Preparation and Lithium Storage Properties of LiV$_3$O$_8$ as a Cathode Materials

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Abstract. The LiV$_3$O$_8$ cathode materials was successfully synthesized by PEG-assisted freeze drying combination with calcination treatment process. The annealing temperature affected the electrochemical properties of the LiV$_3$O$_8$ cathode materials. The LiV$_3$O$_8$ cathode materials annealed at different temperatures were characterized by X-ray diffraction, Scanning electron microscopy, and Galvanization charge/discharge profile measurement. The results demonstrated that with the increase of sintering temperature, accompanied with the change of the morphology of the nanoparticles to nanorods. The LiV$_3$O$_8$ fabricated at 500 °C (LVO500) showed the high capacity and good rate capability (after 100th, a reversible discharge capacity up to 218 mAh g$^{-1}$).

1. Introduction
In recent years, the high-performance lithium-ion batteries (LIBs) has been a hot research spot in the field of electrochemical energy storage systems because of their high power density, low cost, and better safety[1,2]. However, the commercial cathode materials have a low practical application capacity, safety concerns, high cost of Co elements and environmental problem of the LiCoO$_2$, Jahn-Teller effect and dissolve of Mn$^{3+}$ for the LiMn$_2$O$_4$, and low electrical conductivity of LiFePO$_4$, which cannot meet the increasing requirements of the LIBs [3,4]. In recent years, LiV$_3$O$_8$ have attracted much attentions as an cathode materials because of easy preparation, their high theoretical capacity, good safety, special layer structure, and low cost [5]. Similarly the V$_2$O$_5$ structure, two structural units of distorted triangular bipyramid VO$_5$ and octahedron VO$_6$ are constituted the three-dimensional layered V$_2$O$_5$ structure [6]. Adjacent V$_2$O$_5$ layers are connected by strong ionic bond with the lithium ion, making up of the stable LiV$_3$O$_8$ frame structure, promote the rapid transport of Li$^+$ [7]. In addition, layer LiV$_3$O$_8$ structure can effectively accommodated three Li$^+$ ions (~ 280 mAh g$^{-1}$) and not caused the irreversible deformation of crystal structure [8].

Different morphologies (nanosheets, nanobelts, nanotubes, nanorods, nanospheres, etc.) and different synthesis methods (hydrothermal, sol–gel, rheological phase reaction, freeze drying, etc.) have been deployed to prepare the high performance LiV$_3$O$_8$ material. Wang and Deng et.al [9] prepared LiV$_{3.9}$Nb$_{0.6}$O$_8$ nanorods by an electrospinning method and post low-temperature calcination. It can give the capacity of 401 mAh g$^{-1}$ at 0.1 C and 91 mAh g$^{-1}$ at 20 C. for the LiV$_{2.94}$Nb$_{0.06}$O$_8$ electrode. Feng and Zhang et.al [10] prepared LiV$_3$O$_8$ crystal by sol-gel combination with calcination treatment process. The annealing time, annealing temperature, and amount of Li$^+$ ion affected the electrochemical properties of the LiV$_3$O$_8$ materials. The obtained sample (Li:1.15, 5h, and 400 °C ).
Huang and Wang et.al [11] prepared cookies LiV$_3$O$_8$ samples via a sol-gel method, ethylene glycol as the adjuvant. The cookies LiV$_3$O$_8$ samples display a good rate capability and high reversible capacity. Thanks to hierarchical plate array structure that can effectively strengthen structural stability and enhance interface stability. The LiV$_3$O$_8$ samples with hierarchical plate array structure display a good rate capability and high reversible capacity [12].

Herein, the LiV$_3$O$_8$ electrode materials were prepared via a PEG-assisted freeze drying combination with calcination treatment process. The effects of annealing temperature on the morphology, structure, and electrochemical performances for LiV$_3$O$_8$ have been carefully studied.

2. Experiment
The LiV$_3$O$_8$ samples were synthesized by using LiAc·2H$_2$O, NH$_4$VO$_3$ and PEG (molecular weight of 40000) as reactants. The molar ratio of LiAc·2H$_2$O, NH$_4$VO$_3$ was 1.05 : 3. These reactants were dissolved in 50 mL water. Then, 5 g of PEG-40000 was added into the transparent solution, and heated to 80 °C, until the formation of transparent solution. The transparent solution was transferred to a refrigerator at -1 °C for 24 h, and freeze dried at 100 Pa (-45 °C) for 12 h, calcined at 400, 450, 500, 550 °C for 3.5 h to obtain final products. The final products were marked as LVO400, LVO450, LVO500, and LVO550.

An X-ray diffractometer (XRD, D8 Advance, Bruker AXS), SEM (JEOLJSM-7400F, Japan) and X-ray photoelectronic spectrometry (XPS, VGESCA-LABMK II) were used to detect structure, morphology and ion valence states of the LiV$_3$O$_8$ samples.

The mixed slurry (LiV$_3$O$_8$ cathodes (80%), acetyleneblack (10 wt%) and PVDF (10 wt%), N-Methy-1-2-pyrrolidone (NMP) as a solvent) was smeared on Al foil, and dried at 120 °C for 12 h in a vacuum drying to obtain work electrodes. The mass loading of each sample was ~2.3 mg·cm$^{-2}$. The electrochemical performance was assessed using CR2032-type cells which were assembled in glove box full of argon gas. 1 M LiPF$_6$ solution (ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume) as solvent) as the electrolyte, Li foil as the counter electrode. The electrochemical performances were tested by Land CT2001A battery testers.

