Recovery and Reuse of Spent LiFePO₄ Batteries

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ABSTRACT

LiFePO₄ has been widely used as cathode materials for lithium-ion battery with the development of electric vehicles and energy storage, which will cause a large quantities of spent batteries. Recycling of spent lithium-ion batteries can not only reduce impact on environment, while also bring some economic benefits. In this paper, parameters of recycling process were studied. The results showed that leaching efficiency of Iron ion was controlled by simultaneous interface chemical and surface diffusion reaction. The discharge specific capacities of resynthesized LiFePO₄/C at 0.1C, 1C, 2C, 5C and 10C were 151.4, 141, 139.8, 132.4 and 115.6 mAh/g, respectively.

Keywords: spent batteries; lithium iron phosphate; recycling

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely used in portable electronic devices, such as mobile phones, laptops and other small-sized electrical equipment, and are increasingly demand for large-scale applications [1-2]. Olivine type lithium iron phosphate (LiFePO₄, LFP) is one of excellent cathode materials for application in large electric vehicles or energy storage facilities with its outstanding safety, good cycling performance, non-toxicity and structural stability [3]. The increasing consumption of LIBs in electronic equipment and electric vehicles, leading to boost growth of spent LiFePO₄ batteries [4-5]. Although spent LIBs are typical hazardous solid wastes, rich metal resources in spend batteries can also be reused rationally [6-8].

In general, recycling of spent LIBs mainly focus on cathode material. At present, there are many kinds of recycling methods, which are broadly divided into the following processes: disassemble batteries, separate cathode material and current collector, recovery and reuse of valuable metals, etc. [9-10]. Leaching and extraction are essential to recover metal ions effectively from cathode material, which is considered as the most important fraction of LIBs. Separation and purification process mainly include chemical precipitation method, solvent extraction method and electrochemical method. Chemical precipitation method need to add specific precipitant to leachate and control the pH of solution to precipitate metal ions for obtaining metal compound product [11]. However, it is inevitable that some ions will co-precipitate during the precipitation process, resulting in impurities of the finally obtained precipitated product. Furthermore most research focus on recovery process parameters, rarely on the reuse of recovered product and analysis on corresponding mechanism.

In this paper, we demonstrate an efficient recycling process by recovering iron and phosphorus selectively and regenerating FePO₄ and LiFePO₄ successfully. The parameters of separating cathode material from aluminum foil, leaching process, leaching kinetics and properties of regenerated FePO₄ and LiFePO₄ were studied.

2. EXPERIMENTAL

2.1. Materials and reagents

Spent LiFePO₄ batteries were collected by our lab. First, batteries were discharged by immersing in 5wt% sodium chloride solution to avoid self-ignition and short-circuiting. Then dismantled the batteries and separated into cathode scraps, anodes scraps, plastic separators and metal cases. All reagents were analytical grade and all solutions were prepared with deionized water.

2.2. Experimental

The cathode scraps were cut into small pieces and dissolved in alkaline solution with ultrasound-assisted dissolution to separate the cathode material from aluminum foil. The leaching efficiencies of aluminum foil under factors including reaction temperature, concentration of alkaline, reaction time, solid-to-liquid ratio (S/L, cathode scraps to alkaline solution, g/L) were studied. The cathode material was collected by filtration and it was subsequently calcined in air at 600 °C for 1h to burn off organics and conductive agent. Harmful gases were managed by an exhaust gas-recovery unit during the calcination process. The leaching experiments were performed in a 500 mL three-necked round bottom flask, which was installed with a reflux condenser. A heating bath with magnetic stirrer was used to ensure optimized kinetics condition and temperature control. During the experiments, a certain amount of filter residue was added into a 250 mL mixed solution including sulfuric acid (H₂SO₄) as a leaching solution and hydrogen peroxide (H₂O₂) as a reductant. The leaching efficiencies of Fe and P under factors including temperature, concentration, reaction time, solid-to-liquid ratio (S/L, filter residue to mixed solution, g/L), the volume ratio of leachate to reductant agent (H₂SO₄/H₂O₂ (v/v), L/L) were considered.

