
A facile recovery process of cathodes from spent lithium iron phosphate batteries by using oxalic acid

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Abstract

A facile and novel leaching process has been developed to dispose spent lithium iron phosphate (LiFePO₄) batteries. In this work, oxalic acid is selected as leaching reagent to recover lithium as resources and remove phosphorus of LiFePO₄ benefiting from its low natural effects. The physical properties of spent cathode materials (before leaching) and residues (after leaching) were characterized by X-ray diffraction (XRD) and scanning electronic microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS). The total amounts of Li and Fe were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The process was under the condition of a 0.3 mol·L⁻¹ oxalic acid concentration, a temperature of 80 °C, a reaction time of 60 min and a solid/liquid ratio of 60 g·L⁻¹. It could effectively precipitate ~92% ferrum in terms of FeC₂O₄·2H₂O from LiFePO₄, with the leaching efficiency of Li up to 98%. This method demonstrates a new strategy for dealing with spent lithium iron phosphate batteries with low cost and low environmental effect.

Keywords: spent lithium-ion batteries; iron phosphate cathode; leaching; oxalic acid; precipitation

1. Introduction

Lithium ion batteries (LIBs) have been used widely in modern society since first produced by SONY in 1991[1]. LIBs can be applied not only on portable electronic equipment such as cell phones, laptop computers and digital cameras, but also on larger devices like electric vehicles (EVs), hybrid electric vehicles (HEVs) and uninterruptible power system (UPS). With the increasing use of LIBs-powered devices in our daily life, the safety of LIBs has been taken more and more attention especially for electric vehicles[2]. LiFePO_4 cathode materials are abundant, relatively environmentally benign, and also with excellent thermal stability. However, drawbacks such as low electronic conductivity, low volume energy density, and poor low temperature performance are necessary to be solved step by step and get better development in the future [3]. On the other hand, as dealing with other types of spent LIBs, the treatment of spent lithium iron phosphate batteries (LIPBs) cannot be ignored as well. Improper and irresponsible disposal of spent LIPBs will cause environmental problems due to the hazardous electrolyte and phosphorus in LiFePO_4 . These hazards can lead to eutrophication once getting into natural water. Therefore, it is necessary for the recovery of lithium from LiFePO_4 and harmless treatment of phosphorus. In this respect, however, only a few studies have been reported[4-6].

A simple thermal treatment method was proposed by calcining the spent LiFePO_4 cathodes at different temperature (400 °C, 500 °C, 600 °C) for 30 min under the flow of nitrogen gas. The product was mixed with styrene butadiene rubber (40 wt% in water) and sodium carboxymethyl cellulose (1 wt% in water) binder (3.14 wt%) at 5,000 rpm for 30 min in a homogenizer. After that, the separated LiFePO_4 active materials was obtained, and its XRD patterns showed no impurity phases[7]. Though this method is easy manipulating, the dispose of styrene butadiene rubber and sodium carboxymethyl cellulose may

lead to secondary pollutants. A hydrometallurgical process was developed to recycle LIBs economically which aimed at disposing mixed cathode materials including LiCoO_2 , LiMn_2O_4 , $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$, and LiFePO_4 . By adjusting pH, ferrum could get deposited from the mixture, leaving Mn^{2+} , Co^{2+} , and Ni^{2+} in solution. The Mn^{2+} , Co^{2+} , and Ni^{2+} could get recycled for synthesis cathode materials by co-precipitating method with addition of Li_2CO_3 [8]. This recycling process is viable for commercial adoption with high recovery efficiencies. However, it is probably inconvenient for adjusting the necessary concentration ratio of Co^{2+} , Ni^{2+} , and Mn^{2+} to 1 : 1 : 1 with additional CoSO_4 , NiSO_4 , and MnSO_4 in each batch of experiments.

The achievements on LiCoO_2 recovery are helpful for dealing with the recovery of LiFePO_4 from LIPBs. The pre-treatment is essential and important to all recycling process, with its aim to separate different component of spent batteries and concentrate valuable metals for recovery. Usually, it consists of crushing, screening, heat treatment, et al. Then the obtained spent materials will subject to the main recycling process, which are mainly based on three types: hydrometallurgical process[9-15], pyrometallurgical method[5, 16, 17] and bioleaching process[18-20]. However, the pyrometallurgical methods are not suitable due to its large energy consumption. As for bioleaching, concentrated metallic contents were considered to be toxic for cells which gradually decreased bacterial activity in the process[18]. In fact, lots of studies were focusing on hydrometallurgical methods which could be approximately classified into inorganic acid leaching[4, 21, 22], organic acid leaching[11-13, 23], chemical precipitation[12, 24-26], organic solvent extraction [9, 26, 27] and others. Through the analysis and comparisons, this process showed the advantage of recovery with simpler process flow, lower cost, less second pollution, and more energy-saving with high efficiency. Benefiting from these advantages,

we here proposed an economical and environmental friendly process using oxalic acid as leaching reagent. The different influence factors on leaching such as oxalic acid concentration, temperature, reaction time and solid/liquid ratio are discussed in detail in this paper.