3. Result and Discussion
The powder X-ray diffraction was used to check the crystalline phase of as-prepared samples in Figure 1a. The diffraction pattern shows the presence of LiV$_3$O$_8$ (JCPDS No.72-1193, space group: P21/m), and the characteristic peaks at 2θ =13.8°, 15.6°, 23.3°, 26.1°, 28.5°, 30.7°, 40.3°, 40.9°, 42.1°, and 50.8° corresponding to diffraction planes of (100), (002), (003), (-202), (-111), (103), (-301), (-205), (203), and (020), respectively. To be compared with the samples of the annealed at different annealed temperature, the crystal structures of the these samples have not been changed and not impurity. XPS experiments were performed to identify the chemical composition and the oxidation states of the LVO500 in Figure 1b. The complete XPS spectra indicate the existence of V, O, and Li elements. The V XPS spectra show two peaks, at 524.3 and 517.05 eV, correspond V 2p1/2 and V 2p3/2, which verifies the presence of the V$^{5+}$ in the sample. The peak at 529.8 eV corresponds to O 1s, corresponding to metal-oxygen (Li-O and V-O) bonds and absorbed oxygen.
Figure 1. XRD patterns of all LiV$_3$O$_8$ samples, (b) XPS survey spectrum of LVO500 and high-resolution XPS spectra of (c) V 2p and (d) O 1s.

Scanning electron microscopy (SEM) were used for morphological investigation of all LiV$_3$O$_8$ samples. The non-uniform size and coterminous morphology of LVO400, LVO450, LVO500, and LVO550 samples can be found out with SEM images in Figure 2. The morphology of the LVO400 samples marked up for a largely of nanoparticles and a small amount of nanorods in Figure 2a. The morphology of the LVO450 samples consists largely of nanorods and a small amount of nanoparticles in Figure 2b. When the calcination temperatures are 500 and 550 °C, the non-uniform nanorods (a diameter with 0.5–2.0 μm) have been founded in Figure 2c and d. The result implied that with the increase of sintering temperature, accompanied with the change of the morphology of the nanoparticles to nanorods.
To investigate the electrochemical properties of the as-prepared samples performed to understand the storage capacity of the material at 2.0–4.0 V. Fig. 3 shows the cycle performances of the as-prepared electrodes at 100 mAh g⁻¹. The first discharge capacity of the LVO400, LVO450, LVO500, and LVO550 were 247, 278, 276, and 265 mAh g⁻¹, and the specific capacity of 132, 187, 218, and 150 mAh g⁻¹ after 100 cycle, retention were 53.4, 67.3, 78.9, and 55.6 % from the first cycle, respectively. The rate capability of the as-prepared electrodes is illustrated in Figure. 3f. It showed specific capacities of 292, 173, 160, 127, 99, 67, and 41 mAh g⁻¹ at 100, 300, 600, 1500, 3000, 6000, and 10000 mA g⁻¹ for the LVO400 electrode, respectively. The electrode retained its capacities 167 mAh g⁻¹ when current density backs to 100 mA g⁻¹. The LVO450 electrode showed specific capacities of 267, 195, 174, 155, 107, 97, and 50 mAh g⁻¹ at 100, 300, 600, 1500, 3000, 6000, and 10000 mA g⁻¹, respectively. The electrode retained its capacities 167 mAh g⁻¹ when current density backs to 100 mA g⁻¹. The LVO550 electrode display a good rate capability, a specific capacities of 319, 219, 182, 171, 150, 115, and 91mAh g⁻¹ at 100, 300, 600, 1500, 3000, 6000, and 10000 mA g⁻¹, respectively. The electrode retained its capacities 205 mAh g⁻¹ when current density backs to 100 mA g⁻¹. The LVO500 electrode showed specific discharge capacities of 290, 190, 160, 145, 116, 81, and 45 mAh g⁻¹ at 100, 300, 600, 1500, 3000, 6000 and 10000 mA g⁻¹, respectively, its capacities 168 mAh g⁻¹ are retained when current density backs to 100 mA g⁻¹. It demonstrated the LVO500 sample behaved better discharge capacity than that of those electrodes.

Figure 2. SEM images of (a) LVO400, (b) LVO450, (c) LVO500, and (d) LVO550.
Figure 3. Discharge–charge curves of (a) LVO400, (b) LVO450, (c) LVO500, and (d) LVO550, (e) cycling performance and (f) rate performance of the LVO400, LVO450, LVO500, and LVO550.

The EIS experiments were performed from 100 kHz to 0.01 Hz as shown in Figure 5e. The straight line and semicircle are attributed to the solid phase diffusion and charge transfer resistance. The $R_c$ value of the LVO400, LVO450, LVO500, and LVO550 electrodes are 255 Ω, 230, 112, and 279 Ω, indicating that LVO500 electrode own rapid charge transfer and lithium ion diffusion with the others sample. Thus, an eminent lithium storage property of the LVO500 electrode can effectively restrain the mixing of cations, effectively decreases the electrochemical reaction resistance and increase the lattice parameters.

Figure 4. EIS of the LVO400, LVO450, LVO500, and LVO550
4. Conclusions
In summary, the LiV$_3$O$_8$ nanorods samples were synthesized by a freeze drying method. The effects of LiV$_3$O$_8$ cathode materials on the morphology, crystal structure and lithium storage performance of the as-prepared electrodes have been carefully studied. The results demonstrated that with the increase of sintering temperature, accompanied with the change of the morphology of the nanoparticles to nanorods. Especially, the LVO500 nanorods electrode delivered an outstanding electrochemical performance.

5. Acknowledgments
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6. References
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