

Effect of PEG molecular weight on the crystal structure and electrochemical performance of LiV_3O_8

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Abstract This paper describes systematic studies on the effect of polyethylene glycol (PEG) molecular weight on the crystal structure and particularly the electrochemical performance of LiV_3O_8 . Scanning electron microscopy results indicate that after the decomposition of PEG, the structure of resultant products exhibits differences in morphology (shape, particle size, and specific surface area). The electrochemical results show that LiV_3O_8 cathode material treated by PEG (mean molecular weight of 10,000) has greater initial discharge capacity and better cyclic stability than other materials treated with PEG of different molecular weight. Its initial discharge capacity is 282.1 mAh g^{-1} and maintains 222.2 mAh/g after 50 cycles in 0.5 C rates (150 mA g^{-1}).

Keywords Polyethylene glycol (PEG) · LiV_3O_8 · Cathode material

Introduction

LiV_3O_8 has been investigated as a cathode material for nearly 20 years, after the first investigation by Panero et al. [1]. Recently, LiV_3O_8 with a layered structure [2] has attracted significant interest as cathode material for Li-ion batteries because of its low cost, large specific capacity, and a long potential cycle. It is also well known that the

preparation methods and posttreatments have significant influence on the electrochemical properties of LiV_3O_8 . The traditional solid-state method for the synthesis of LiV_3O_8 is carried out by the reaction between Li_2CO_3 and V_2O_5 at high temperature (HT). It could effectively avoid the occurrence of concentration gradient in precursor and simplify the preparation process. But the disadvantage of the HT method is that it is difficult to control the composition and homogeneity of the final products and the product LiV_3O_8 has a low capacity, such as 180 mAh g^{-1} in the range of 2.0–3.7 V [3]. Afterward, many improved solution methods are proposed to improve the electrochemical performance of LiV_3O_8 , such as doping other metal ions [4, 5], new synthetic methods [6–9], coating organic polymers [10], and so on.

In these methods, some solution methods are attracted extensive attention, such as sol–gel method. The sol–gel method has unique advantages in the synthesis of oxide materials because the starting materials can be blended homogeneously; meanwhile, the products with higher homogeneity and capacity could be obtained from this method. But the main disadvantage of the method is that it is easily to obtain different concentration gradient and its products shows bad capacity performance. The template method is a significant method to prepare cathode materials [11] because the homogeneous particles can be obtained simply in this method, so this method can solve problems of the different concentration gradient in the sol–gel method. It is useful to research into new synthesize methods which include the advantages of sol–gel method and template method. In this paper, we use sol–gel template method to synthesize LiV_3O_8 cathode material. Polyethylene glycol (PEG) is used by Hui Yang et al. as a surfactant to synthesize LiV_3O_8 nanocrystallites [12]. As a novel carbon source, PEG has improved the electrochemical

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performance of LiFePO_4 cathode material [13]. It also plays an important role in electric conductivity of electrolytes [14]. In this work, PEG with different molecular weight as templates to treat LiV_3O_8 cathode materials is investigated, and the structure, morphology, and electrochemical performance of the layered LiV_3O_8 powder are also studied.

Experimental

Preparation of the LiV_3O_8 electrode

V_2O_5 gel was prepared by reacting 1.25 g of V_2O_5 (99.6%) in 40 mL of H_2O_2 15 mol%. pH measurements were performed with a pH meter using 3.5 points for calibration. $\text{LiOH}\cdot\text{H}_2\text{O}$ (90.7%) and V_2O_5 gels with stoichiometric ratio were mixed and stirred for 2 h. Six grams PEG (analytically pure PEG, $M_w=2,000$, 10,000, and 1,000,000) was added together with 15 mL ethanol (99.6%) and the resulting mixture was stirred for 24 h. Then, the mixture was dried at 100 °C for 12 h. Finally, the precursors were calcined at 300 °C for 10 h to yield brown crystalline products and the samples obtained were named PEG1 (means molecular weight of 2,000), PEG2 (means molecular weight of 10,000), PEG3 (means molecular weight of 1,000,000), and LVO (the pristine sample).