2. Experimental

2.1. Materials and reagents

The A123-18650 cylindrical spent lithium iron phosphate batteries were collected from electronics market. N-methyl-2-pyrrolidone (NMP) was used to separate the cathode active materials from the aluminum foil. Aqua regia (3:1 HCl:HNO₃ ratio) was used to digest the spent LiFePO₄ powder extracted from the cathode at 90 °C. The obtained solution was analyzed for Li and Fe contents determination. Oxalic acid solution with different concentrations was used for leaching studies.

2.2. Preliminary treatment

To avoid short-circuiting or self-ignition, a discharge pretreatment was applied to remove the remaining capacity. Fig. 1 is a flow chart of the process designed in this work. The anodes and cathodes can be separated from spent LIBs by manually dismantling. Being immersed in NMP 1 h at 100 °C, the cathode active materials were fully detached from the aluminum substrates. After filtration and drying, the spent LiFePO₄ powders were calcined at 400 °C for 1 h to eliminate impurities, such as acetylene black and polyvinylidene fluoride (PVDF) binder. Then the obtained powders were grounded for 30 min in a planetary ball mill to increase leaching efficiency.

2.3. Metal leaching

The separated LiFePO₄ powder and oxalic acid solution were placed into a three-necked round-

bottomed flask reactor. The reactor was equipped with an impeller magnetic stirrer to assist leaching reaction and a vapor condenser to reduce the loss of water by evaporation. The flask was kept at a constant reaction temperature in a water bath during the leaching. To determine the optimum conditions, the operation variables were set as oxalic acid concentration ($0.1\text{--}1.5\text{ mol}\cdot\text{L}^{-1}$), temperature ($40\text{--}90\text{ }^{\circ}\text{C}$), reaction time ($10\text{--}120\text{ min}$) and solid/liquid ratio ($10\text{--}90\text{ g}\cdot\text{L}^{-1}$) at 300 rpm mixing speed. After leaching, the raffinate and insoluble residue were separated by filtration and washed with distilled water, resulting in a yellow green filtrate and a black residue. Then the black leach residues were filtered, dried and characterized.

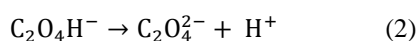
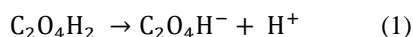
2.4. Analytical method

To determine the total amounts of lithium and ferrum, a sample of cathodic active material was dissolved completely in concentrated HNO_3/HCl (ratio:1/3) solution. After the digestion of the LiFePO_4 powder sample, the total amounts of Li and Fe were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The leaching efficiency is defined as the ratio of the amount of a chemical species in the leachate to the total amount of that species in the original cathode powder. The cathode materials and leaching residues were characterized using X-ray diffraction (XRD Rigaku, $\text{Cu-K}\alpha$). Scanning electron microscopy (SEM, Hitachi S-570) combined with energy dispersive X-ray spectroscopy (EDS) was used to analyze the morphology. Thermogravimetric analysis (TGA) was performed on a Seiko TGA/STDA 6200. The measurements were performed in flowing air atmosphere, with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

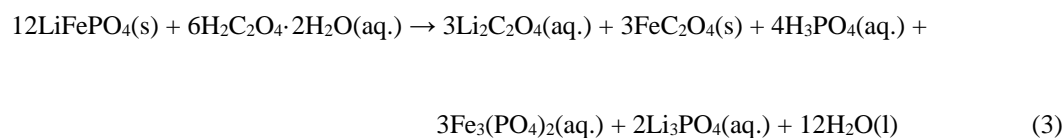
3. Results and discussion

3.1. Leaching of waste LiFePO_4

Oxalic acid is a relatively strong acid among organic acids. At room temperature, the equilibrium constant (K_a) for loss of the first H^+ is 5.37×10^{-2} ($pK_a = 1.27$). The loss of the second H^+ leads to the yields of oxalate ion with an equilibrium constant of 5.25×10^{-5} ($pK_a = 4.28$). The dissociation reaction of oxalic acid can be described in following equations:



