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Insight into thermal behavior mechanism of Li₃VO₄ anode for safety design of Li-Ion batteries

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ABSTRACT

With the widespread implementation of lithium-ion batteries, their safety properties have attracted intensive attention. Among various anode materials, Li₃VO₄ is emerging as one of the most promising anode candidates for Li-ion batteries due to its appropriate lithiation voltage and superb kinetic properties. However, there are few researches on the thermal stability of Li₃VO₄ anodes. In fact, the exothermal reactions between electrode materials and electrolytes at elevated temperature may trigger serious thermal runaway of batteries, which is a critical factor affecting battery safe performance. For the first time, the thermal reaction mechanism of Li₃VO₄ anode is systematically studied by the differential scanning calorimetry method. The whole exothermic process between Li₃VO₄ and electrolyte and decomposition of passivation film taking place below 225 °C, while the reduction of electrolyte and the thermal reaction of binder occur only when T > 225 °C. The results reveal that the thermal stability of Li₃VO₄ anodes is highly relevant to the depth of lithiation, cycling numbers and binder type, which provides important guidance for the safety design of Li₃VO₄ anode for lithium ion batteries in the future commercialization.

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1. Introduction

In recent years, due to the harm of non-renewable energy such as oil and fossil to the natural environment, developing green and sustainable clean energy has become a major challenge for researchers all over the world [1]. Lithium-ion batteries (LIBs), as a new generation of chemical energy storage technology, have replaced nickel-cadmium/nickel-hydride batteries, and become the preferential choice for energy storage devises [2–4]. Therefore, the safety feature of LIBs is critically important and closely related to the future direction of consumer electronics and electrical vehicles [5–7]. Anode is an indispensable component of LIBs and greatly affect the safe performance of battery. Generally, the anode

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materials for LIBs are divided into three types by electrochemical reaction mechanisms: the intercalation/deintercalation mechanism, the conversion reaction mechanism, and the alloying mechanism [8,9]. The anode materials based on conversion and alloying mechanisms [10] are currently not widely commercialized due to some intrinsic obstacles such as low conductivity and huge volume expansion during cycling. Nowadays, there are mainly two types of anode materials (graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) that have been commercialized. Both are all based on the intercalation/deintercalation mechanism, affording the prominent advantages of minimal structure change during cycling and good cycling performance [11,12].

The state-of-the-art anode material is graphite with the theoretical specific capacity of ~372 mAh g⁻¹, and the relatively small volume change (~7.6%) after Li⁺ insertion ensures good cycling performance [13]. However, owing to its low lithiation potential (<0.2 V versus Li+/Li), lithium metal may deposit on the surface of the electrode and forms lithium dendrites especially during highrate cycling, and cause severe safety hazards. On the other hand,







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Li₄Ti₅O₁₂ is a well-known "zero volume effect" anode material, and its high lithiation potential (~1.55 V versus Li⁺/Li) prevents the formation of Li dendrites essentially. However, the low theoretical specific capacity (~175 mAh g⁻¹) and excessively high potential of Li₄Ti₅O₁₂ may sacrifice the energy density too much when it is matched with the cathodes [14]. In addition, the Li_{3.08}Cr_{0.02}-Si_{0.09}V_{0.9}O₄, Zn₂Nb₃₄O₈₇ and Al_{0.5}Nb_{24.5}O₆₂ were also popular anode materials in the Li-ion batteries [15–17].

