

# Optimization of Lithium iron phosphate delithiation voltage for energy storage application

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**Abstract**—Olivine-type lithium iron phosphate (LiFePO<sub>4</sub>) has become the most widely used cathode material for power batteries due to its good structural stability, stable voltage platform, low cost and high safety. The olivine-type iron phosphate material after delithiation has many lithium vacancies and strong cation binding ability, which is conducive to the large and rapid insertion of alkaline ions such as lithium, sodium and potassium. Therefore, the investigation of delithiation technology is of great significance. Electrochemical delithiation is a common method for preparing olivine-structured FePO<sub>4</sub>, which can maintain the structural stability and integrity of the material. In this work, the effect of voltage on the delithiation of LiFePO<sub>4</sub> material was investigated by the electrochemical delithiation method in Na<sub>2</sub>SO<sub>4</sub> as delithiation solution. The results show that 2.0 V is the best delithiation voltage, and the as-prepared FeO<sub>4</sub> exhibits the highest specific capacity of 137.7 mAh g<sup>-1</sup>.

## 1. Introduction

Nowadays, with the rapid development of the economy, the number of waste lithium-ion batteries (LIB) is increasing. The treatment of waste lithium batteries has become a problem that cannot be ignored. It is a feasible treatment strategy to delithiate the cathode material in the waste lithium battery and realize lithium recovery. Among many cathode materials for LIB, olivine-type LiFePO<sub>4</sub> has attracted wide attention due to its good stability, cost-effective and high safety. Compared with chemical delithiation, electrochemical delithiation is a common method for preparing olivine-structured FePO<sub>4</sub>, which can maintain the structural stability and integrity of the material. The electrolyte system used in electrochemical delithiation is divided into two types: organic electrolytes and aqueous electrolytes. The use of organic electrolyte for delithiation requires harsh conditions. It is necessary to assemble the battery in the glove box, charge and discharge, and then disassemble the battery to obtain the pole piece after delithiation. This series of operations must ensure an anhydrous and anaerobic environment, the process is cumbersome, and the organic electrolyte is toxic, which will pollute the environment and costly. The delithiation of aqueous electrolyte only needs to be completed in the electrolytic cell, without an anoxxygen-free environment, and the aqueous electrolyte is also non-toxic and harmless. The setting of different delithiation voltage will affect the rate of delithiation reaction and the degree of delithiation. However, the commonly used aqueous electrochemical delithiation electrolyte has the problems of slow delithiation rate and incomplete delithiation. For example, the chloride solution has the

corrosion problem of an aluminum-made current collector during the electrochemical delithiation process. Therefore, the neutral aqueous electrolyte of the sulfate system and nitrate system is commonly used for electrochemical delithiation. Different delithiation voltage settings will affect the rate of delithiation reaction and the degree of delithiation, so it is very necessary to determine the appropriate delithiation voltage for electrochemical delithiation.

In this work, the commonly used Na<sub>2</sub>SO<sub>4</sub> solution was selected as electrolyte and the delithiation voltage was adjusted to obtain the best delithiation condition. And the as-prepared FeO<sub>4</sub> showed the highest specific capacity of 137.7 mAh g<sup>-1</sup> at the delithiation voltage of 2.0 V.

## 2. Experimental section

### 2.1 Electrochemical Delithiation Process

LiFePO<sub>4</sub> powder was brought from B&M Science and Technology Co., Ltd, Tianjin, China. 90 wt% LiFePO<sub>4</sub>, 5wt% (poly(vinylidene fluoride)) (PVDF) and 5wt% conductive carbon (Super P) were mixed in N-methylpyrrolidinon (NMP) to form a uniform slurry. And this slurry was coated onto Al foil with a mass loading of 6 mg cm<sup>-2</sup> to prepare LiFePO<sub>4</sub> electrode. In the electrochemical delithiation process, titanium foil was used as the counter electrode, and 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution was employed as electrolyte. The LiFePO<sub>4</sub> electrode was cut into 5\*10 cm<sup>2</sup> pieces and potentiostatically delithiated until the specific capacity reached 170 mAh g<sup>-1</sup> at different voltages.

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## 2.2 Electrochemical tests and Materials characterization

The electrochemical impedance spectroscopy (EIS) was obtained by a CHI660E electrochemical workstation in the frequency range of 100 kHz to 0.01 Hz. The electrochemical tests were carried out on the Land

CT2001A battery tester. Scanning Electronic Microscopy (SEM), Brunauer Emmett Teller (BET) and X-Ray Diffraction (XRD) were used to analyze the materials.

