere (the purity > 99.999%) at different temperatures for different times.

2.2 Measurements

The product was characterized by X-ray powder diffraction carried out on a Rigaku D/max2550VB⁺ diffractometer with $\text{Cu K}\alpha$ radiation (40 kV, 300 mA, $\lambda=0.154\ 06\ \text{nm}$, $10^\circ \leq 2\theta \leq 80^\circ$). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed by TAS100 analyzer (12.8 mg, argon, and $10^\circ/\text{min}$). Morphology of the powder was studied by using a JSM-5600LV scanning electron microscopy. Fourier transform infrared (FTIR) spectroscopic measurements were made with a NEXUS470 instrument.

2.3 Electrochemical behaviors of VO_2 at 500°C

The electrochemical measurements of Li-B/LiCl-KCl/ VO_2 (obtained at 500°C and 2 h, and the mass ratio between $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{R})$ is about 3 : 7) pellet single cell were performed at 500°C and two voltage vs time curves were monitored by an x - y function recorder. The mass of positive pellet was 0.4 g (active materials 70%). The diameter of the electrodes was 17.5 mm and two pieces of molybdenum plates (thickness 1.0 mm) were used as the collector. The process has been described elsewhere in detail [21].

3 Results and discussion

Fig.1 shows the evolution of the X-ray diffraction patterns of the sample heated at various temperatures for 2 h. The precursor dried at 200°C in vacuum shows a broad hump around $2\theta=28^\circ\text{--}30^\circ$ without any discernible reflections, indicating the amorphous nature of the precursor. The sample heated at 300°C shows the development of reflections corresponding to $\text{VO}_2(\text{B})$, which also corresponds to a weak exothermic peak of DTA curve at 302°C . The reflections of $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{R})$ become more clearly defined on raising the temperature to 400°C , which indicates that the layered-structure metastable $\text{VO}_2(\text{B})$ has begun to transform irreversibly to the thermodynamically more stable tetragonal rutile $\text{VO}_2(\text{R})$ as the temperature increases. It is well known that at room temperature and

below, the stable form of VO_2 is a monoclinic distortion of the rutile structure, which undergoes a metal-insulator transition at 67°C that is a result of a structure change to the normal tetragonal rutile type. The reflections corresponding to the rutile phase become more prominent as the heating temperature increases to 500°C , while the intensity of $\text{VO}_2(\text{B})$ decreases. TSANG et al [13] have reported the transformation of nano-crystallite $\text{VO}_2(\text{B})$ to rutile-type $\text{VO}_2(\text{R})$ at 320°C , with a complete conversion around 500°C . So the $\text{VO}_2(\text{B})$ obtained by this method shows higher thermal stability and still appears at least up to 500°C , which is consistent with the results obtained by GUI et al [4] from the evolution of phases of needle-like nano-crystallites $\text{VO}_2\cdot\text{H}_2\text{O}$. The peaks become sharper with the temperature rising, indicating the degree of crystallinity of the product increases further.

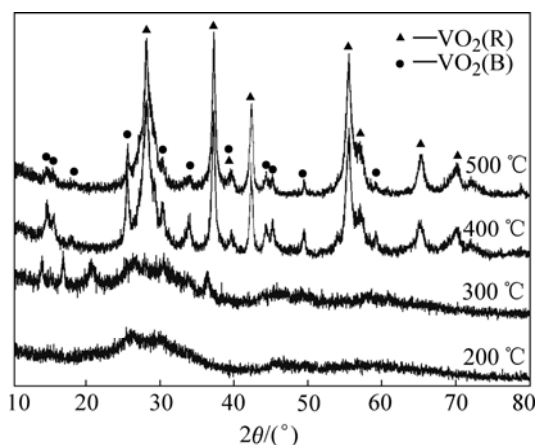


Fig.1 XRD patterns of vanadium dioxide powder obtained at different heating temperatures for 2 h

Fig.2 shows the influences of heating time at 400°C on the crystal structure. The resultant product is mainly amorphous because the heating time of 1 h is too short to become crystallization. The crystal reaction takes place as the heating time extends to 2 h, in which both $\text{VO}_2(\text{B})$ phase and $\text{VO}_2(\text{R})$ phase are obtained. Although the phases are the same as those of 2 h as further prolong time, the reflections and intensity of $\text{VO}_2(\text{B})$ and $\text{VO}_2(\text{R})$ become sharper and swell, respectively, indicating the crystal degree of product further increases as the heating time postpones.