Recently, the emerging Li₃VO₄ (denoted as LVO) [18], an anode material also based on the intercalation/deintercalation mechanism has received widespread concern. LVO possesses an appropriate lithiation potential (0.5–1.0 V versus Li⁺/Li) between graphite and Li₄Ti₅O₁₂, and a theoretical specific capacity (592 mAh g^{-1} , corresponding to x = 3 in Li_{3+x}VO₄) higher than that of graphite and Li₄Ti₅O₁₂, making it a promising high-safety LIB anode [14,19]. Based on this, the researchers have been made a lot of modifications to the LVO anode, such as carbon hybridization [20], structural design [21], etc, to improve its electrochemical performance. Compared to the ionic conductivity, the electronic conductivity of LVO is poor, which would arouse large over potential between the discharge/charge processes and deteriorate the rate capacity. The carbon coating strategy have been implemented to improve the electronic conductivity as well as the rate capability of LVO, as shown in Table S1. Through the efforts of many researchers, the high-rate performance and cycling stability of LVO has been enhanced remarkably, and may be developed for commercial products in the future [22,23]. However, for high-safety battery materials in practical applications, the thermal stability is also critical [24–26]. The thermal safety issues and the thermal abuse behavior of the LVO anode also affects its future development direction [27,28]. It has been reported that the thermal runaway and spontaneous combustion of most batteries are due to the selfexothermic reaction between the electrode materials and the electrolyte [29,30]. This short-term self-exotherm is caused by many side reactions, such as active materials compositions, binder, electrolyte, passivation film and some other factors such as degree of lithium insertion and number of cycles. Similarly, for the LVO anode, although its relatively high lithiation potential can effectively prevent lithium dendrite growth, there may be still some thermal safety problems caused by the reaction of some side reactions [31,32]. Then, what is the thermal reaction mechanism and how is the thermal stability of the LVO/Li battery system during cycling?

For the first time in this paper, the thermal stability and reactivity between the active materials, the binder and the electrolyte in the LVO/Li battery system are investigated by the differential scanning calorimetry (DSC) method. And the degree of intercalation, number of cycles and nature of different binders are also explored. This research has a guiding significance for the safety design in the future commercial development of the LVO material.

2. Experimental

2.1. Synthesis

The LVO materials were prepared by a typical simple solid-state method [18]. 0.624 g of V_2O_5 , 0.76 g of Li_2CO_3 and 0.6 g of glucose were weighed and uniformly mixed by using a mortar. The mixed sample was placed in a tube furnace and pre-calcined at 350 °C for 5 h under a hydrogen/argon (10:90 v/v) atmosphere, and then taken out and fully ground, calcined at 750 °C for 8 h in the same atmosphere at a heating rate of 5 °C min⁻¹. The LVO sample was finally obtained. And the pure LVO were synthesized without glucose under the same preparation process.

2.2. Materials characterization

X-ray diffraction (XRD) data was recorded with CuKa radiation operated at 40 kV on a Rigaku miniflex 600 X-ray diffractometer. A scanning electron microscopy (SEM, S-4800, Hitachi) and Transmission Electron Microscope (TEM, Tecnai F30) were used to observe the morphology and structure of the sample. The simultaneous thermal analysis (449 F3, Netzsch) were used to test the DSC performance of the anode materials.

2.3. Electrochemical measurement

For preparation, the LVO sample, acetylene black (AB), and poly(vinylidene fluoride) (PVDF) or polyvinylidene fluoridehexafluoropropylene (PVDF-HFP) were mixed in N-methyl pyrrolidone (NMP) with weight ratio of 8:1:1, and stirred to form an electrode slurry. Subsequently, the slurry was uniformly coated on a Cu foil current collector, then placed in a vacuum oven at 80 °C, and dried overnight to remove solvent and moisture. Then, the dried sheet was made into a circular electrode with a diameter of 12 mm, and the active materials loading mass amount per electrode was about 3 mg/cm². The prepared working electrode was tested for electrochemical performance using a CR2016 type coin cell with lithium metal as the counter electrode and the reference electrode. Among them, the compositions of the electrolyte were 1 M of $LiPF_6$ with the ethylene carbonate (EC) and diethyl carbonate (DEC) (v/ v = 1: 1). Celgard 2400 was used as a separator. The preparation process of graphite system cell was the same as above, in which the active material was replaced by the graphite (MGS-2). The entire process of the cell preparation was carried out in an Ar filled atmosphere glove box. And the fabricated batteries were tested at 25 °C on Neware BTS cell testers at a current density of 0.02 and 0.2 Ag^{-1} . The test process was in a constant current (CC) mode over a voltage range of 3.0-0.01 V.

To examine the full-cell properties, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) was used as the cathode material. For preparation, NCM523, AB, and PVDF were mixed in NMP with a weight ratio of 8:1:1. After stirring overnight, the slurry was uniformly spread on aluminum foil, and dried at 80 °C overnight. The test charging and discharging cut-off voltages were controlled to 4.2 V and 1.5 V, respectively.