## 3. Results and discussion

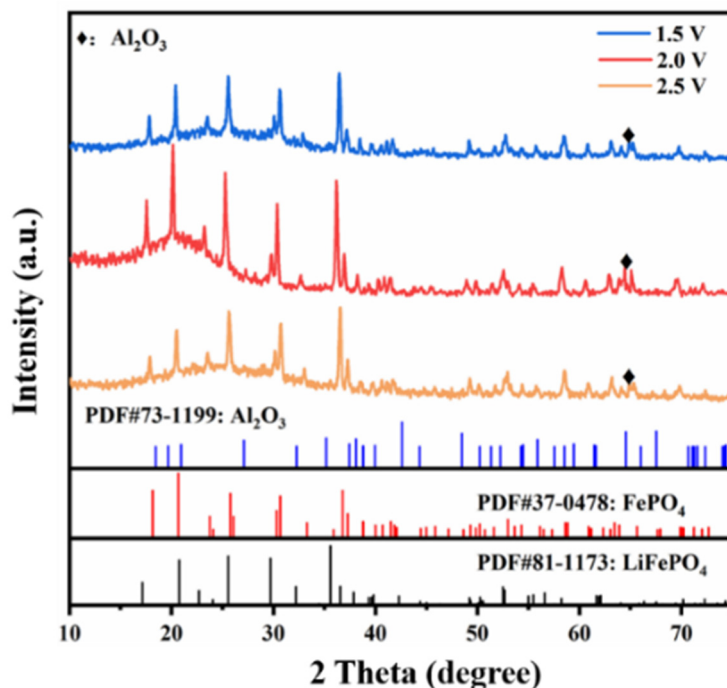


Fig.1 XRD patterns of LiFePO<sub>4</sub> cathode materials after delithiation at different voltages

The structural changes of the LiFePO<sub>4</sub> after delithiation at three different voltages were analysed by XRD (Fig. 1). It can be seen that the materials obtained under three different voltages are mixed phases and not completely delithiated. The characteristic peaks can be attributed to FePO<sub>4</sub> (PDF# 37-0478), and LiFePO<sub>4</sub> (PDF# 81-1173), in which the FePO<sub>4</sub> phase is more obvious. There are sharp and obvious characteristic crystal diffraction peaks near 20.1 °, 25.4 °, 30.4 ° and 36.2 °, which are consistent with FePO<sub>4</sub>. Although it is a mixed

phase, it can be seen that at 2.0 V, the diffraction peak intensity ratio is stronger than at 1.5 V and 2.5 V, indicating that the intensity of the phase is relatively high, and the crystallinity of the material is better. XRD results indicate that 2.0 V is the best voltage to realize lithium removal.

The SEM images of the LiFePO<sub>4</sub> after delithiation at different voltages are shown in Fig. 2. At 1.5 V, the shape and size of the particles are different from those of 2.0 V and 2.5 V. The particles are larger and gather in a cluster.

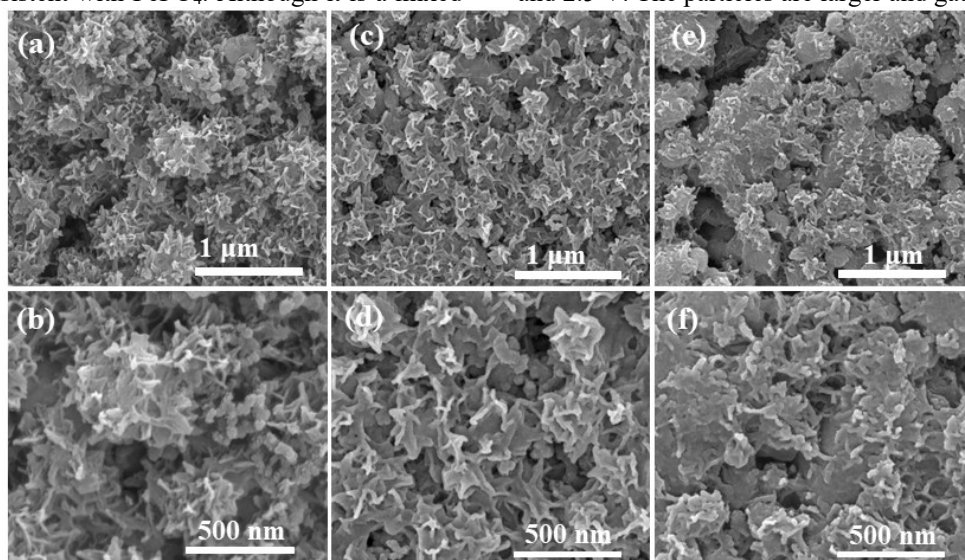


Fig. 2 SEM images of LiFePO<sub>4</sub> cathode materials with different magnifications after delithiation at different voltages. (a-b) 1.5 V; (c-d) 2.0 V; (e-f) 2.5 V