After leaching, the leachate which contained Fe³⁺ and P⁵⁺ was analyzed and adjusted to molar ratio of 1:1. Then NH₃·H₂O was added to the leachate to adjust pH value and regenerated FePO₄ precursor was obtained, which was filtered, washed, dried, and calcined. Finally

FePO$_4$ precursor was mixed with Li$_2$CO$_3$ and carbon sources to resynthesize LiFePO$_4$/C cathode material.

2.3. Characterization

Crystal structures of resynthesized FePO$_4$ and LiFePO$_4$/C were examined by X-ray diffract meter (XRD) with Cu Kα radiation. The concentration of Al^{3+}, Fe^{3+} and P^{5+} in leaching solution were measured by inductively coupled plasma (ICP). Morphology of resynthesized FePO$_4$ and LiFePO$_4$/C was observed by scanning electron micrometer (SEM). Electrochemical performance of resynthesized LiFePO$_4$/C was measured by constant current charge and discharge testing (CT2001A) at cut off voltage 2.5-4.2V at 0.1C, 1C, 2C, 5C, 10C respectively.

3. RESULTS AND DISCUSSION

3.1. The leaching parameters

Cathode scraps were cut into small pieces and dissolved in alkaline solution with ultrasound-assisted dissolution to separate cathode material from aluminum foil. During separating procedure, leaching efficiency of aluminum foil under the factors e.g. temperature, concentration of alkaline, reaction time and solid-to-liquid ratio (S/L, cathode scraps to alkaline solution, g/L) are studied.

The effect of concentration of alkaline on leaching of aluminum was tested at 60 °C for 60 min and S/L was 20g/L. As shown in Fig.1 (a), the leaching efficiency increased from 78wt% to 98.5wt%, with concentration increased from 0.1 to 1.0 mol/L, which implied higher concentration of alkaline may help destroy the structure of aluminum foil. However, the leaching efficiency did not increase significantly with the concentration of alkaline increased beyond 1.0 mol/L. Therefore, concentration of 1.0 mol/L was employed in the subsequent leaching experiments. As shown in Fig. 1(b), the effect of reaction time on leaching of aluminum was tested at 1mol/L(concentration of alkaline) for 60 min and S/L was 20g/L. About 85wt% of aluminum was leached within 60 min, and the leaching efficiency reached 98wt% after 80 min, indicated that leaching equilibrium was reached within 80 min. Therefore, in the subsequent experiments, the leaching time was set to be 80 min. The effect of temperature on leaching of aluminum was tested at 1mol/L (concentration of alkaline) for 80 min and S/L was 20g/L. As shown in Fig. 1(c), the leaching efficiency increased from 86.3wt% to 99wt% when the temperature increased from 30 °C to 60 °C. This can be attributed to the fact that higher temperature could accelerate mass transfer. In addition, the leaching efficiency increased slowly when temperature was beyond 60 °C. Hence, in this study, reaction temperature of 60 °C was determined. As shown in Fig.1 (d), the effect of S/L on leaching of aluminum was tested at 1mol/L (concentration of alkaline) and 60 °C. The leaching efficiency decreased from 98wt% to 71wt% with the S/L increased from 10 g/L to 50 g/L and it decreased rapidly when S/L was 30g/L. It could be attributed to the fact that insufficient reaction. Therefore, 30 g/L of S/L was employed in the leaching experiments.

In summary, aluminum foil could be completely separated under the optimized condition: concentration of alkaline was 1mol/L, temperature was 60°C, reaction time was 80min and S/L was 30g/L.