Measurements

The cathodes were prepared by pressing a mixture of active materials, conductive material (acetylene black), and binder (polytetrafluoroethylene) in a weight ratio of 8:1:1. Li metal was used as the counter and reference electrode. The electrolyte was 1 M LiPF_6 in a 6:3:1 mixture (vol/vol/vol) of ethylene carbonate, propylene carbonate, and dimethyl carbonate. The galvanostatic method was used to measure the electrochemical capacity of the samples at the current density of 0.5 C (150 mA/g), with cutoff voltages (1.8–4.0 V) for charge and discharge processes.

The precursor was analyzed by thermogravimetry and differential thermal analysis (TG/DTA) using a thermogravimetric–differential thermal analyzer (Standard Type High temp. Type, Rigaku). The tests were conducted in air. The morphology was investigated with a scanning electron microscope (SEM; FEG SEM Sirion scanning electron microscope). X-ray powder diffraction (XRD) was carried out using a Rigaku D/Max-2500 apparatus. A CHI 660b electrochemical workstation was used for cyclic voltammetry (CV; scan rate 0.1 mV s^{-1} , 1.8–4.0 V) and electrochemical impedance spectroscopy experiments (open circuit potential, amplitude 5 mV, 10^4 to 10^{-1} Hz). All experiments were conducted at room temperature.

Results and discussion

Figure 1 shows the DTA/TG curves of the precursor PEG2. It can be seen that the thermal decomposition of precursor prepared in this method possesses two main steps. The first step is the temperature ranging from room temperature to about 257 °C. The weight loss of the sample was about 31.2 wt.%. Two obvious absorbing heat peaks are observed near 46 °C and 114 °C from DTA curve. The dehydration reaction of PEG might lead to the exothermic peak near 46 °C and the loss of crystal water probably results in the other peak near 114 °C. The second step is from 257 °C to 585 °C, which is the decomposition of PEG existing in the precursor. A big exothermic hump is observed on DTA curve near 257 °C. The PEG may be decomposed to form CO_2 and H_2O . At about 585 °C, an endothermic peak is observed on the DTA curve, but the weight of the sample keeps constant; this should be due to the melting of LiV_3O_8 . PEG can be completely eliminated after simply calcining at 300 °C. So it is possible to synthesize LiV_3O_8 without other impurities.

The SEM images of all as-synthesized lithium vanadium oxides are demonstrated in Fig. 2. It can be seen that all the samples show very different configurations, indicating that different PEG molecular weights lead to different changes. It is obvious that the sample PEG2 shows the smallest particle size ($\leq 2 \mu\text{m}$), while the precursor of PEG2 shows lumpish configuration ($\geq 15 \mu\text{m}$). It can be observed that inhomogeneous particles are distributed in the precursor of PEG1 (2–10 μm), almost the same morphology as that of LVO, while the image of PEG3 shows a uniform rod-like structure (about 5 μm). It has been reported by several researchers that the morphology can have an important effect on electrochemical performance of cathode materials,

