

Effect of citric acid dosage and sintered temperature on the composition, morphology and electrochemical properties of lithium vanadium oxide prepared by a sol–gel method

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Abstract. A lithium vanadium oxide cathode material was synthesized via sol-gel processing using citric acid as the chelating agent. Different dosage of citric acid and sintered temperature were introduced to investigate their effects on the products composition, morphology and electrochemical properties. The results showed that the V_2O_3 yield was inhibited and the crystallization of grain was accelerated with the increasing dosage of citric acid. Furthermore, V_2O_3 was oxidized to LiV_3O_8 and $Li_{0.3}V_2O_5$ with the increase of sintered temperature.

Keywords: sol-gel method, lithium vanadium oxide, thermal battery, citric acid, electrochemical performance

1. Introduction

The vanadium-based oxides have become one of the most attractive candidates in the field of lithium batteries in the past several decades. Among the vanadium-based oxides, LiV_3O_8 has been extensively investigated as potential and promising substituted cathode materials due to its attractive electrochemical properties such as high specific discharge capacity, good rate capacity, long cycle life, good safety, low cost and facile preparation [1,2]. LiV_3O_8 has a layered structure composed of VO_6 octahedra and VO_5 distorted trigonal bipyramid units to form stable V_3O_8 sub-lattices [3], accommodating additional three lithium-ions per formula unit without any structural change in the tetrahedral sites [4].

It is generally known that the synthesized routes and processing factors have significant influences on the crystal structure and electrochemical performances of LiV_3O_8 [5]. Various methods have been developed to prepare the LiV_3O_8 materials such as the sol–gel method, solid-state reaction, combustion synthesis, hydrothermal reaction and flame spray pyrolysis method [6]. Among these methods, sol–gel process is supposed to be an excellent method for the synthesis of cathode active materials due to its unique advantages in the synthesis of oxide materials. The raw materials can be mixed at the molecular level via sol–gel methods so that the products possess homogeneous composition and higher capacity [7]. Many works have been done to fabricate LiV_3O_8 crystallites by using sol–gel methods in which citric acid was mostly used as chelating agent [6-9].

The vanadium-based oxides also have been used for thermal battery cathode in the past years [10-11]. In the present work, we utilized a sol–gel process to synthesize the LiV_3O_8 cathode material



used in thermal battery which using citric acid as chelating agents. The influences of citric acid dosage and sintered temperature on the phase composition, morphology and electrochemical properties of the products were particularly investigated.

2. Experimental

Analytical pure $\text{LiOH}\cdot\text{H}_2\text{O}$, V_2O_5 and citric acid ($\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$) were used as raw materials without any purification. Stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ and V_2O_5 (Li: V=1.05: 1.5, molar ratio) were mixed in deionized water. Then the saturation solution of citric acid was slowly dripped into the reaction system with continuous magnetic stirring. The molar ratio of total metal ions to citric acid was 1:1, 1:1.5, 1:2, respectively. After stirred for 1 h and dried the sol at 80°C in air, the gel was obtained. The three piece of obtained gel was dried in a vacuum oven at 120°C for 6 h to form the bulky honeycombed precursor. Subsequently each precursor was grinded through 100 mesh sieve and was divided into three portions. One portion sieved powder of each sample was handled as one group and heated at 400°C , 450°C and 500°C for 12 h in a muffle furnace respectively. The samples obtained were designated LVO-1-400, LVO-1-450, LVO-1-500, LVO-1.5-400, LVO-1.5-450, LVO-1.5-500, LVO-2-400, LVO-2-450 and LVO-2-500, respectively.

The crystal structures of the samples were determined using Oxford Instruments Company type 7718 X-ray spectroscopy in the range of $10^\circ\sim 80^\circ$. The morphology of the samples was observed with a Tescan VEGA 2 XMU SEM.

The cathode powder was fabricated by a mixture of 80 wt% active materials and 20wt% eutectic salt which is made up of LiCl and KCl (45:55, wt %). Every cell was assembled from a pelletized cathode material having a diameter of 20mm, Li-Si anode, eutectic salt and MgO (65:35, wt %) separator, nickel collector. The assemblage and measurement were conducted under a dry air atmosphere (1% humidity). The cells were introduced into a home-built instrument set to the test temperature (500°C). While testing, the peak value of open circuit potential (OCP) and elevated temperatures discharge measurements were recorded on CorrTest CS 350 electrochemical workstation.