Oxalic acid is consist of two carboxyl groups which are directly connected, in which the oxygen of O-H and C=O in the carboxyl groups has electron-withdrawing effect with carbon atoms. Although conjugated system of the carboxyl can help some for charge distribution, the electron-withdrawing effect is not able to be eliminated. When two carboxyl groups are directly connected, the electron clouds shift toward C-C bond leading to unstable bonding and much easier to be oxidized and broken. Therefore, Fe(II) of $LiFePO_4$ will not be oxidized during the leaching and precipitate with oxalate to produce FeC_2O_4 . During leaching, most of the $LiFePO_4$ will be dissolved to precipitate as FeC_2O_4 , and other possible products such as $Li_2C_2O_4$, Li_3PO_4 and $Fe_3(PO_4)_2$ are soluble in acid medium. The leaching reaction mechanism of waste $LiFePO_4$ with $H_2C_2O_4 \cdot 2H_2O$ solution are proposed as follow:



The leaching process is a solid-liquid reaction. The efficiency could be affected by several factors, such as acid concentration, leaching temperature, reaction time and solid/liquid ratio. The molar ratio of Li to Fe in the spent materials was close to 1:1, indicating no significant loss of metals in the spent

LiFePO₄ material. To optimize the operational conditions, we conducted a series of experiments to comprehensively investigate the influences from those factors.

3.1.1 Effect of oxalic acid concentration

The effect of oxalic acid concentration on leaching efficiency was studied in the range from 0.1 to 1.5 mol·L⁻¹ at temperature of 80 °C, reaction time of 60 min, and solid/liquid ratio of 60 g·L⁻¹. As shown in Fig. 2, with increased oxalic acid concentration, the leaching efficiency of Li increased significantly till 98% at 0.3 mol·L⁻¹, then stayed stable over 98% from 0.3 to 1.25 mol·L⁻¹, but finally decreased to 86% at higher concentration of 1.5 mol·L⁻¹, probably due to the resistance from high concentration of ions in the solution. Meanwhile, the leaching efficiency of Fe was lower than that of Li, indicating that most of Fe was precipitated out. It decreased with the oxalic acid concentration increased from 0.1 to 0.3 mol·L⁻¹, and then kept about 10% from 0.3 to 1.5 mol·L⁻¹. Oxalic acid could provide proton and acid radicals to leach metals. With increased concentration, it could release more proton to promote the dissolution of LiFePO₄. At the same time, ferrous ion could precipitate with oxalate to form FeC₂O₄. In consideration of the follow up treatment to separate Li and Fe from the leaching solution, high Li and low Fe leaching efficiencies are desirable. Therefore, the suitable choice of oxalic acid concentration is 0.3 mol·L⁻¹.

3.1.2 Effect of temperature and reaction time

Fig. 3 shows the influence of temperature and reaction time on leaching efficiency with the conditions of oxalic acid concentration of 0.3 mol·L⁻¹, and solid/liquid ratio of 60 g·L⁻¹. In general, the leaching efficiency of Li (Fig. 3a) increased with the increasing temperature and reaction time. It increased evidently at beginning and then remained stable. With longer reaction time, oxalic acid solution could

mix with the LiFePO_4 powder more sufficiently to promote the solid-liquid reaction. At the temperature of $80\text{ }^\circ\text{C}$, the Li leaching efficiency increased rapidly from 78% to 98.7% due to longer reaction time. However, there was no benefit for reaction time longer than 60 min. On the other hand, the reaction time showed very little influence on the leaching efficiency of Fe as shown in Fig. 3(b), which was kept about 8.3% without obvious fluctuations from 10 to 120 min. Consequently, 60 min is the optimal reaction time for the leaching efficiency of both Li and Fe.

After reacting for 60 min, the leaching efficiency of Li increased from 93% to 98.7% with temperature increased from 40 to $70\text{ }^\circ\text{C}$, and stayed stable when the temperature is over $70\text{ }^\circ\text{C}$. On the contrary, the leaching efficiency of Fe decreased. The high temperature successfully activates the reactants and thus accelerates reactions, which is mainly attributed to the endothermic reactions. In addition, temperature has more effect on Fe than Li due to the enhanced ionization degree of oxalic acid. At higher temperature, more oxalate ions were released to react with Fe ions to form precipitations. However, the 13% efficiency of Fe at $70\text{ }^\circ\text{C}$ was not a desirable result. At the temperature of $80\text{ }^\circ\text{C}$, the Li leaching efficiency was 98% while the Fe leaching efficiency was 8%. Since there was only 1% improvement of the Li leaching efficiency by increasing 10 degrees (from 80 to $90\text{ }^\circ\text{C}$), the temperature of $80\text{ }^\circ\text{C}$ is a suitable selection in consideration of both leaching efficiency and energy consume.