After the aluminum foil was completely dissolved, the cathode material was collected by filtration, washed several times with deionized water and dried it was subsequently calcined in air at 600 °C for 1 h to burn off organics and conductive agent. The filtrated residue was added into mixed solution including H$_2$SO$_4$/H$_2$O$_2$ as a leaching solution. After reacting for a preset period, the mixture (leachate and reaction residue) was filtered immediately. During leaching experiments, the effects of a range of factors including temperature, concentration of acid, solid-to-liquid ratio (S/L, filtrated residue to mixed solution, g/L) and the volume ratio of leachate to reductant agent (H$_2$SO$_4$/H$_2$O$_2$ (v/v), L/L) were
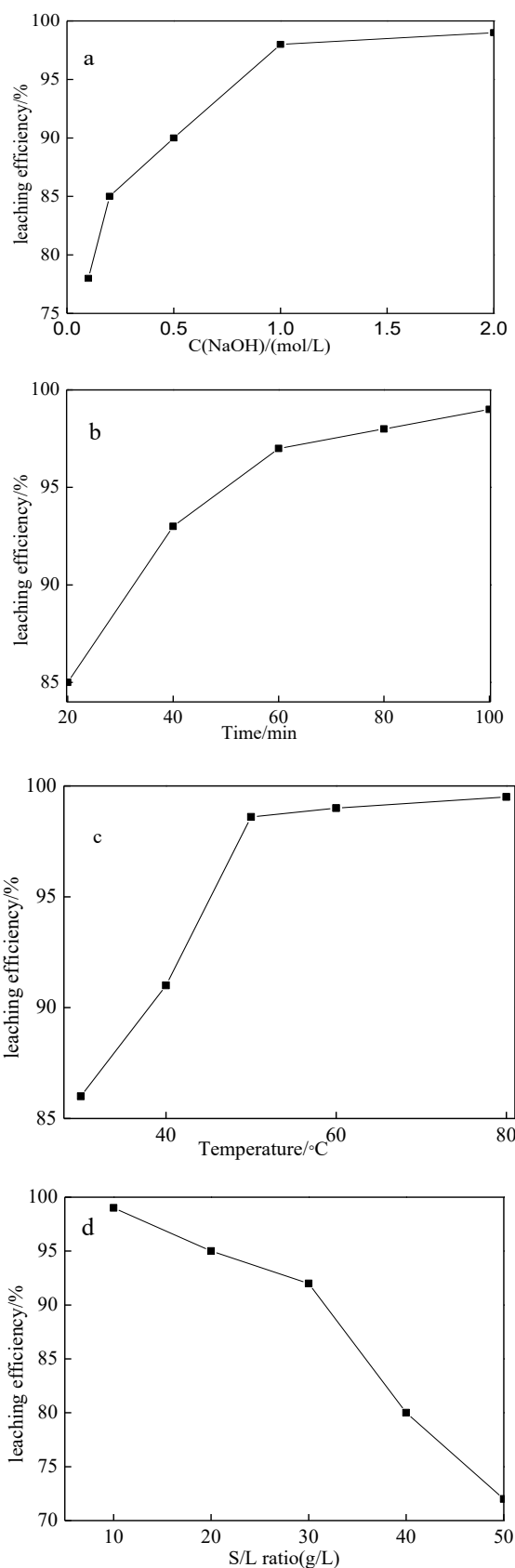