Nanostructured sheets appeared in all the materials under voltage. At 1.5 V, the sheets are small and composed of more rods. At 2.0 V, the sheet structure is mainly composed of large specific surface area. As the voltage increased to 2.5 V, the sheet structure gradually

become smaller and the aggregation degree is looser. Therefore, it is speculated that the lamellar structure of the material obtained at 2.0 V has a larger specific surface area. The specific surface area has a certain influence on the subsequent electrochemical performance.

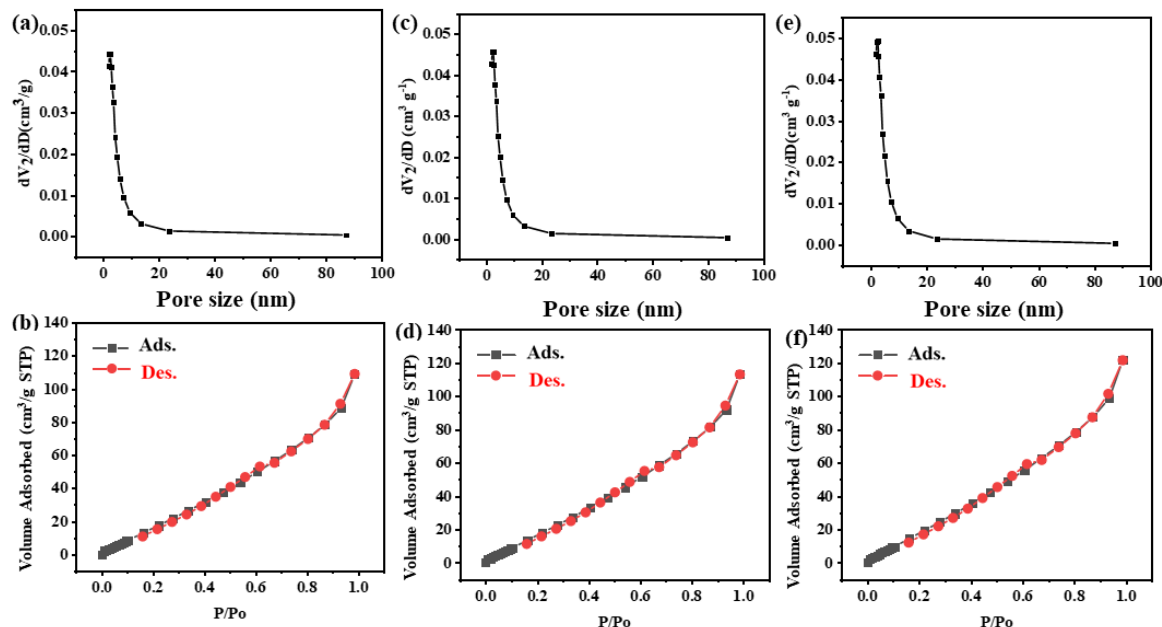


Fig. 3 The pore size distributions and adsorption-desorption curves of  $\text{LiFePO}_4$  cathode material after delithiation at different voltages. (a-b) 1.5 V; (c-d) 2.0 V; (e-f) 2.5 V

Fig.3 shows that the specific surface areas of the electrode obtained at 1.5 V, 2.0 V and 2.5 V are 168.271, 209.083 and 187.984  $\text{m}^2\text{g}^{-1}$ , respectively. It can be seen that the specific surface area of the material is large when the dissociation voltage is 2.0 V. The large specific surface area of the material obtained at 2.0 V contributes to the full contact between the electrolyte and the electrode, which has a certain influence on the electrochemical performance.

Figs.4a-e shows the first discharge curves of different delithiated materials at different rates. At 0.1 C, the initial discharge voltage is close to about 3.35 V. The discharge specific capacities of the delithiated materials obtained at 1.5 V, 2.0 V and 2.5 V are 118.3, 137.7 and 133.2  $\text{mAh g}^{-1}$ , respectively. At 0.2 C, the same voltage of 2.0 V and 2.5 V is 3.32 V, while the initial voltage of 1.5 V is 3.38 V.