3.1.3 Effect of solid/liquid ratio

The effect of different solid/liquid ratio from 10 to $90\text{ g}\cdot\text{L}^{-1}$ on the leaching efficiency are presented in Fig. 4. During the leaching processes, the temperature was maintained at $80\text{ }^\circ\text{C}$, the leaching time was set at 60 min, and the oxalic acid concentration was fixed at $0.3\text{ mol}\cdot\text{L}^{-1}$. The results indicate that the leaching efficiency of Li and Fe decreased as the solid/liquid ratio increased. Actually, the leaching

efficiency of Li stayed unchanged about 97% when solid/liquid ratio increased from 10 to 60 g·L⁻¹, and decreased at the range between 60 g·L⁻¹ and 90 g·L⁻¹. The low solid/liquid ratio with high Li leaching efficiency resulted from the adequate photon amount for leaching reaction. However, the leaching efficiency of Fe decreased when solid/liquid ratio increased from 10 to 50 g·L⁻¹ and then kept stable about 8% with the solid/liquid ratio higher than 50 g·L⁻¹. The possible reason for the high Fe leaching efficiency at low solid/liquid ratio was due to the dissolution of FeC₂O₄ precipitation in the excessive oxalic solution. Apparently, a solid/liquid ratio of 60 g·L⁻¹ was optimal for both throughput and leaching efficiency.

3.2 Characterization of spent cathode materials and leach residues

Fig. 5 shows XRD patterns of the leach residues as well as the cathode materials obtained in pretreatment. The XRD patterns of spent cathode materials were presented in Fig. 5(a), and the characteristic peaks of LiFePO₄ as crystalline structure were clearly identified. Some weak peaks of FePO₄ were observed as well overlapping with the LiFePO₄ ones. After leaching, most of the LiFePO₄ was dissolved since its intensity is almost invisible in XRD patterns, as shown in Fig 5(b). Meanwhile, it can be seen that the main part of leaching residues was FeC₂O₄·2H₂O, though with characteristic peaks of impurity H₂C₂O₄·2H₂O appeared as well.

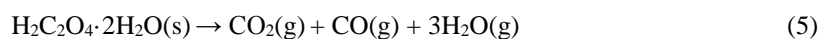
Fig. 6 shows scanning electron micrographs (SEM) of spent cathode materials and the leach residues. Obviously, the morphology of cathodic materials changed after leaching. The spent LiFePO₄ cathodes showed nanoscale particles about 200~500 nm in diameter. The particle size of residues became larger with rod like shape, which is the typical morphology of oxalates. Meanwhile, surface scan of EDS was applied to analyze the distribution of elements of the two samples and the results were shown in Fig. 6

as well. The reduction of phosphorus was evident by comparing the elements distribution in Fig. 6 (a) and (b). According to Equation (3), it could be concluded that phosphorus existed in the form of phosphate ions in the solution.

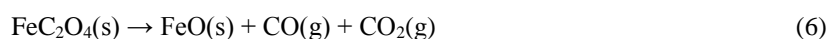
After filtration of leaching solution, lithium ions in the raffinate can be extracted by ionic sieve[28, 29]. And then calcium hydroxide can be applied to precipitate phosphate ion in order to avoid its eutrophication. The residues were sintered in air flow with a temperature range from ambient to 800 °C. As shown in Fig. 7, two peaks on the DTG curve stands for that the mass loss of residues was taking place in two stages. The first stage was the loss of crystalized water from 120 to 210 °C, and the second stage was the decomposition of FeC₂O₄ to FeO, CO and CO₂ from 210 to 300 °C. Theoretically, the mass loss of the first stage should be 20% if the residues were pure FeC₂O₄·2H₂O. However, the actual value was 2.4% more than theoretical one, which might result from the decomposition of impurities in oxalic acid. In addition, the total mass loss of FeC₂O₄·2H₂O was 59.6%, approaching 60% in theory. For the slight difference, the weight gain from FeO to Fe₂O₃ during second stage was a reasonable explanation.

Therefore, the reactions during thermogravimetry may be represented as follows:

First stage:



Second stage:



4. Conclusion

A novel environmental friendly recovery process has been developed for the recovery of valuable lithium element from cathodes of spent lithium iron phosphate batteries. The main processes contain manual dismantling, separation of cathode materials and oxalic acid leaching. Low cost oxalic acid is selected as leaching reagent to avoid secondary pollution. The lithium can be leached out from the bulk LiFePO_4 . The XRD results shown that the main composition of the leaching residues was $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, which is the raw materials for the synthesis of LiFePO_4 . During the leaching process, experimental conditions such as temperature, reaction time, acid concentration and solid/liquid ratio have been investigated. In consideration of using less energy and chemicals to achieve relatively better leaching efficiency, the optimal conditions were determined as $0.3 \text{ mol} \cdot \text{L}^{-1}$ oxalic acid, reaction temperature of $80 \text{ }^\circ\text{C}$, leaching time of 60 min and solid/liquid ratio of $60 \text{ g} \cdot \text{L}^{-1}$. Under such condition, around 98% Li was able to be extracted from the spent lithium iron phosphate batteries.

Acknowledgements

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(CERC-CVC).