Figure 1. The leaching efficiency of aluminum at diffident reaction conditions; a: concentration of alkaline/(mol/L), b: time/min, c: temperature/°C, d: S/L (g/L)
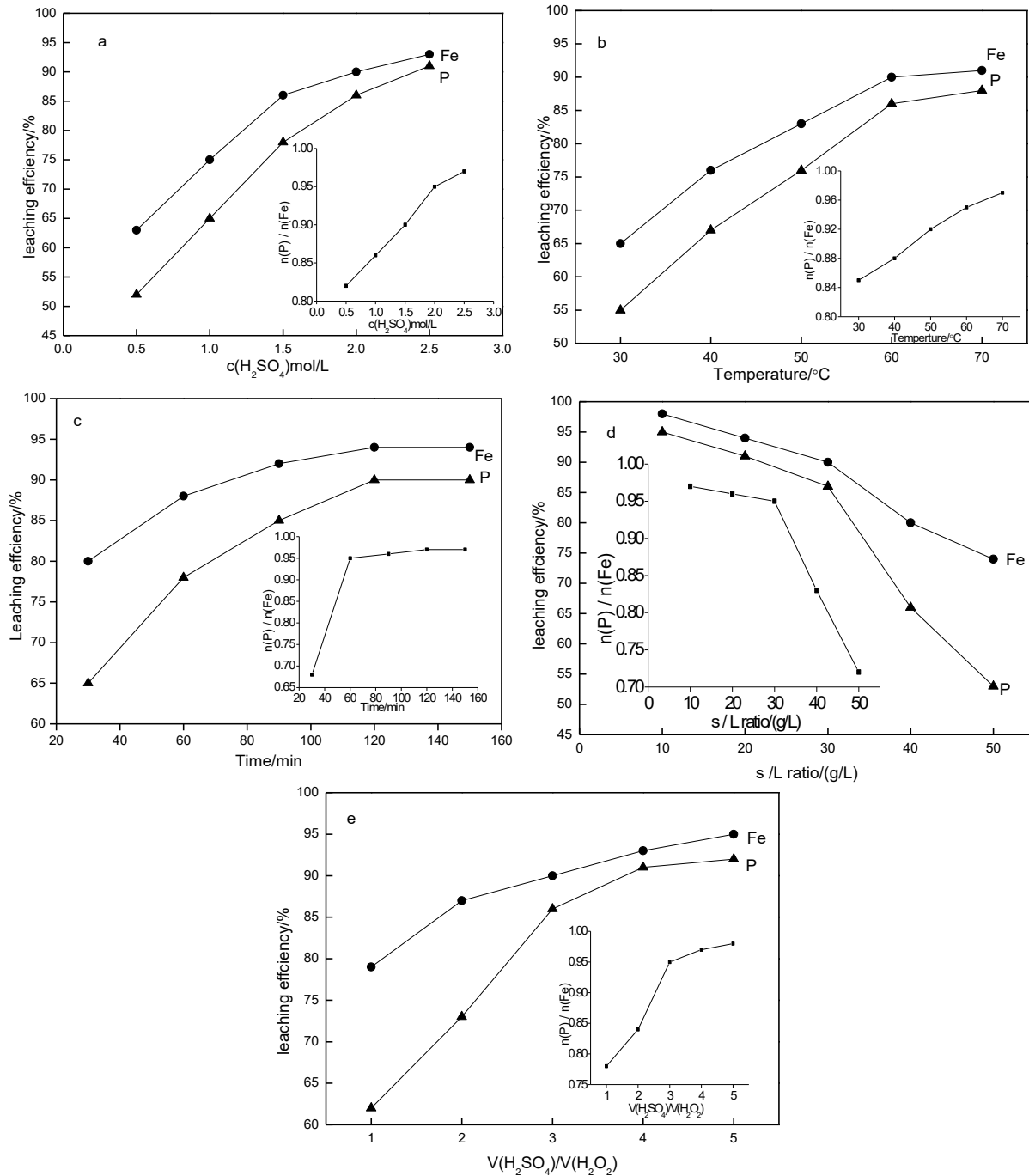
Figure 2. The leaching efficiency of Fe, P and molar ratio at diffident parameters; a:concentration /(mol/L), b: temperature/°C, c: time/min, d:S/L (g/L)e: H_2SO_4/H_2O_2 (v/v,L/L)

considered. The leaching efficiency of Fe^{3+}, P^{5+} and molar ratio of Fe/P under each reaction condition were shown in Fig.2.

The effect of concentration of mixed solution on the leaching of Fe and P and molar ratio of Fe/P was tested at 50 °C for 60 min, S/L was 10g/L and H_2SO_4/H_2O_2 (v/v) was 3. As shown in Fig.2 (a), the leaching efficiencies increased with increasing concentration, which implied that reaction between protons and lithium ions is promoted in higher concentration. Fe/P was approximate to 0.96 when concentration reached 2.0mol/L, indicating that most of Fe and P have been released from the spent LiFePO₄. Therefore, concentration of 2.0mol/L was employed in

