Preparation and Electrochemical Performances of Magnesium and Zircon Doped Lithium Iron Phosphates

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Abstract. Magnesium and zircon doped lithium iron phosphates (LiFePO₄) were synthesized via combustion method without inert gas, then they were characterized by X-ray diffraction and Scanning electron microscopy, and their electrochemical performances including discharge performance and cycle performance were measured by galvanostatic charge-discharge cycling technique. The results indicate that both doped LiFePO₄ still keep the structure of olivine but their electrochemical performances greatly improve compared with the undoped LiFePO₄. In addition, zircon doped LiFePO₄ exhibits the best discharge specific capacity of 143.4 mAh/g at 0.2 C discharge rate and the discharge specific capacity of it remains 126.3 mAh/g after 50 charge/discharge cycles, showing good cycle performance.

Introduction

LiFePO₄ cathode materials have become one of the hot point in the research of lithium ion batteries at present. LiFePO₄ materials have advantages of low cost, high cycle characteristics, high open circuit voltage (3.5 V) and environmental protection, but at the same time, they have shortcomings of intrinsic low electronic conductivity and low rate of Li⁺ migration which limit their electrochemical performance.

In order to improve the electrochemical properties of LiFePO₄ cathode materials, Some measures like surface coating, ion doping and control particle morphology have been used [1]. Ion doping is one of the most effective means, a lot of testing results show that the doping can indeed improve the electrochemical performance of LiFePO₄ electrode materials. Chung et al think that LiFePO₄ possess electrons and holes with large effective mass, the mixed ion will cause material internal lattice defects, which will improve the hole mobility, so as to improve the conductivity of the material, but in the study of Chung, they ignored the doping effect relationship between the ionic radius and the electric charge.

In this paper, Magnesium and zircon doped lithium iron phosphates were synthesized via combustion method, on this basis, the effect of Mg²⁺ and Zr⁴⁺ doping on crystal structure and electrochemical of LiFePO₄ electrode materials have been studied.

Experimental

Materials and Synthesis

LiNO₃, Fe(NO₃)₃.9H₂O and (NH₄)₂HPO₄ were weighed and mixed at the molar ratio of 1:1:1 [12-14], then a suitable amount of distilled water and citric acid were added, and the mixing time were 30 min, after that, they were put into vacuum for drying oven 5 h, next, they were put into muffle furnace at the temperature of 600 °C, The sample was taken out immediately When the bright flame is observed, pure LiFePO₄ was prepared and marked as S1. In the weighing mixing stage, 1% Mg(NO₃)₂/Zr(NO₃)₄ were added into mixture, then Mg²⁺/Zr⁴⁺ doped LiFePO₄ were made and marked as S2/ S3.
Characterization

X-ray diffraction (XRD) instrument (bruKer, D8 ADVANCE, Germany) was used for analysing the phase composition of these samples, Cu K was used for alpha radiation sources, accelerating voltage and charging current were respectively 40 kV and 40 mA, scanning Angle were 10° ~ 60°, scanning speed was 6 (°)/min.

Scanning electron microscope (SEM) was used to observe the micromorphology of doped and undoped samples.

The samples were prepared as the positive active material with acetylene black and PVDF, which were carried out at the quality ratio of 8:1:1, then a small amount of NMP were added into mixture, they were put into ultrasonic oscillators for 30 min, next, they were prepared for cathode materials. celgard 2300 was used for the diaphragm assembly of button cell. The charging and discharging performance and cycling performance of the assembled battery are made on the LAND-CT2001A battery tester, while charging and discharging voltage is 2.5 V~4.2 V. The cyclic voltammetry test of the assembled battery was completed at the CHI650C electrochemical workstation (Shanghai chenghua). The scanning speed was 0.1 mV/s, and the scanning voltage was 2.4 V~4.2 V.

Results and Discussion

XRD patterns of S1, S2 and S3 are shown in Figure 1 According to the standard JCPDS card, it is obviously that three samples are considered to be LiFePO₄ with high purity crystalline. However, compared with S1, the diffraction peak of S2 and S3 slightly shift to high angle. This indicates that the unit cell volume of LiFePO₄ is decreased after doping Mg²⁺/Zr⁴⁺, and the distance of crystal face is reduced.