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Figures and Tables

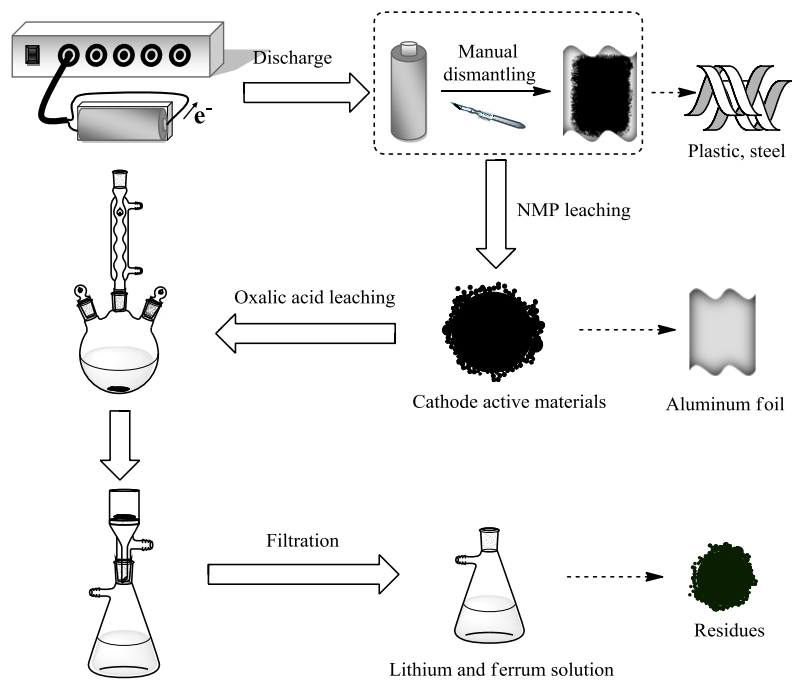


Fig. 1. Flow chart of the recovery of Li from spent lithium iron phosphate batteries.

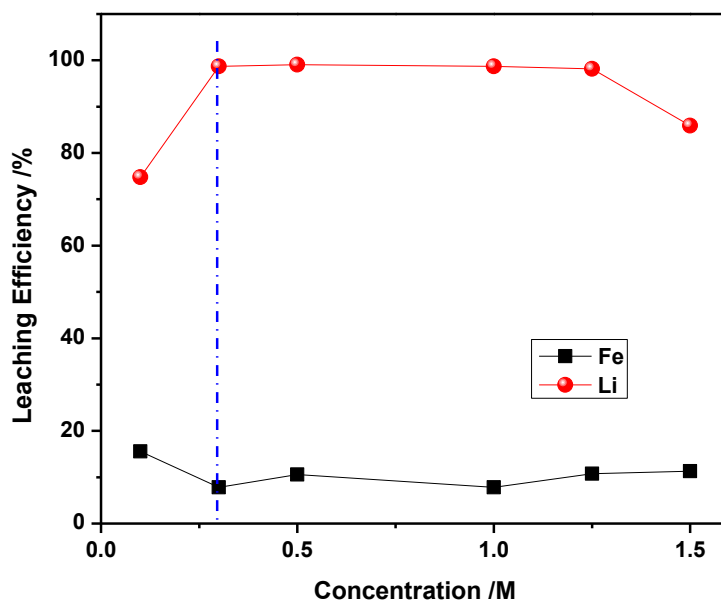


Fig. 2. Effect of oxalic acid concentration on the leaching of Fe and Li from spent LiFePO_4 ($T = 80\text{ }^\circ\text{C}$, $t = 60\text{ min}$, solid/liquid = $60\text{ g}\cdot\text{L}^{-1}$, agitation speed = 300 rpm).