To understand the evolution of phases upon thermal treatment, the precursor powder was subjected to thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in a flowing argon atmosphere (Fig.3). The DTA curve shows a strong, broad endothermic peak around 94°C , indicating the temperature of the loss and evaporation of free water absorbed by the precursor powder exposed to air before the examination, which corresponds to a mass loss of about 10% of the TGA. A

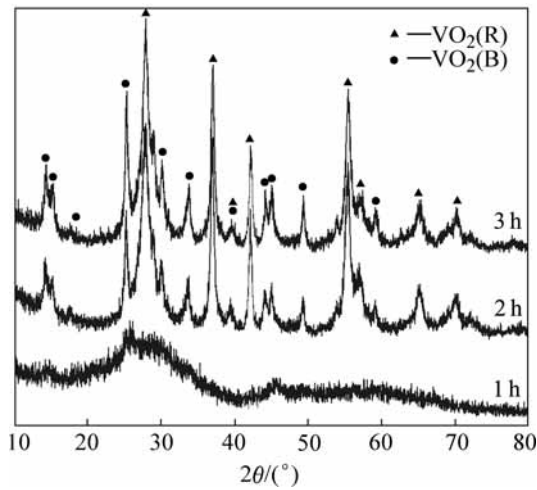


Fig.2 XRD patterns of vanadium dioxide powder obtained by different heating time at 400

mass of about 20% corresponds to the loss of absorbing and bound water between 100–350 . The two weak exothermic peaks around 244 and 302 may correspond to the transformation to VO₂(B) and VO₂(R), respectively. But, because no sharp exothermic peaks are

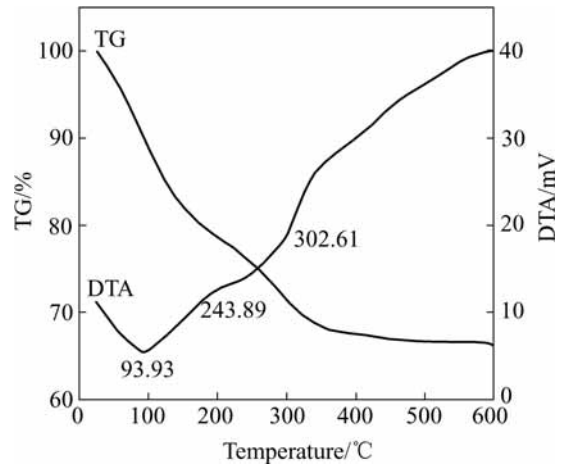


Fig.3 TG and DTA curves of precursor of VO₂

observed, these transformations may occur over a wide temperature range. These phase transformation temperature is consistent with the previous literatures[5, 15]. The mass shows no apparent change after 350 .

The FT-IR spectra of V₂O₅ and products obtained at different temperatures are compared in Fig.4. The characteristic lines of V₂O₅ are at 1 020 cm⁻¹, 826 cm⁻¹,