the subsequent leaching experiments. The effect of temperature on the leaching of Fe and P and Fe/P was tested at 2.0 mol/L for 60 min, S/L was 10 g/L and H_2SO_4/H_2O_2 (v/v) was 3. As shown in Fig. 2(b), the leaching efficiencies of Fe and P were 91wt% and 86wt% at 60°C, with temperature increased did not cause a significant change in leaching efficiencies. Since leaching processes of metal ions are of endothermic in nature, high reaction temperature create favorable thermodynamic condition during leaching. In this study, a temperature of 60 °C was used. Reaction time are also important factor influencing the leaching efficiencies of metal ions. The experiments were carried out at acid
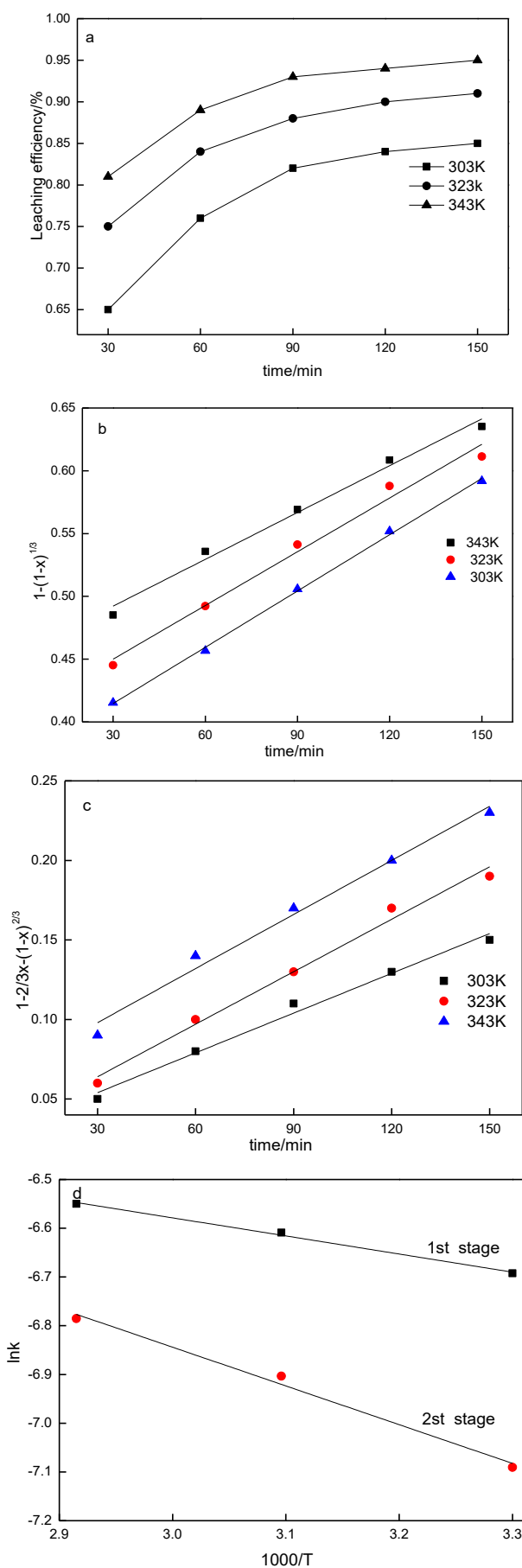
concentration of 2.0mol/L, reaction temperature was 60 °C, S/L was 10 g/L and H_2SO_4/H_2O_2 (v/v) was 3. As shown in Fig.2(c), the leaching efficiencies increased with increasing reaction time and Fe/P was approximate 0.98 when reacted for 80 min, indicated that leaching equilibrium was reached within 80 min. Therefore, in the subsequent experiments, leaching time was set to be 80 min. To examine the effect of S/L on the leaching efficiency, as given in Fig.2(d), experiments were carried out at acid conversation of 2.0 mol/L, the temperature was 60 °C for 80min, and H_2SO_4/H_2O_2 (v/v) was 3. It can be found that S/L has an unfavorable effect on the extraction rate of Fe and P from the spent $LiFePO_4$. The leaching efficiencies of Fe and P were decreased with increasing of S/L, when S/L is less than 30 g/L, the leaching efficiency was achieved about 90wt% for Fe and 85wt% for P. In general, a small amount of S/L could be beneficial for the increasing of leaching efficiency. S/L of 30 g/L was employed in the leaching experiments. The effect of the H_2SO_4/H_2O_2 volume ratio on dissolution of Fe and P were carried out at acid conservation of 2.0 mol/L for 80 min, the temperature was 60 °C, and the solid-liquid ratio was 30 g/L. As shown in Fig.2 (e), the leaching efficiencies of Fe and P with increasing H_2SO_4/H_2O_2 volume ratio more than 90wt% of Fe and P could be recovered when the H_2SO_4/H_2O_2 volume ratio was 4. Therefore, the H_2SO_4/H_2O_2 volume ratio of 4 was employed in the leaching experiments.