![Figure 1. XRD patterns of undoped, Mg²⁺ and Zr⁴⁺ doped LiFePO₄ powders.](image)

Figure 2 is SEM images of S1 in 20000 magnification, it can be seen that LiFePO₄ particles dispersed evenly, particle size are about 0.3 microns. It shows the combustion method can be used to synthesize small LiFePO₄ powders, Figure.3 is SEM images of S2 and S3 in 20000 magnification, compared with S1, doping Mg²⁺/Zr⁴⁺ had no significant change in microscopic morphology of LiFePO₄ powder, but it is worth noting that all the samples have marked reunion in a certain extent. powder produced by combustion method belong to nanoscale particles, which have large specific surface area, high activity and are easy to gather. In addition, clumps have been reduced after Mg²⁺ and Zr⁴⁺ doping.
Figure 2. SEM image of undoped LiFePO$_4$ powder.

Figure 3. SEM images of (S2) Mg$^{2+}$ doped and (S3) Zr$^{4+}$ doped LiFePO$_4$ powders.

Figure 4 shows cycle of performance curves of S1, S2 and S3 in 0.2 C discharge ratio, it is observed that three samples reached maximum of specific capacity of the battery in the second cycle, in ascending order: S3 (143.4 mAh/g), S1 (135.2 mAh/g), S2 (123.3 mAh/g). After 50 cycles, their discharge specific capacity were 99.5 mAh/g, 118.2 mAh/g and 126.3 mAh/g separately, the capacity retention rate were 81.7%, 88.4% and 89.4% separately, and the test results also showed that Zr$^{2+}$ doping can effectively improve the cycle performance of LiFePO$_4$ than Mg$^{2+}$ doping.

Figure 4. Cycling performance of undoped, Mg$^{2+}$ and Zr$^{4+}$ doped LiFePO$_4$.

Figure 5 showed circular curve of S1, S2, S3 samples under different discharge ratio, it is found that discharge capacity of three samples fell very slowly under the same discharge ratio, which reveal that the cycle stability of three samples are good. Under the discharge ratio of 0.2c, 1C, 2C and 5C, the cycle performance of Mg$^{2+}$ and Zr$^{4+}$ doped samples were better than that of undoped samples, in addition, Zr$^{4+}$ doping has better effect.
Figure 5. Rate performance of undoped, Mg$^{2+}$ and Zr$^{4+}$ doped LiFePO$_4$.

Figure 6. showed cyclic voltammetric curve of S1, S2 and S3 respectively. Compared with S1, the peak current of S2 and S3 increased. It is obvioued that Mg$^{2+}$ and Zr$^{4+}$ doping enhanced the Li$^+$ migration rate in crystal lattice, to a certain extent, increase the battery capacity, what is more, Zr$^{4+}$ doped LiFePO$_4$ have greater peak current and smaller redox peak potential than that of Mg$^{2+}$ doped LiFePO$_4$.

Figure 6. Cycle voltammetry curve of undoped, Mg$^{2+}$ and Zr$^{4+}$ doped LiFePO$_4$.

The results of electrochemical properties showed that the addition of Mg$^{2+}$ and Zr$^{4+}$ not only enhanced the multiplier performance, but also improved the circulation performance of LiFePO$_4$. What's more, the addition of Zr$^{4+}$ was more beneficial to the improvement of the electrochemical performance of LiFePO$_4$ than that of Mg$^{2+}$.

Conclusions

We successfully integrate Mg$^{2+}$, Zr$^{4+}$ into the crystal lattice of LiFePO$_4$ using combustion method, the adulterated LiFePO$_4$ still maintains a complete peridot structure. The addition of Mg$^{2+}$ and Zr$^{4+}$ can not only improve the discharge ratio of LiFePO$_4$, but also improve the circulation performance of LiFePO$_4$ effectively, and the improvement effect of Zr$^{4+}$ is even more significant.

References