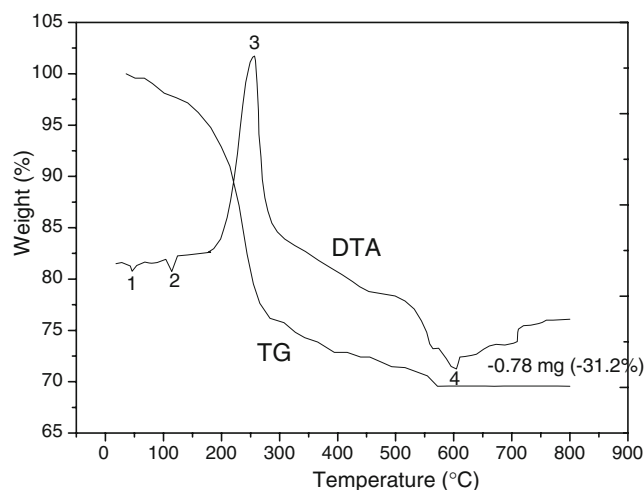
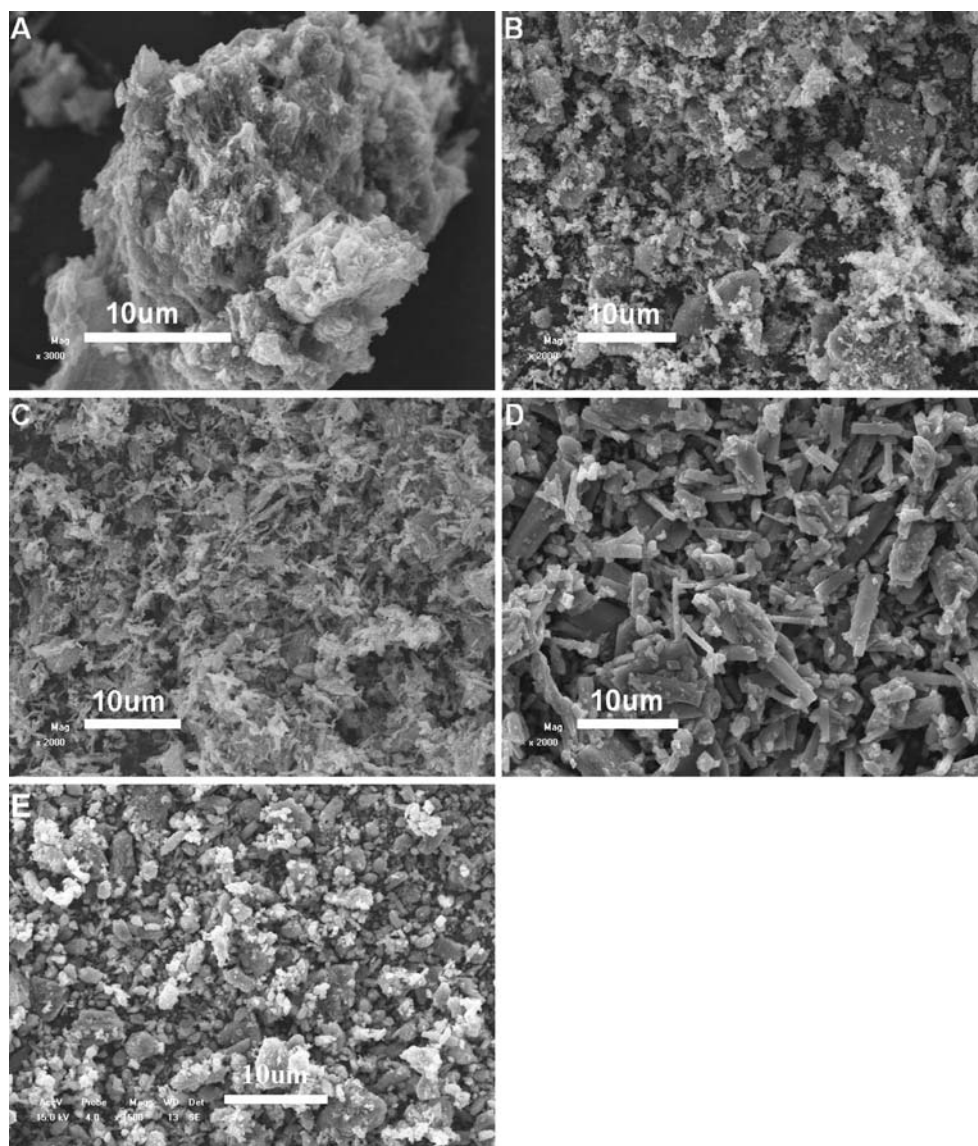


Fig. 1 TG/DTA curves of the precursor PEG2 (1 46 °C, 2 114.5 °C, 3 257 °C, 4 585 °C)

Fig. 2 Scanning electron micrographs of all gained lithium vanadium oxides: **a** the precursor of PEG2, **b** PEG1, **c** PEG2, **d** PEG3, **e** LVO



and the intercalation process of Li ion between the layers of the cathode material is a diffusion process. Therefore, the larger grains are not advantageous to intercalate lithium ion [15]. So the sample PEG2 should have better electrochemical performance.