2.4. DSC characterization

The thermal behaviors and stability of the LVO electrode were tested by DSC measurement. The heating range is from 35 °C to 400 °C with the heating rate of 5 K min⁻¹ under an argon flow. In order to isolate water and oxygen, the cycled cell was disassembled in the argon-filled glove box. After natural drying at room temperature in the glove box, the sample was carefully scraped off with a ceramic knife. Finally, the scraped materials and the electrolyte with a ratio of 1 mg: 1 μ L were placed in a sealed steel crucible for DSC testing.

3. Results and discussion

In this study, we didn't choose pristine LVO without carbon coating as our research object owing to its poor cycling performance resulting from the low electronic conductivity (Fig. S1), which only keeps the capacity of 102 mAh g^{-1} during 100 cycles with current density of 0.2 A g^{-1} . In order to achieve the reversible capacity of LVO approaching its theoretical capacity, we synthesized the LVO/ amorphous carbon composite by a conventional solid phase method as the study subject. And the detailed synthesis process is demonstrated in the experimental part. The carbon

content of LVO is approximately 6.2% (Fig. S2). Moreover, to ensure the universality of the analysis results about LVO, no special morphology design has been carried out for the composite. Fig. 1a shows the XRD pattern of the prepared LVO. The diffraction peaks are in full agreement with the electrochemically active orthorhombic LVO (JCPDS No. 38-1247), indicating the successful synthesis of the LVO [18]. The Raman spectrum is also showed in the Fig. 1b, the vibration of the VO₄ tetrahedron is attributed to two main peaks at about 789.3 cm⁻¹ and 818.6 cm⁻¹. Other weak peaks in the range of 200–600 cm⁻¹ and 880–980 cm⁻¹ are also in good agreement with previously reported LVO [18,21]. In addition, the two characteristic bands near 1344.7 cm⁻¹ and 1592.4 cm⁻¹ are assigned to the D and G bands, respectively, originating from the carbonization of glucose after annealing.

The morphology of the product obtained by the solid phase method is checked by SEM and TEM (Fig. 2). According to the SEM and TEM images (Fig. 2a–c), it can be found that the obtained product exhibits a random block morphology. The HRTEM image (Fig. 2d) shows the existence of a carbon layer on the outer surface of the material, and in Fig. 2e, clear lattice fringes with a spacing of 0.41 nm corresponding to the orthorhombic LVO (110) plane can be distinguished [19]. Mapping analysis (Fig. 2f–i) of C, V and O elements indicates that LVO particles are uniformly distributed in the carbon matrix (Fig. S3). Moreover, the overlay image of V and C element mapping can indicate the carbon coating is very uniform (Fig. S4). Next, the as-prepared LVO is assembled into a half- cell as an anode material for LIBs, and the thermal reaction mechanisms are further investigated by DSC measurement.

Fig. 3a shows the typical galvanostatic charge-discharge profiles of the LVO at 0.2 A g^{-1} from 3.0–0.01 V. The initial discharge capacity of LVO is 533 mAh g^{-1} and the initial coulombic efficiency (ICE) is 64.2%. LVO is intercalated by Li⁺ mainly between 0.5 and 1.5 V, the electrochemical reaction equation is concluded as follow:

$$\text{Li}_3\text{VO}_4 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_{3+x}\text{VO}_4 \ (0 \le x \le 3)$$

$$[1]$$

The cycle performance of the LVO during the 100 cycles is also investigated (Fig. 3b). The reversible capacity of LVO still maintained at 412 mAh g^{-1} after 100 cycles, and there is almost no fading in the overall capacity. Moreover, the LVO material can keep stable coulombic efficiency of 99.7%, which demonstrate the material stability. In addition, the as-fabricated LVO//NCM523 full battery can retain a reversible capacity of 325 mAh g-1 after 30 cycles at 1 C, which demonstrates the feasibility of LVO material to be use as practical lithium-ion battery anode (Fig. S5). This also shows that the LVO material has a great cycle stability as a lithiumion cell anode, and is an excellent potential for future commercial anode materials.