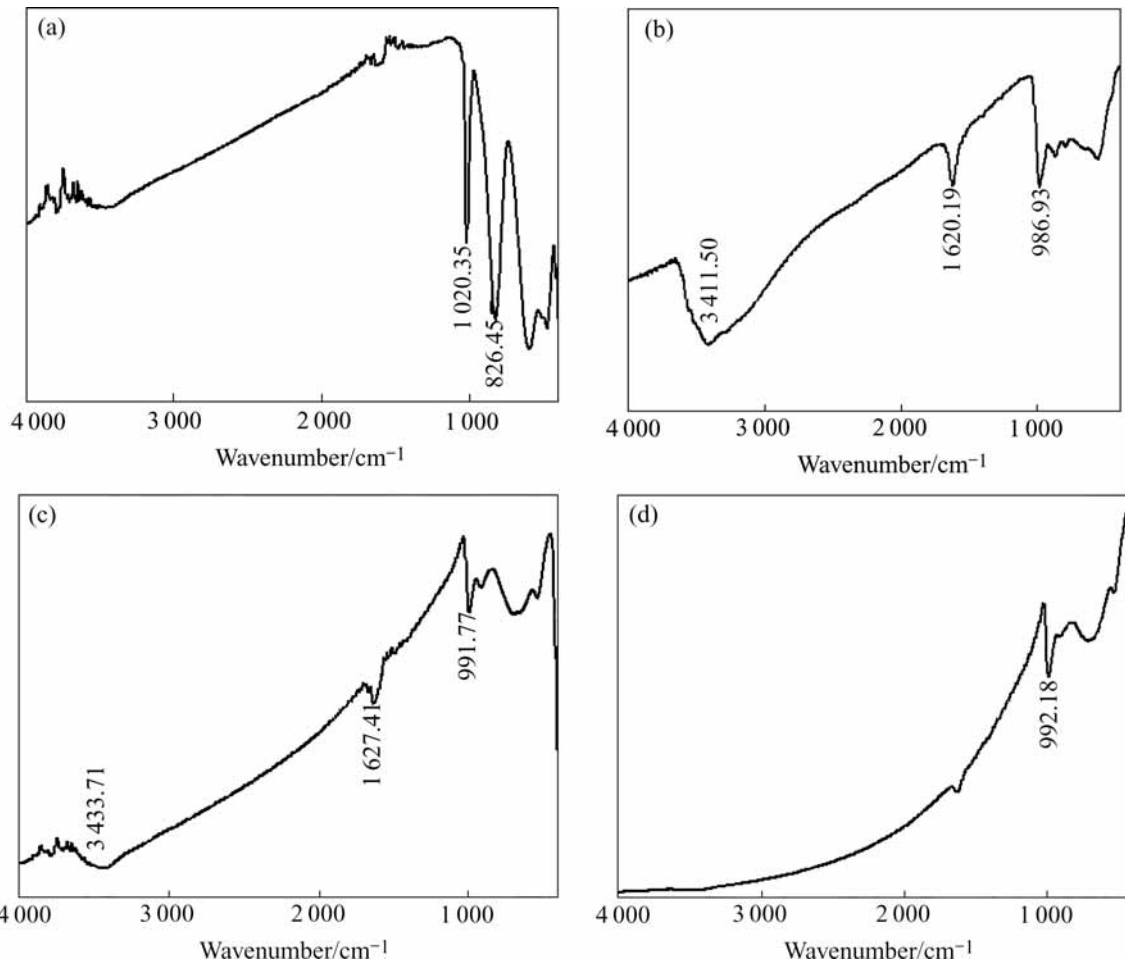


Fig.4 FTIR spectra of V₂O₅ and products obtained at different heating temperatures: (a) V₂O₅; (b) Precursor; (c) 400 , 2 h; (d) 500 , 2 h

597 cm^{-1} , 477 cm^{-1} , of which the line at 1 020 cm^{-1} originates from the shortest $\nu(\text{V}=\text{O})(0.158 \text{ nm})$ bond of V_2O_5 and disappears quickly in the course of phase transition[5]. The other lines result from the $\nu(\text{V}-\text{O}-\text{V})$ vibration. As the ionic radius of V () (0.060nm) is larger than that of V () (0.059nm), the V—O bond length increases with the consequent softening of the vibration. The comparison of the IR spectra of VO_2 with V_2O_5 shows a gradual shift to lower wave numbers and a varying intensity as the vanadium ionic radius becomes larger. This behavior may be related to the increased weakness of the surface $\text{V}=\text{O}$ bonds and to the decreased oxidation state at the surface[22]. The intense line at 826 cm^{-1} of V_2O_5 is not observed in the spectra of VO_2 . The line at 1 620 cm^{-1} of precursor and resultant product at 400 for 2 h stems from the $\delta(\text{O}-\text{H})$ bond, which is in accordance with a slight loss of mass of the TGA curve above 400 and disappears with increasing temperature and prolonging time, indicating the wet of precursor has been completely decomposed.