In summary, filtered residue was then dissolved in the following solution: concentration of acid was 2 mol/L, reaction temperature was 60 °C and reaction time was 80 min, S/L was 30 g/L ,and volume ratio (H_2SO_4 /H_2O_2, v/v) was 4.

3.2. Apparent kinetics of leaching

To determine the most probable mechanisms involved in the leaching of spent $LiFePO_4$ using the electrochemical cathode reduction method [12,13], kinetics analysis was carried out at various temperatures and leaching durations under concentration of acid was 2 mol/L, volume ratio H_2SO_4/H_2O was 4, S/L was 30 g/L .

Based on the characteristics of the leaching process, the leaching of single particle of spent $LiFePO_4$ involves the following steps [14, 15]: (1) diffusion of reactive ions within the liquid film, (2) diffusion of reactive ions through the product layer of the particle up to the surface of the inner core, (3) chemical reaction at the surface of the inner core. According to previous studies, the surface chemical reaction model (Eq. (1)) and the diffusion control model (Eq. (2)) can be applied to analysis the control mechanism of the leaching process. The two models are presented as follows:

$$1 - (1-x)^{\frac{1}{3}} = k_1 t \tag{1}$$

$$1 - \frac{2}{3}x - (1-x)^{\frac{2}{3}} = k_2 t \tag{2}$$

Where x is the fraction of the leaching efficiency, k_1 and k_2 are the rate constants of the control model, and t (min) is the leaching time.

As shown in Fig. 3(a), the leaching of the spent $LiFePO_4$ can be divided into two stages: the first stage was for 30-90 min, and the second stage was for 90 -150 min. We fitted the leaching data of the two stages based on the above models. It was clear that Eq. (1) (surface chemical reaction control) and Eq. (2) (diffusion control) exhibit the best fitting relevance for the first stage (Fig. 3(b)) and second stage (Fig. 3(c)),

Table 1. The kinetic fitting parameters of iron ion

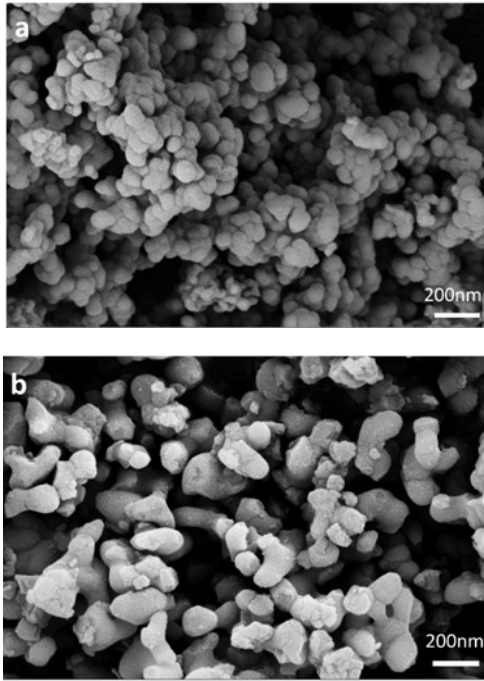| T	1st stage		2st stage	
	k_1	R^2	k_2	R^2
303K	0.00124	0.9857	0.000833	0.9852
323K	0.00149	0.9985	0.00111	0.9867
343K	0.00143	0.9826	0.00113	0.9818
lnk	-0.3712	0.9914	-0.7946	0.9818