The X-ray diffraction patterns of the untreated/treated samples are shown in Fig. 3. It shows that surely all patterns can be indexed to a signal phase of LiV_3O_8 structure (JCPDS: 72-1193), demonstrating no impurities or new products. The calcined temperature is chosen at 300 °C, which agrees well with the TG/DTA results.

The first discharge curves of all gained samples are illustrated in Fig. 4. It is found that PEG-treated samples show obvious discharge voltage plateaus, while the initial discharge curve of pristine material shows several indistinct voltage plateaus. It is clear that several intercalation processes are possibly hindered in the treated samples.

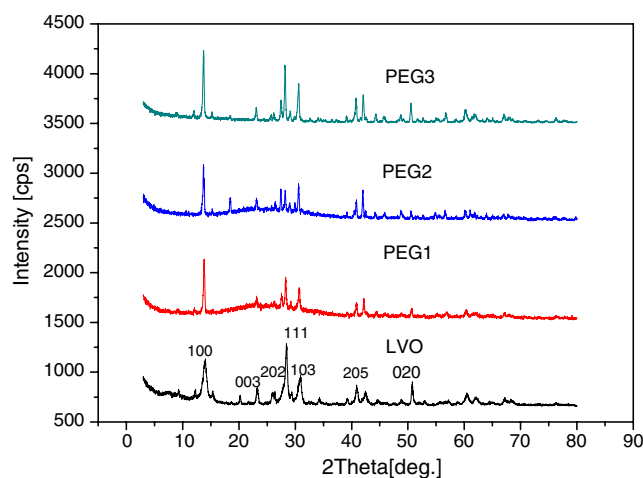


Fig. 3 XRD patterns of all gained samples

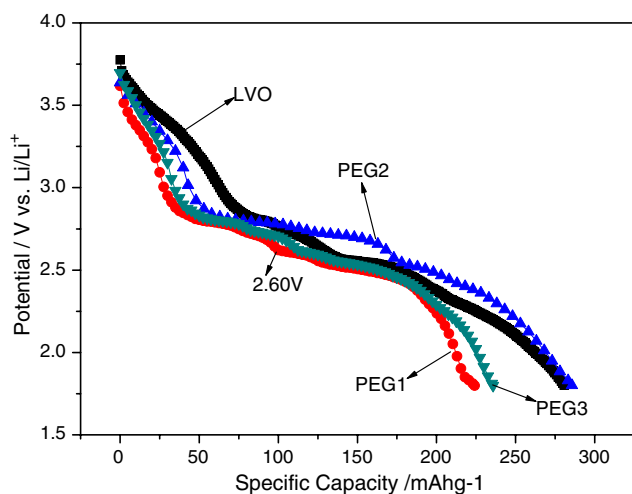


Fig. 4 Initial discharge curves of all gained samples (discharge 4–1.8 V at 0.5 C rates)

The disappearance of the voltage plateaus might be due to the rearrangement of Li ion for adding PEG. The sample PEG2 clearly exhibits the highest and longest first discharge plateau between 2.75 and 2.81 V, which corresponds with the highest specific discharge capacity among all the samples. The sample PEG1 shows a redundant voltage plateau at 2.60 V and the sample PEG2 shows narrow voltage plateaus. Therefore, the discharge curves show that the addition of PEG ($M_W=10,000$) can effectively improve the capacitance of LiV_3O_8 electrode.