Fig.5 shows the SEM photographs of the precursor and sample obtained at 500 for 2 h. The precursor is bulky. The particle size of precursor is far larger than 5 μm and consists of small and compact reuniting powder granules. This indicates that the sintering does not happen at 200 yet. The smaller grains in the sample obtained at 500 for 2 h loosely combine and the spacing between the grains is larger.

The discharge plots of $\text{VO}_2(\text{B})/\text{VO}_2(\text{R})$ mixed phase material at different current densities at 500 are shown in Fig.6. The open-circle voltage of the single cell

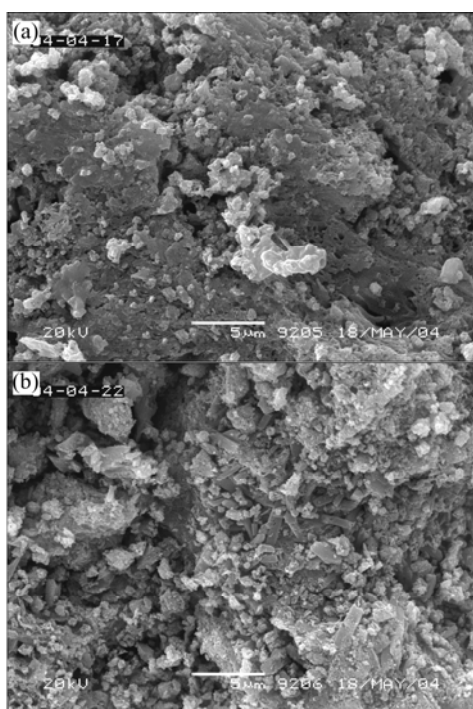


Fig.5 SEM photographs of precursor(a) and sample obtained at 500 for 2 h(b)

of $\text{Li-B}/\text{LiCl-KCl}/\text{VO}_2$ is 2.6 V. During the discharge process the transient voltage pinnacle does not exist in the beginning, which is very important to a thermal battery. About 9.1 min and 5.5 min can be achieved at the cut-off voltage of 1.4 V for the current density of 100 mA/cm^2 and 200 mA/cm^2 , respectively. Then the specific capacities are 449 $\text{A}\cdot\text{s}/\text{g}$, 539 $\text{A}\cdot\text{s}/\text{g}$, respectively. When the current density is 100 mA/cm^2 the initial work-voltage is 2.52 V, and then the voltage begins to decrease slowly because of the influences of the ohm resistance and polarization.

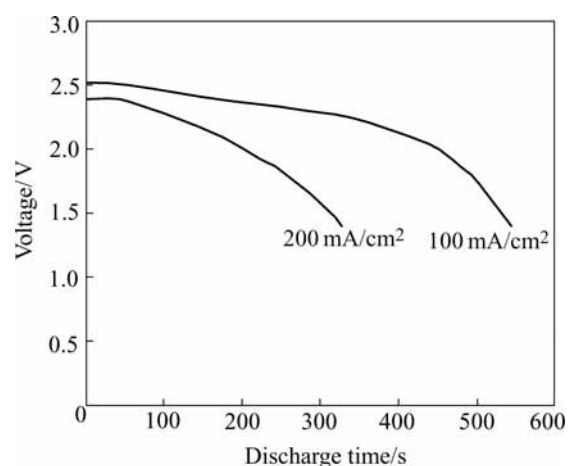


Fig.6 Electrochemical characteristics of $\text{VO}_2(\text{B})/\text{VO}_2(\text{R})$ composite