The corresponding discharge capacities of the three delithiation specific capacity electrodes are 107.7, 133.9 and 121.0  $\text{mAh g}^{-1}$ , respectively. At 0.5 C, the initial discharge voltage of 2.0 V is the highest, followed by 2.5 V, and finally 1.5 V. The corresponding discharge capacities of the three delithiation specific capacity electrodes are 87.5, 111.4 and 101.9  $\text{mAh g}^{-1}$ , respectively. At 1.0 C, the initial discharge voltage of 1.5 V is the highest, followed by 2.0 V, and finally 2.5 V. The discharge curve corresponding to the 1.5 V delithiated electrode still retains the discharge platform, which may be due to the incomplete delithiation and thus maintains the original structure. The corresponding discharge capacities of the three delithiation specific capacity electrodes are 62.9, 109.0 and 90.8  $\text{mAh g}^{-1}$ , respectively, and the maximum gap is 47  $\text{mAh g}^{-1}$ .

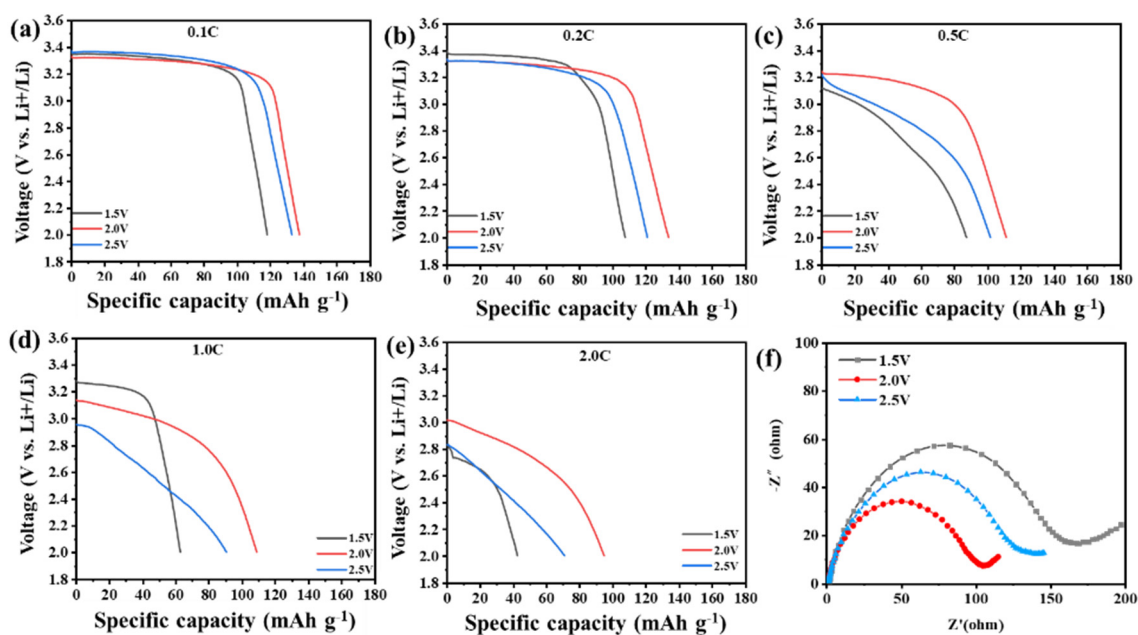


Fig. 4 The discharge capacity curves of  $\text{LiFePO}_4$  after delithiation at different voltages. (a) 0.1 C; (b) 0.2 C; (c) 0.5 C; (d) 1.0 C; (e) 2.0 C; (f) Corresponding EIS curves.

At 2.0 C, the initial voltage corresponding to 2.0 V is the highest, which is 3.05 V, followed by 2.5 V, and finally the initial platform voltage corresponding to 1.5 V is 2.84 V, respectively. The corresponding discharge capacity of the three delithiation specific capacity electrodes are 42.6, 95.0 and 42.6  $\text{mAh g}^{-1}$ , respectively. And the corresponding EIS curves indicate that the  $R_{ct}$  value ( $\sim 98 \Omega$ ) of 2.0 V is lower than that of 2.5 V ( $\sim 125 \Omega$ ) and 1.5 V ( $\sim 160 \Omega$ ) (Fig. 4f).

## 4. Conclusion

In this work,  $\text{LiFePO}_4$  was delithiated by the electrochemical delithiation method with  $\text{Na}_2\text{SO}_4$  solution as electrolyte. Under this condition, the delithiated material has a surface area of up to  $209.083 \text{ m}^2\text{g}^{-1}$  and a high specific capacity of  $137.7 \text{ mAh g}^{-1}$  (0.1 C) at the optimal delithiation voltage of 2.0 V. This work provides a new direction for the efficient delithiation of LIB cathode materials.

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