Then, for such a high-safety cell material, in the future development of commercialization, it is crucial to identify the side reaction between the LVO electrode and the electrolyte. Fig. 4 shows the DSC curve of the fully lithiated LVO anode containing electrolyte, and the anode is pre-activated between 0.01 and 3.0 V (vs. $Li^+/$ Li) for 5 cycles. Five main exothermic peaks can be observed and denoted as I. II. III. IV. and V from low to high temperature. respectively. According to the analysis of the compositions of the prepared electrode, the main components that may participate in the self-exothermic reaction in the fully lithiated electrode are: the active materials, the passivation layer (contains the solid electrolyte interface (SEI) film and side reaction products), conductive agent (AB) and binder (PVDF). And the composition of the electrolyte mainly contains lithium salt (LiPF₆) and solvent (EC and DEC). It is reported that the self-exothermic reactions that may occur in electrode materials in low temperature areas (before 225 °C) are: decomposition of SEI films, reactions of active materials and electrolytes, and side reactions such as reduction of electrolytes and self-exothermic reaction of binders are more likely to occur in a higher temperature area (after 225 °C) [29,30]. Moreover, the DSC peak shape of bare LVO material is similar to that of carbon coated LVO. However, the heat amount seems to be different due to the diverse discharging capacities (Fig. S6). The coexistence of solid and liquid components in systems leads to complex interactions and synergies, resulting in complex thermal runaway behavior of LIBs. Therefore, a series of experiments are designed to accurately identify the exothermic peaks obtained from the DSC test results based on the component analysis of possible side reactions.

The DSC tests are performed by reducing the corresponding influencing factors, respectively, to analyze the contributions of each component to the observed thermal peaks position. For the sake of analysis, the entire thermal reaction process is divided into two parts: the first part of the thermal reaction occurs during 35–225 °C, labeled as the low-temperature reaction region, and the other part is the thermal reaction zone during 225–400 °C, labeled as the high-temperature reaction region. Firstly, the lowtemperature region is analyzed. The two exothermic reactions (peak I and II) occur almost simultaneously, and the onset reaction temperature are about 100 °C. The maximum values of the two peaks (the value of max heat flow) correspond to the temperatures of 136 °C and 155 °C, respectively. To determine the reaction mechanism of these two peaks, the fully lithiated LVO anode in the same conditions is thoroughly cleaned by (dimethyl carbonate) DMC in the glove box under Ar atmosphere, and then naturally dried to remove the excess solvent. Next, the corresponding electrolyte is added for DSC test. The result is shown in the Fig. 5a, it can



Fig. 1. (a) XRD patterns and (b) Raman spectra of the LVO composite.



Fig. 2. (a-b) SEM, (c) TEM and (d-e) HRTEM images of the LVO composite; (f-i) SEM image and corresponding element mapping of the LVO composite.



Fig. 3. (a) Galvanostatic charge-discharge profiles of LVO system from 3.0-0.01 V at 0.2 A g⁻¹; (b) Cycling performance of LVO system during the 100 cycles.

be clearly found that before the temperature of 225 °C, the original two exothermic peaks (I and II) disappeared, and only a sharp peak appeared at 117 °C. After the integral calculation, the value of the exothermic heat of this sharp peak (480.8 J g^{-1}) is basically the same as the value of the peak I (497.0 J g^{-1}), so it is deduced that the sharp peak located at 117 °C and the peak I represent the same thermal reaction process. This result shows that after washing with DMC, the peak II (the second self-exothermic reaction process)

disappeared. This because after the DMC washing, the SEI film on the materials surface of the LVO anode is dissolved and washed away by DMC. The amorphous layer on LVO sample without DMC washing seems more obvious and thicker, as shown in Fig. S7 [29,33,34]. So this means that the disappearing peak II is contributed by the decomposition reaction of the SEI film, while the exothermal peak I is generated by the reaction between the active materials and electrolyte. Since there is no SEI film on the surface of



Fig. 4. DSC trace of the reactions occurring in a fully lithiated LVO anode containing electrolyte (activated 5 cycles at 0.02 A g^{-1}).

the active materials, the reaction kinetics of the active materials and the electrolyte are accelerated, and the melting process become faster, so the peak I shift to a lower temperature and the peak width is narrowed. In addition, it is corroborated by another experiment that the exothermic peak II is a typical passivation layer decomposition reaction. DSC tests of the fresh LVO anode without cycled and the cycled delithiated LVO anode were conducted. In the Fig. 5b, the DSC curve of the cycled delithiated LVO anode shows two exothermic peaks (I' and II') in the low-temperature region, while the fresh uncycled LVO anode shows only one peak [35]. This further indicates that the peak II' corresponding to the temperature position of the peak II is also generated by the breakdown process of the SEI film. In addition, the curve shows that the heat release of delithiation is less than the heat release of lithiation, indicating that the heat release effect of lithiated LVO is more obvious. Since the fresh uncycled LVO anode has no encapsulation of the SEI film, the decomposition of the SEI film process is not observed on the corresponding DSC curve.