3. Results and discussion

The composition and crystallinity of the materials synthesized using a sol-gel method followed by different heat treatments (400 , 450 or 500°C) were determined using XRD analysis. As shown in figure 1, the powder shows diffractions peaks at 2θ of 13.9° and 28.5° indicating the gradual crystallization of LiV_3O_8 (JCPDS No. 72-1193) phase. The presence of the V_2O_3 (JCPDS No. 34-0187) and $\text{Li}_{0.3}\text{V}_2\text{O}_5$ (JCPDS No. 18-0755) was also detected in the XRD pattern. The impurity of V_2O_3 has rarely been reported in previous literature. From figure 1, it can be found that the diffraction peaks of V_2O_3 decreased with increasing dosage of citric acid. The dosage of citric acid has a great influence on the decomposition of the precursor. The more citric acid used, the less V_2O_3 deoxidized. In addition, the increased citric acid obviously accelerates crystallization of LiV_3O_8 and $\text{Li}_{0.3}\text{V}_2\text{O}_5$ grain. The effect of sintered temperature on the composition of the sample was analyzed at the same dosage of citric acid. The V_2O_3 produced was decreased gradually even disappeared with the increasing sintered temperature may because the V_2O_3 was oxidized to LiV_3O_8 and $\text{Li}_{0.3}\text{V}_2\text{O}_5$. Moreover, the crystallinity of LiV_3O_8 and $\text{Li}_{0.3}\text{V}_2\text{O}_5$ enhances with increasing sintered temperature.

The SEM images of as-synthesized LiV_3O_8 powders are shown in figure 2. It can be seen that the citric acid dosage and sintered temperature has a visible influence on the morphology of the samples. The SEM images reveal the process of the grain emerged and grew with the increasing citric acid at the same sintered temperature. Besides, the citric acid acts as an organic fuel during the sintering process [8] that is the reason why the increasing citric acid accelerates crystallization of grain. Review the images from vertical orientation; it reveals that the sintering temperature has obvious effect on the morphology of the as-synthesized material. The crystallites grain just appeared at 400°C , and then grew with the increasing temperature. In these samples, LVO-1-500, LVO-1.5-500 and LVO-2-450 reveal the rod-shaped crystallites with regular geometric shape and even size distribution. In addition,

the volatilized citric acid also causes much interspace in sintering process so that the samples are propitious to infiltration of melting eutectic salt, which may lead to good electrochemical performance at the same dosage of citric acid.

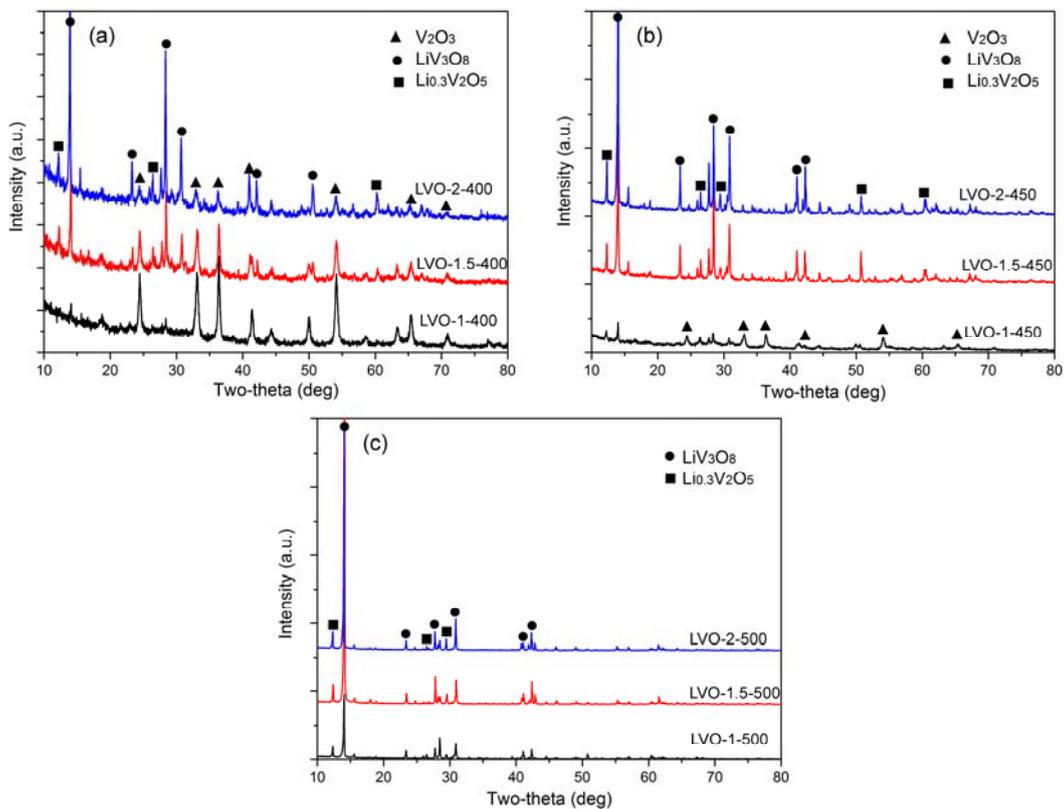
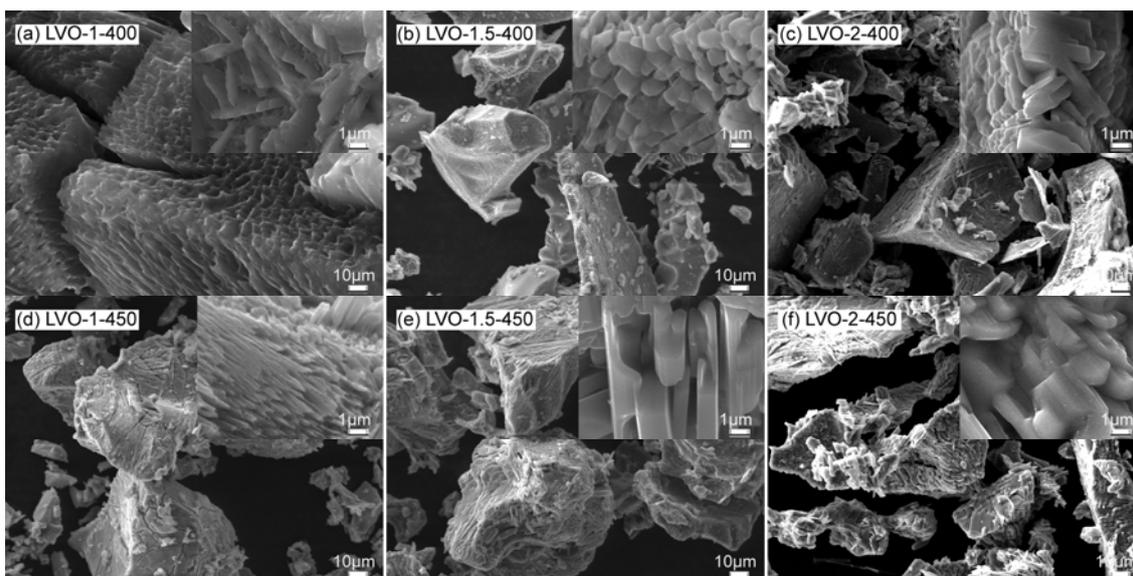