The structure of $\text{VO}_2(\text{B})/\text{VO}_2(\text{R})$ mixed phase material after discharge is shown in Fig.7. The following reactions take place as the cell makes up of a $\text{VO}_2(\text{B})/\text{VO}_2(\text{R})$ cathode and a Li-B alloy anode:

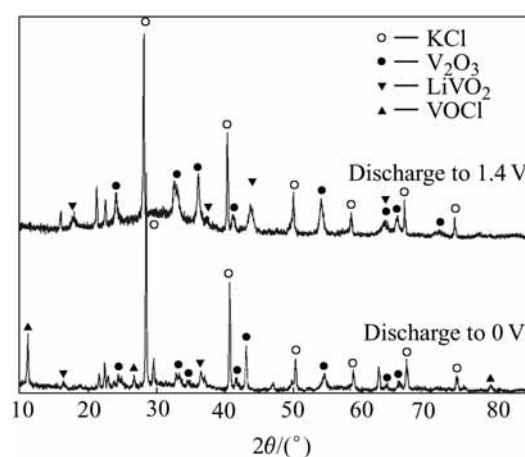


Fig.7 XRD patterns of $\text{VO}_2(\text{B})/\text{VO}_2(\text{R})$ composite after discharge



During the discharge process Li^+ transfers from the negative to the positive via electrolyte and the redox

reactions happen. V^{4+} of the positive materials has been deoxidized to V^{3+} . The diffractions of KCl result from the molten salt of KCl-LiCl added into the positive materials.

4 Conclusions

Formaldehyde solution has been used as a reductant to obtain VO_2 powder from vanadium pentoxide. $VO_2(B)$ obtained by the soft-chemical method shows higher thermal stability even at 500 °C for 2 h. The open-circle voltage of the single cell of Li-B/LiCl-KCl/ VO_2 is 2.6 V. During the discharge process the voltage is very stable and V^{4+} of the cathode materials is deoxidized to V^{3+} . When the current density is 100 mA/cm² the initial work-voltage is 2.52 V. The specific capacities of 100 mA/cm² and 200 mA/cm² at cut-off voltage of 1.4 V are 449 A·s/g and 539 A·s/g, respectively.