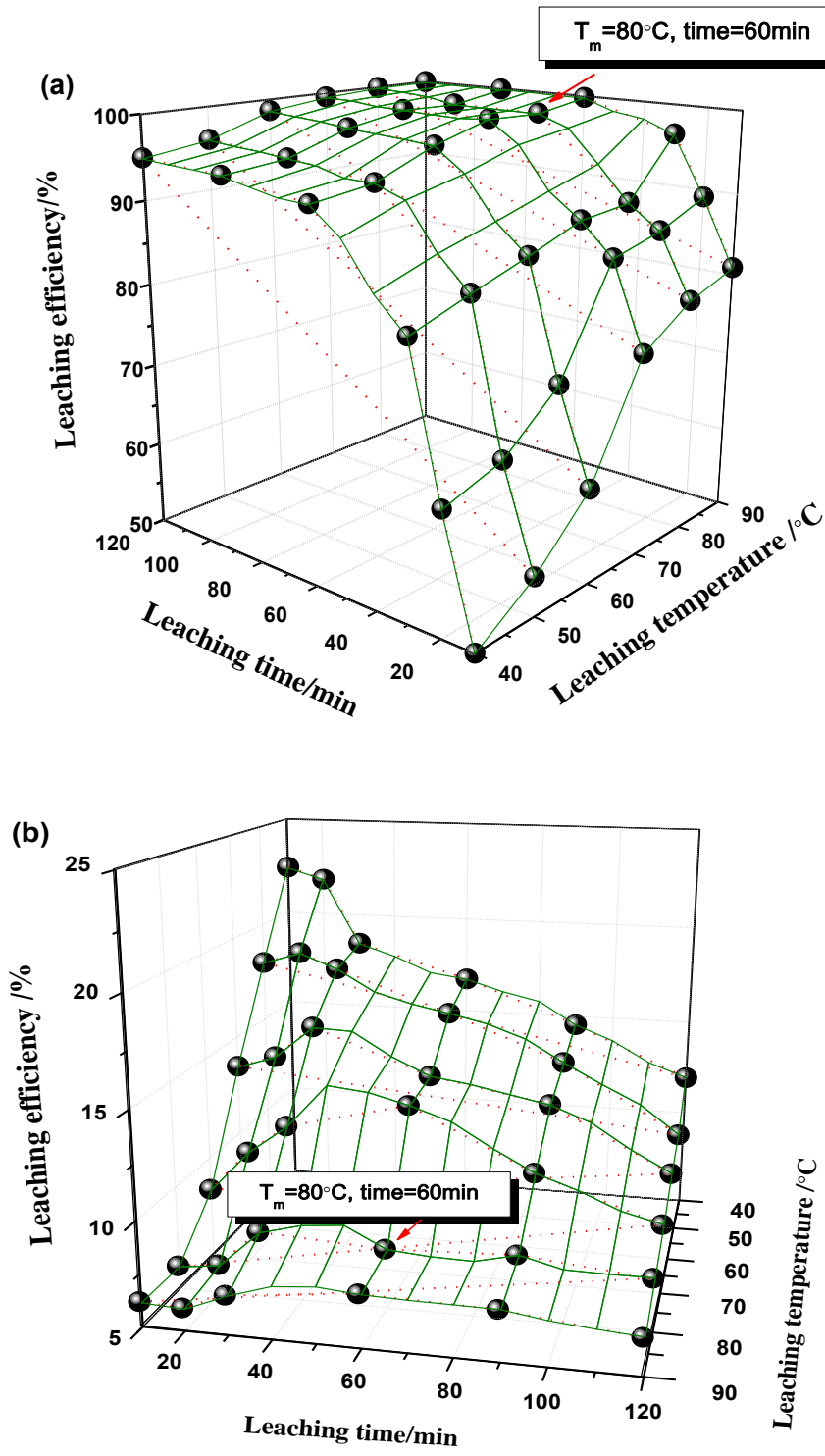


Fig. 3. Effect of temperature and reaction time on the leaching of Li (a) and Fe (b) from spent LiFePO_4 ($C = 0.3 \text{ mol}\cdot\text{L}^{-1}$, solid/liquid = $60 \text{ g}\cdot\text{L}^{-1}$, agitation speed = 300 rpm).

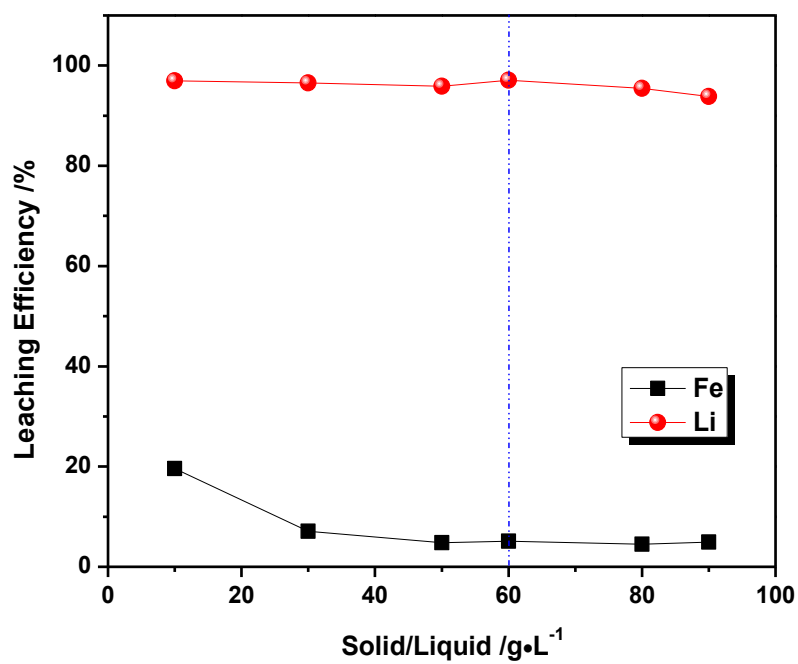


Fig. 4. Effect of solid/liquid ratio on the leaching of Fe and Li from spent LiFePO_4 ($C = 0.3 \text{ mol}\cdot\text{L}^{-1}$, $T = 80 \text{ }^\circ\text{C}$, $t = 60 \text{ min}$, agitation speed = 300 rpm).