Figure 1. XRD pattern of specimen sintered at (a) 400°C; (b) 450°C; (c) 500°C.



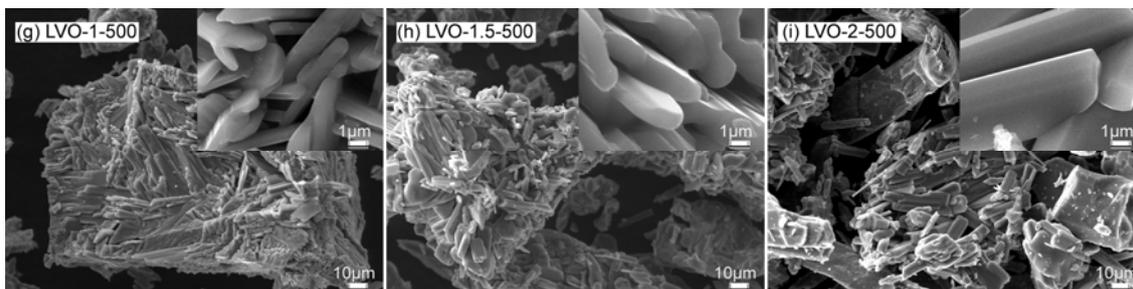


Figure 2. SEM images of prepared specimen (a) LVO-1-400, (b) LVO-1.5-400, (c) LVO-2-400, (d) LVO-1-450, (e) LVO-1.5-450, (f) LVO-2-450, (g) LVO-1-500, (h) LVO-1.5-500, (i) LVO-2-500.

The peak value of open circuit potential (OCP) is shown in figure 3(a). Combining with XRD analysis, we find that the peak value is seriously affected by the composition of material. The presence of $\text{Li}_{0.3}\text{V}_2\text{O}_5$ and V_2O_3 decrease the OCP of the cathode materials. When the dosage of citric acid is equal, the V_2O_3 is oxidized to LiV_3O_8 and $\text{Li}_{0.3}\text{V}_2\text{O}_5$ with the increasing temperature, so the peak value of OCP increase. At the same temperature, the V_2O_3 yield was inhibited and the content of LiV_3O_8 and $\text{Li}_{0.3}\text{V}_2\text{O}_5$ increase with the increasing dosage of citric acid. It has proved that the percentage of LiV_3O_8 is augmented which is according with the XRD analysis.