In the high-temperature reaction region, the three exothermic peaks III (located at 268 °C), IV (located at 300 °C) and peak V (located at 336 °C) in Fig. 4 are presumed to be contributions of the thermal reaction of the electrolyte, acetylene black (AB) and the binder. Fig. 6a shows the DSC curve for the individual electrolyte obtained for the solution of LiPF₆ in EC/DEC, it can be clearly observed that there are three typical thermal effect peaks after 225 °C. An endothermic peak at 230 °C followed by two exothermic peaks, the first sharp exothermic peak located at 251 °C and the

wide one at 313 °C. The first endothermic process is attributed to the melting of LiPF₆ and the followed exothermic process is due to the redox reaction of LiPF₆ and its decomposition products such as PF₅ in a carbonate solvent [36–38]. The DSC curve of the blend of pure AB and electrolyte are shown in the Fig. 6b, there are also no thermal reaction occurs before 225 °C. Due to the synergistic effect of AB and electrolyte reaction, the intensity of two endothermic peaks between 250 °C and 350 °C are enhanced. Similarly, the thermal effect of the electrolyte and AB are both after 225 °C, corresponding to peaks III and IV in Fig. 4, and it is also proved that the reaction before 225 °C is only related to the LVO materials. Then washing the fully lithiated LVO anode with pure anhydrous DMC, no electrolyte is added for DSC testing. The result is shown in Fig. 6c, after this treatment, only peak V remines after 225 °C. Since there is no electrolyte in reaction, only the exothermic reaction process of the binder occurs (341 °C). And the weak and broad peak centered before 225 °C is observed for reaction of LVO materials and residual trace electrolyte.

The above experiments demonstrate the thermal behavior mechanisms of the fully lithiated LVO anode with electrolyte system. The main thermal reaction can be divided into two parts. The first part occurs before 225 °C, which is the synergistic exotherm of active materials and passivation layer. The onset temperatures of both thermal reactions are 100 °C, and the peak temperatures are 136 °C and 155 °C, respectively. And the total heat released during the first part is 646.5 J g⁻¹. The second part is the thermal reaction after 225 °C, which is the contribution of the thermal reaction process of the electrolyte system and the binder. The exothermic peaks located at 268 °C and 300 °C are attributed to the reduction reaction of the electrolyte and the synergistic effect of acetylene black and electrolyte. When the temperature reaches 336 °C, the binder of the system will thermally decompose.

In addition, this article comprehensively compares the thermal reactivity process of the commercial graphite anode and LVO anode. The graphite is lithiated in a half-cell containing the same electrolyte as the LVO system and is subjected to a DSC test under the same treating procedures as the LVO electrode (Fig. S8), Fig. S8a shows the DSC curves of the fully lithiated LVO and fully lithiated graphite with electrolyte system. The exothermic accumulation of the reaction between the electrode material and the electrolyte before 200 °C is main cause of the heat shrinkage of separator [39–41]. During the low-temperature region before 200 °C, it can be clearly seen that the onset temperature of the thermal reaction of the graphite system and the LVO system are all 100 °C, and the value of the max heat flow of the graphite (2.36 W g^{-1}) is much higher than that of the LVO (1.77 W g^{-1}). In the high-temperature region after 200 °C, the graphite system also shows three exothermic peaks, and the heat release of this part of the graphite system is lower than that of the LVO. Then, the thermal reaction



Fig. 5. DSC trace of (a) the fully lithiated LVO anode washed with DMC or not and (b) the fresh uncycled and cycled delithiated LVO anode.