Figure 3. The kinetic analysis of iron ion

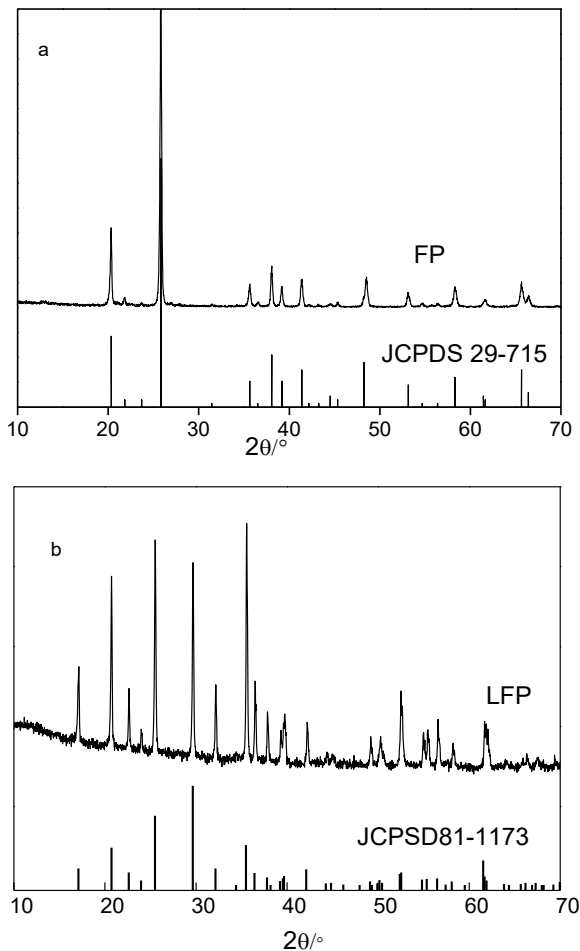Figure 4. The SEM images of resynthesized FePO₄ and LiFePO₄/C

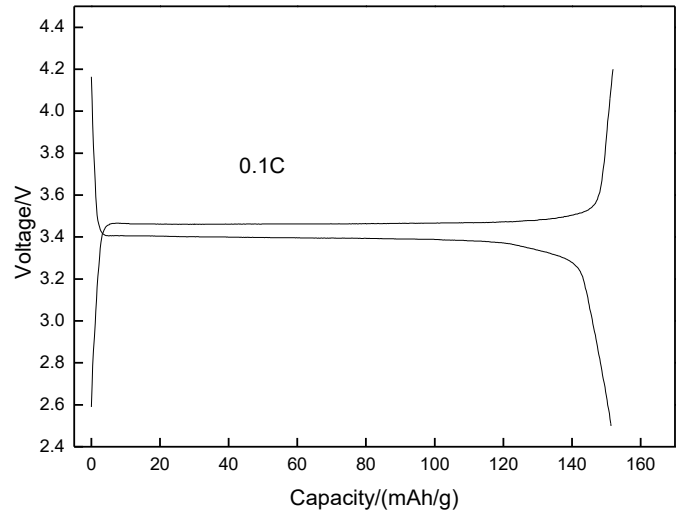Figure 5. The XRD patterns of resynthesized FePO₄ and LiFePO₄/C

Figure 6. Initial charge and discharge curves of resynthesized LiFePO₄/C at 0.1C rate

respectively. This indicates that the leaching of Fe is controlled by a surface chemical reaction within a leaching time of 90 min. Thereafter, the leaching process may be controlled by the diffusion of reactive ions. To explain clearly the control mechanism, the apparent activation energy was calculated using the empirical Arrhenius law (Eq. (3)):

$$k = Ae^{-\frac{Ea}{RT}} \tag{3}$$

Where k is the rate constants, R is the gas constant (8.314 J/K·mol), A is the preexponential factor, and E_a is the apparent activation energy.

By plotting lnk vs. 1000/T in Fig. 3(d) and Table 1, the apparent activation energy of the two stages can be obtained as 74.72 kJ/mol and 11.65 kJ/mol, respectively. This implies that the leaching of Fe at the second stage was controlled by a combination of the surface chemical reaction and diffusion [16, 17].

3.3. The analysis of regenerated FePO₄ and LiFePO₄
(1) SEM

The morphology of resynthesized FePO₄ and LiFePO₄/C are shown in Fig. 4. The particles of resynthesized FePO₄ are spherically distributed, the surface of the particles is relatively smooth, the particle size distribution is about 50-100 nm. The particles of resynthesized LiFePO₄/C are well-dispersed and ranged from 100 to 200nm, which was caused by the high temperature reaction.