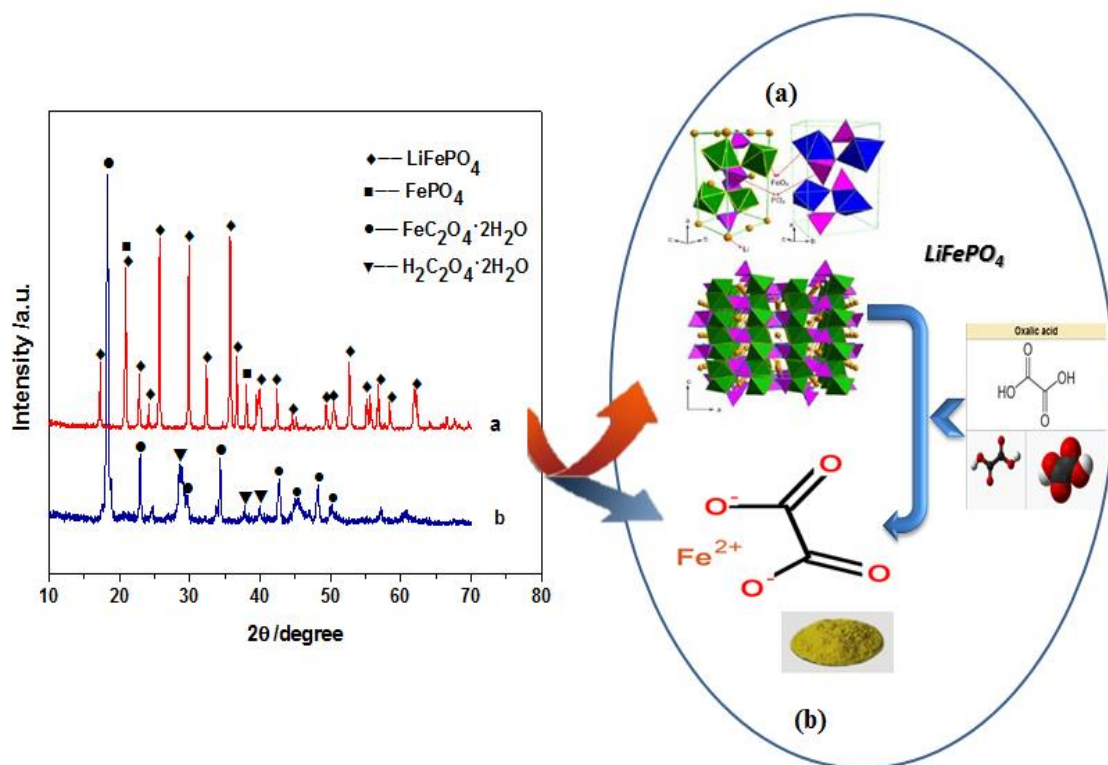


Fig. 5. XRD patterns of samples: (a) spent cathode materials after pretreatment, (b) the residues after leaching and filtration.