Fig. 6. DSC profiles of (a) the 1 M LiPF₆ in EC/DEC electrolyte solution, (b) the AB with electrolyte system and (c) the fully lithiated LVO anode without electrolyte.

peaks of the two systems are calculated by integral to obtain the overall heat release at different temperatures. Before 200 °C, the total heat release of graphite system (683.8 J g^{-1}) is higher than that of the LVO (646.5 J g^{-1}). However, the value of the heat release in the high-temperature region after 200 °C of the graphite system (200.6 Jg^{-1}) is lower than that of the LVO (695.6 Jg⁻¹). Fig. S3b also shows the overall exotherm curves of these two systems. The total heat release of the LVO system (1342 Jg^{-1}) is higher than that of the graphite (884 J g⁻¹), and the value of the heat release curve before 250 °C is slightly lower than that of graphite. By calculation, the average total heat of 231 J g^{-1} will be increased for each lithium ion inserted into LVO. So, ensuring that the LVO material has better thermal stability by the way of controlling the lithium intercalation is vital. The thermal runaway of most cell systems occurs before 200 °C, and the heat release of LVO in this region is equivalent to that of graphite, and LVO has a suitable lithiation potential to avoid safety problems caused by lithium dendrites. Therefore, compared with the commercial graphite, LVO is a relatively safe anode material of the lithium ion batteries.

The influences factors of the thermal reactivity process of the LVO system such as degree of intercalation, number of cycles and chemical nature of the binder are also studied. Fig. 7a shows the discharge curve after 5 cycles of pre-circulation activation. The DSC tests are carried out on the several samples in different discharge states. Five different degrees of lithium intercalation points have been selected, which corresponds to the insertion of 0, 0.66, 1, 1.8 and 3 lithium atoms into the structure of Li_3VO_4 ($Li_{3+x}VO_4$, x = 0, 0.66, 1, 1.8, 3). Then these five groups of cells are added to the electrolyte for DSC experiments (Fig. 7b). It can be observed that in the low-temperature region before 225 °C, as the degree of lithiation increases, the exothermic peak intensity of the thermal reaction process of the active materials and the electrolyte is continuously increased, corresponding to an increase in the value of the heat flow. This indicates that the more lithium intercalation, the greater the exothermic strength of the reaction of the active materials with the electrolyte. The heat flow of the passivation film on the surface of the active materials is also gradually increased, because as the amount of lithium x inserted in LVO increased, the surface passivation film (SEI and side reaction products, etc.) gradually thickens [42,43], resulting in a stronger decomposition peak of the passivation film.

For a clearer analysis of the exotherm process of LVO system in different state of discharge, Fig. 7c shows the exotherm heat release of the low-temperature region (35–225 °C) and high-temperature region (225–400 °C), as well as the total thermal reaction process in all regions, respectively. These values are obtained by integrating the corresponding DSC heat flow curves of Fig. 7b. It is found that the amount of heat released in the low-temperature region continued to rise when x is lower than 1 lithium atom, and it is basically flat and slowed down when x exceeds 1. In the second region, the overall heat shows a trend of rising, and only when x reaches 1 does the value decrease slightly. The total heat generated by these two regions increases with the degree of lithiation, and the rate of rise gradually slows down. Since the synergistic effect of passivation film composition on heat release is relatively complex, further DSC tests are conducted after washing the SEI film with DMC (Fig. 7d). It can be clearly observed that the heat flow in the first region continues to increase with the degree of lithiation. As the amount of lithium x inserted in LVO increased, the heat generated in both the thermal reaction of LVO and electrolyte and the total process increased [44].

Similarly, the thermal stability of the Li-ion cell during cycling is also very important [45]. Further, the thermal effects of number of cycles of the LVO anode are explored. The DSC tests are performed on the LVO system that are cycled for 5, 10, 20, and 30 cycles. And an interesting phenomenon can be found from the test results (Fig. 8a), as the number of cycles increases, the exothermic intensity produced by the reaction of the active materials with the electrolyte gradually decreases, while the heat flow of the SEI film shows the maximum value after 5 cycles, but in the subsequent 10-30



Fig. 7. (a) Galvanostatic discharge curves of the LVO system in fifth cycles; (b) Corresponding DSC curves for five discharge states; (c) Heat curves of exothermic reaction process in two regions and total process with different states of discharge; (d) DSC curves of LVO anode washed by DMC under five states of discharge.