(2) XRD

The XRD patterns of resynthesized FePO₄ and LiFePO₄/C cathode material are shown in Fig.6. All diffraction peaks of resynthesized FePO₄ can be indexed to pure FePO₄ with an orthorhombic olivine-type structure (JCPDS card no.29-715). Resynthesized LiFePO₄/C cathode material could be indexed to pure LiFePO₄ with an orthorhombic olivine-type structure (JCPDS card no. 81-1173). The strong diffraction peaks in the pattern suggest a perfect crystallinity of the synthesized materials with no impurities.

(3) The electrochemical performance

Fig.6 shows the initial charge-discharge profiles of resynthesized LiFePO₄/C at 0.1C at cut off voltage 2.5-4.2V (vs. Li/Li⁺).The initial discharge capacity of the prepared LiFePO₄/C is 151.4 mAh/g, the initial charge specific capacity is 152 mAh/g, and the charge and discharge efficiency is 99.6%.
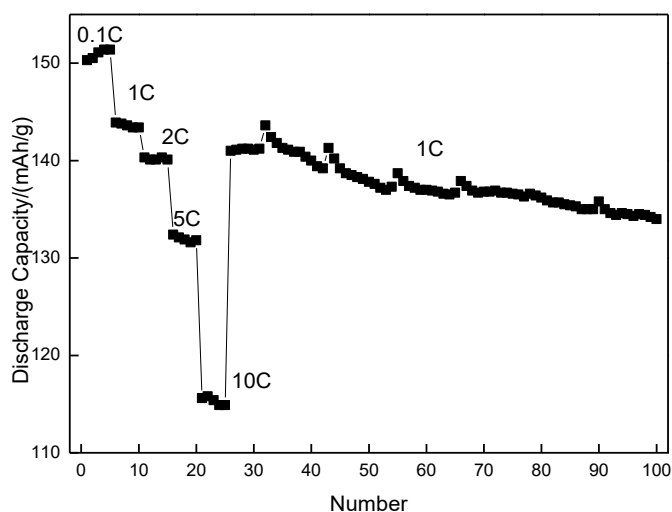
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Figure 7. Cycling performance of resynthesized LiFePO$_4$/C at different rates

The resynthesized LiFePO$_4$/C material showed excellent high-rate capability and good cycle performance, which is displayed in fig.7. The discharge specific capacities of this prepared LiFePO$_4$/C can stabilize at 151.4, 141, 139.8, 132.4 and 115.6 mAh/g at high rates of 0.1C, 1C, 2C, 5C and 10C, respectively. The discharge capacity can still retain 134 mAh/g after 100 cycles at 1C and the capacity retention is 95%.The results indicated that resynthesized LiFePO$_4$/C cathode material has low polarization and good electrical conductivity.

4. CONCLUSION

With comprehensive investigation and evaluation of the recovery process of LiFePO$_4$ from spent LiFePO$_4$ batteries, conclusion can be drawn as follows:

(1) A systematic understanding on the effects of various parameters on recovery of Al^{3+}, Fe^{3+}, P^{5+} and Fe/P were carried out. It can be noticed that the cathode material could be completely separated from aluminum foil under the optimized conditions of leaching (1mol/L of NaOH, S/L of 30 g/L, 60 °C, 80min). Fe^{3+}, P^{5+} could be dissolved with a high recovery efficiency of more than 90% and85% under the optimized conditions of leaching (2 mol/L of H$_2$SO$_4$, H$_2$SO$_4$ /H$_2$O$_2$ of 4, S/L of 30 g/ L, 60 °C , 80 min) .

(2)The apparent kinetics of leaching showed that the leaching of Fe at the second stage was controlled by a combination of the surface chemical reaction and diffusion.

(3) The resynthesized FePO$_4$ and LiFePO$_4$/C had good crystallinity and particle dispersion. The discharge specific capacities of resynthesized LiFePO$_4$/C batteries were 151.4, 141, 139.8, 132.4 and 115.6mAh/g, respectively at 0.1 C, 1C, 2C, 5C and 10C. After 100 cycles at 1C rate, the discharge specific capacity could reach 134mAh/g, and the capacity retention rate was about 95%.

5. ACKNOWLEDGMENTS

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