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References

- [1] FAUL I, GOLDBERGER A J. Electrochemical cell structures and materials therefore [P]. USA 4596 752, 1986-06-24.
- [2] CLARK A J, MCKIRDY I, RITCHIE A G. Lithiated vanadium oxides (LVO) and vanadium dioxide (VO_2) as thermal battery cathode material [A]. Attewell A, Keily T. Power Sources 15. Research and Development in Non-Mechanical Electrical Power Sources. The 19th International Power Sources Symposium [C]. Crowborough, UK: Int Power Sources Symposium Committee, 1995. 488.
- [3] GIBBARD H F. High temperature, high pulse power lithium batteries [J]. J Power Sources, 1989, 26(1-2): 81-91.
- [4] GUI Z, FAN R, CHEN X H, WU T C. A new metastable phase of needle-like nanocrystalline $VO_2 \cdot H_2O$ and phase transformation [J]. J Solid State Chemistry, 2001, 157(2): 250-254.
- [5] FRÉDÉRIC G, JEAN-CHRISTOPHE V, JEAN-RAYMOND G. Nanocrystalline vanadium dioxide: synthesis and mid-infrared properties [J]. Optical Materials, 2000, 15(2): 111-114.
- [6] KIMIZUKA N, ISAHII M, KAWADA M, KIMIZUKA N, ISHII M, KAWADA I, SAEKI M, NAKAHIRA M. Behaviour of vanadium dioxide single crystals synthesized under the various oxygen partial pressures at 1 500 K [J]. J Solid State Chemistry, 1974, 9(1): 69-77.
- [7] OPPERMAN H, REICHEL T, GERLACH U, WOLF E, BRUCKNER W, MOLDENHAUER W, WICH I. The range of homogeneity of VO_2 and the influence of the composition on the physical properties(1): The preparation of defined VO_2 and the determination of its phase boundaries [J]. Physica Status Solidi (A) Applied Research, 1975, 28(2): 439-446.
- [8] BRUECKNER W, MOLDENHAUER W, WICH H, WOLF E, OPPERMAN H, GERLACH U, REICHEL T. Range of homogeneity of VO_2 and the influence of the composition on the physical properties [J]. Physica Status Solidi (A) Applied Research, 1975, 29(1): 63-70.
- [9] KUCHARCZYK D, NIKLEWSKI T. Accurate X-ray determination of the lattice parameters and the thermal expansion coefficients of VO_2 near the transition temperature [J]. Journal of Applied Crystallography, 1979, 12(4): 370-373.
- [10] STANLEY A L, EDWARD A T. Synthesis of vanadium oxide powders by evaporative decomposition of solutions [J]. J Am Ceram Soc, 1995, 78(1): 104-108.
- [11] ZHENG Chen-mou, ZHANG Jie-li, LUO Guo-bin, YE Jian-qing, WU Ming-mei. Preparation of vanadium dioxide powders by thermolysis of a precursor at low temperature [J]. J Materials Science, 2000, 35(13): 3425-3429.
- [12] ZHENG Chen-mou, ZHANG Xin-min, ZHANG Jian-hui, LIAO Kai-rong. Preparation and characterization of VO_2 nanopowders [J]. J Solid State Chemistry, 2001, 156(2): 274-280.
- [13] TSANG C, MANTHIRAM A. Synthesis of nanocrystalline VO_2 and its electrochemical behavior in lithium batteries [J]. J Electrochem Soc, 1997, 144(2): 520-524.
- [14] VALMALETTE J C, GAVARRI J R. High efficiency thermochromic $VO_2(R)$ resulting from the irreversible transformation of $VO_2(B)$ [J]. Materials Science and Engineering B, 1998, 54(3): 168-173.
- [15] KANNAN A M, MANTHIRAM A. Synthesis and electrochemical evaluation of high capacity nanostructured VO_2 cathodes [J]. Solid State Ionics, 2003, 159(3-4): 265-271.
- [16] GUI Z, FAN R, MO W, CHEN X, YANG L, ZHANG S, HU Y, WANG Z, FAN W. Precursor morphology controlled formation of rutile VO_2 nanorods and their self-assembled structure [J]. Chem Mater, 2002, 14(12): 5053-5056.
- [17] DOUGLAS H, JON Z, CHRISTOPHER J W, LINDA M M, MICHAEL M J T, ROBERT C H. A new polymorph of VO_2 prepared by soft chemical methods [J]. J Solid State Chemistry, 1998, 138(1): 178-182.
- [18] LU Song-wei, HOU Li-song, GAN Fu-xi. Preparation and optical properties of phase-change VO_2 thin films [J]. J Materials Science, 1993, 28: 2169-2177.
- [19] MANIVANNAN V, GOODENOUGH J B. Low-temperature synthesis of rutile VO_2 in aqueous solution using $NH_2OH \cdot HCl$ as reducing agent [J]. Materials Research Bulletin, 1998, 33(9): 1353-1357.
- [20] TOSHIYUKI O, YASUHIRO I, KENKYU K R. Synthesis of SnO_2 , VO_2 and V_2O_3 fine particles by laser-insured vapor-phase reaction [J]. J Photopolymer Science and Technology, 1997, 10(2): 211-220.
- [21] LIU Zhi-jian, DUAN Wei, LI Zhi-you, HUANG Ying-hua, QU Xuan-hui, HUANG Bai-yun. Effects of cathode materials on discharge characteristics of Li-B alloy/ $FeSe_2$ thermal battery [J]. Trans Nonferrous Met Soc China, 1999, 9(3): 530-534.
- [22] BOTTO I L, VASSALLO M B, BARAN E J, MINELLI G. IR spectra of VO_2 and V_2O_3 [J]. Materials Chemistry and Physics, 1997, 50(3): 267-270.

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