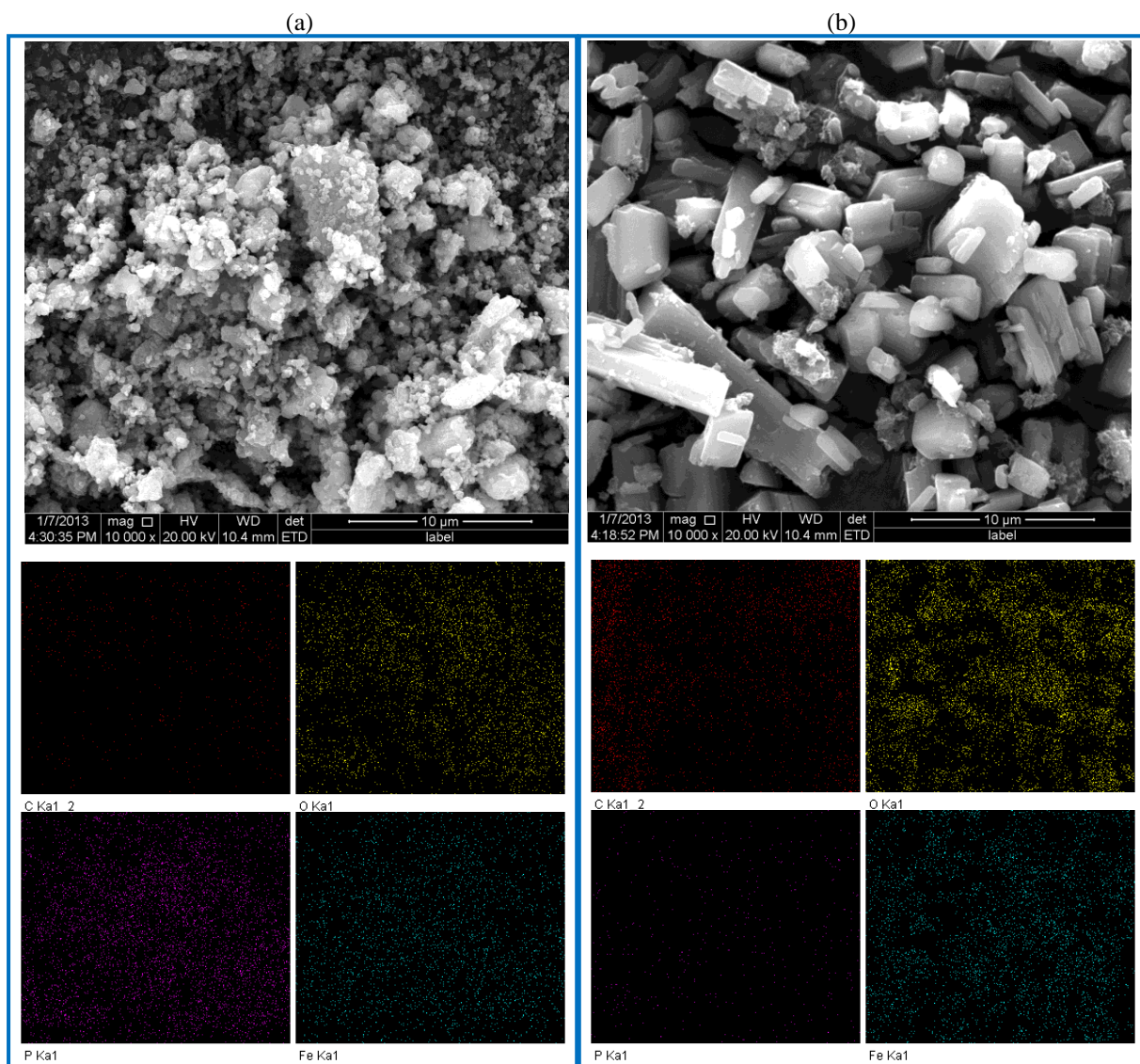


Fig. 6. SEM images and element distributions of samples: (a) cathode materials after pretreatment, (b) residues after leaching and filtration.

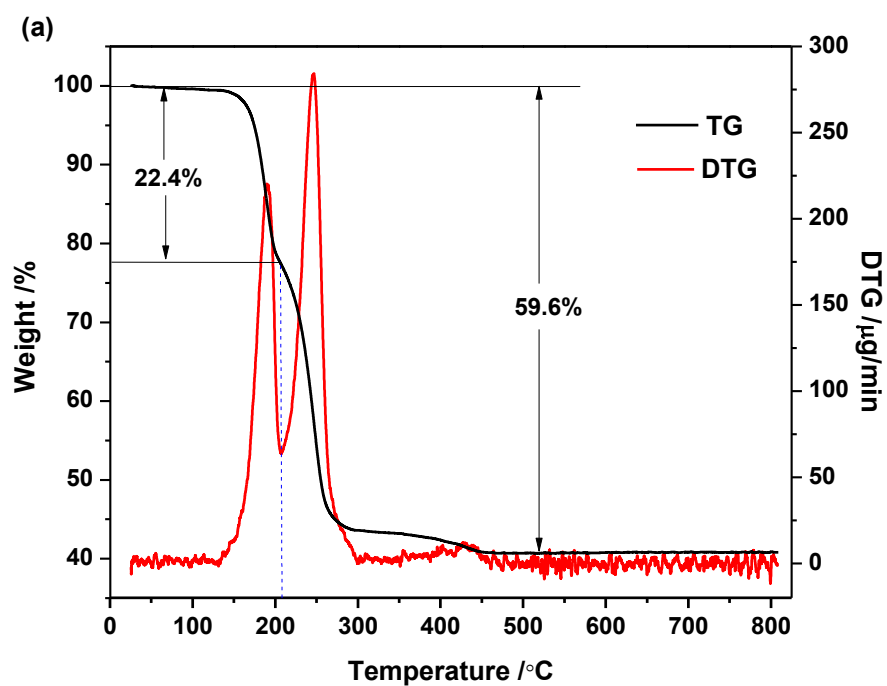


Fig. 7. TG/DTG curves (a) and thermogravimetry reactions (b) for the residues from ambient to 800 °C.