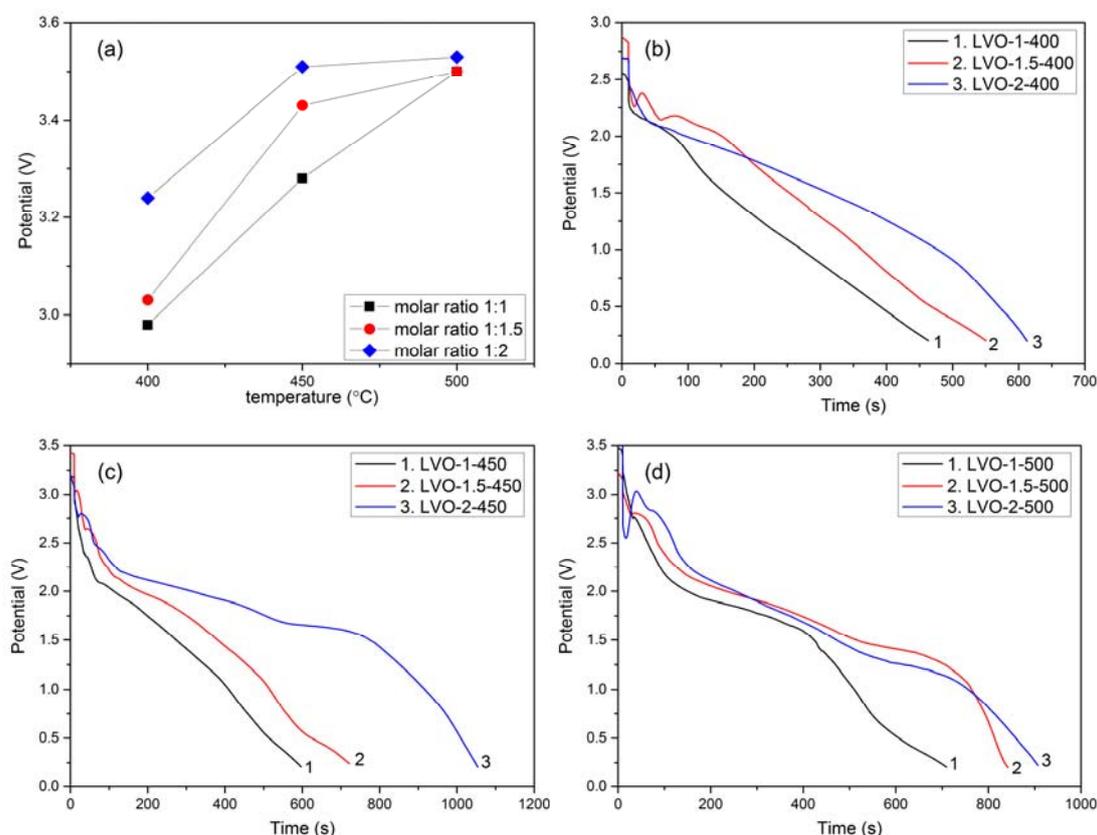


Figure 3. (a) The peak value of OCP, and the galvanostatic discharge curve of samples sintered at (b) 400°C; (c) 450°C; (d) 500°C.

The voltage-time curves of the samples at a current density of 100 mA/cm^2 are illustrated in figure 3(b), (c), (d) (the terminated voltage is 0.2 V). The specific capacity of the electrode material can be calculated according to the current density and the discharge time. Analyzing the discharge curves and specific capacity, we find that the two specimens, LVO-2-450 and LVO-1.5-500, have stable discharge platform which can be used as cathode material of thermal battery. They have a main

discharge plateaus in the potential range of 1.65–2.2 V (maintaining for 500–700 s), and separately delivers a high initial discharge capacity of 312.2 mAh/g and 241.5 mAh/g at a current density of 100 mA/cm². Compared with the traditional cathode of FeS₂ material, the LiV₃O₈ material exhibits higher discharge potential and shorter working time, which can be used as promising candidates for both medium-high voltage and relatively low currents in thermal batteries applications.

4. Conclusion

The lithium vanadium oxide powder were synthesized via sol–gel process with citric acid as chelating agent. The results show that the samples exhibits better electrochemical properties with increasing dosage of citric acid. The increasing citric acid inhibits the produce of V₂O₃ and accelerates the emergence and growth of LiV₃O₈ and Li_{0.3}V₂O₅ grains. While the molar ratio of total metal ions to citric acid is 1:2, the as-synthesized samples exhibits better electrochemical performance.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51302312, 51502341).

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