Figure 5 shows the cyclic curves of all gained samples. It indicates that the addition of PEG ($M_W=10,000$) can improve the cyclic performance. The PEG2 electrode shows a high initial discharge capacity of 281.1 mAh g^{-1} and maintains 240.0 mAh g^{-1} after 30 cycles. While other

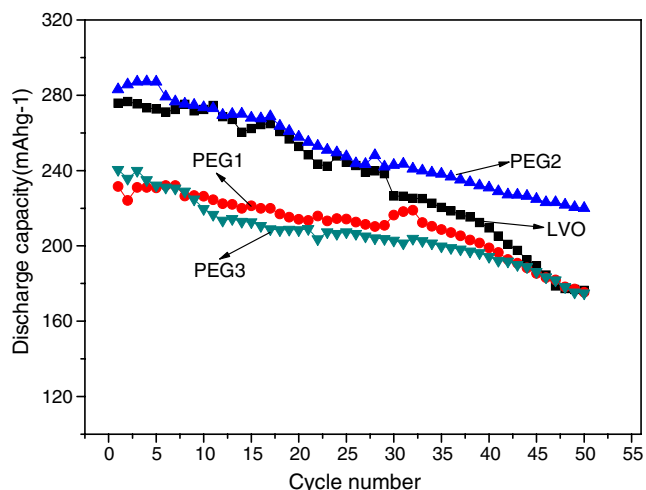


Fig. 5 Cycling curves of all gained samples (discharge 4–1.8 V at 0.5 C rates)

samples added with PEG ($M_W=2,000$ and $1,000,000$) show bad capacity properties and even worse than pristine LiV_3O_8 . So it indicates that the addition of PEG ($M_W=10,000$) is significant in improving the cyclic performances of LiV_3O_8 .

CV profiles of the samples are shown in Fig. 6. As is shown, the sample PEG2 exhibits the sharpest oxidation peak at 2.86 V vs. Li/Li^+ which indicates a charge plateau and several reduction peaks at 2.45, 3.73 V vs. Li/Li^+ , respectively, which indicate multiple discharge plateaus. It can be seen that the product PEG2 shows excellent cyclability. The initial specific discharge capacity of the PEG2 is 281.1 mAh g^{-1} and remains 240 mAh g^{-1} after 40 cycles, which is best among all the samples. This is consistent with the results obtained above. The curve of PEG3 is very different from the other curves. It can be concluded that comparatively large molecular weight of PEG will lead to tiny change of charge/discharge processes. Since different charge/discharge processes do not mean structural change, the X-ray diffraction patterns have attested the fact that the sample PEG3 exhibits the same structure as the pristine LiV_3O_8 .

Conclusions

In this study, different PEG as templates were used to synthesize LiV_3O_8 cathode materials; all treated LiV_3O_8 manifests different surface topography. PEG ($M_W=10,000$)-treated material shows good size distribution and small particle size. It shows the best electrochemical performance with high discharge capacity (remains 240.7 mAh g^{-1} after 30 cycles) and less voltage plateaux.

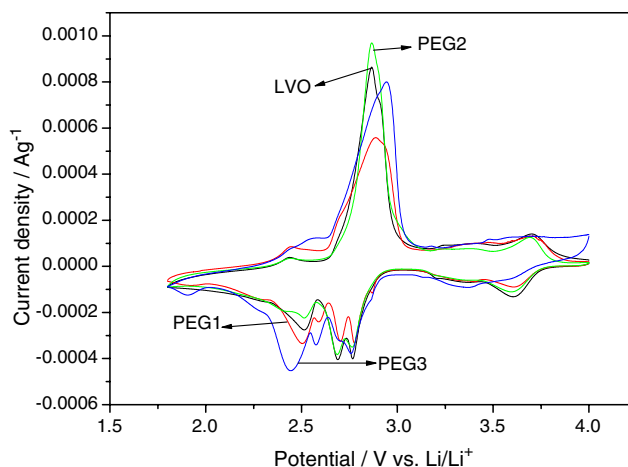


Fig. 6 CV curves (first cycle) of all gained samples. Counter and reference electrode: lithium; area of working electrode 0.5 cm^2 ; scan rate $0.1 \text{ mV}\cdot\text{s}^{-1}$; potential interval 1.8–4.0 V vs. Li/Li^+

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