Fig. 8. DSC traces of (a) the number of different cycles of the fully lithiated LVO anode and (b) the nature of different binder with the fully lithiated LVO anode.

cycles, as the cycle numbers increases, the exothermic intensity of the SEI film gradually increases. The reason for this phenomenon may be that as the cycling continues, the active materials in the cycling are continuously lost, resulting in the decrease in the exothermic intensity of the thermal reaction between the active materials with the electrolyte. And since the first five cycles failed to form a relatively stable SEI film, the thermal reaction kinetics are faster, and the position of the SEI film decomposition peak at five cycles is shifted to lower temperature compared with the subsequent number of cycles, which is further illustrated. In the next cycling, the SEI film is continuously thicker and more stable, and the side products generated during the cycling are continuously attached to the surface, so that the exothermic intensity is increased [43]. Overall, with the increase of cycle numbers, the total heat does not increase significantly, and the effect of the number of cycles is less than the degree of intercalation. This also shows that in the thermal reaction process of the LVO system, as the cycling continues, the overall heat release is relatively stable. To further restrain the exothermic reactions appearing at the high-temperature region, we also tried different binders used in the electrode. Fig. 8b shows the DSC curves of the exothermic reactions of the LVO system using two commonly used binders. The region over 250 C in the Fig. 8a mainly result from the change in electrochemical interface. With the deepening of the cycle, many side reactions occurred at the electrode surface interface, such as the degradation of the binder and electrolyte, which caused the change

in the interface condition. In the previous literature, these side reactions mainly occur above 250 C. During the cycling process, with the continuous consumption of electrolyte and the continuous deterioration of AB and binder, the corresponding heat peak has moved forward and the total heat release has been reduced [46–49]. It can be observed that the peak position and shape of the LVO anode with PVDF-HFP and PVDF as binders are basically the same, while the PVDF -HFP electrode exhibits much lower value of overall heat release than that of the PVDF. The DSC test results of PVDF-HFP in the air (Fig. S9) shows that the decomposition reaction of PVDF occurs mainly at around 340 °C, while the decomposition reaction of HFP occurs around 700 °C. Because the total mass of the binder in electrode preparation process is controlled to be same, the sample using PVDF-HFP contains less ratio of PVDF so the heat flow value shown in peak V is correspondingly lower (Fig. S10). Moreover, the thermal stability of PVDF-HFP also has been recognized in the previous reports [50-52]. Therefore, the thermal stability of LVO electrode can be further improved by replacing PVDF with PVDF-HFP as binders.

4. Conclusion

In summary, LVO materials are synthesized as an anode of a lithium-ion cell by a simple solid phase method. Firstly, the thermal reaction mechanisms of LVO/Li system are analyzed by DSC measurement. The onset and peak temperatures of the thermal reaction of active materials, passivation film, electrolyte and binder are analyzed, and the experimental verification is carried out by using the method of controlling variables. It is found that in the LVO/Li system, the thermal reaction of the active materials with the electrolyte and the decomposition reaction of the SEI film mainly occur in a low-temperature region (35–225 °C), while the reduction of the electrolyte and the thermal reaction of the binder occur in a high-temperature region (225–400 °C). And the exothermic stability of LVO system is compared with that of commercial graphite. In the subsequent conditional experiments, the thermal effects of the amounts of lithium intercalation, the number of cycles, and nature of different binders are also investigated. The experimental results show that the overall exothermic intensity of LVO/Li system increases with the increase of the amount of lithium intercalation. However, the number of cycles has little effect on the overall exothermic intensity. The thermal behavior mechanism of LVO as a lithium ion anode is systematically studied by DSC method, which has guiding significance for the safety design and development direction of its future commercialization. In the future, we will investigate the full cell capacity matching and thermal stability issues.

CRediT authorship contribution statement

Zhipeng Wen: Conceptualization, Methodology, Supervision, Project administration, Writing - original draft. **Min Zhao:** Investigation, Formal analysis, Validation, Writing - review & editing. **Xiangbang Kong:** Formal analysis, Visualization, Writing - review & editing. **Chaoyue Liu:** Formal analysis, Visualization, Writing review & editing. **Yang Yang:** Conceptualization, Data curation, Project administration, Writing - review & editing. **Jinbao Zhao:** Conceptualization, Supervision, Data curation, Project administration, Funding acquisition, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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