Separation of Cathode Material from Aluminum Plate by Ultrasonic Action using Fenton’s Reagent

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Abstract. Polyvinylidene fluoride (PVDF) has been used as a binder in lithium-ion batteries due to its high viscosity, which makes it difficult to separate the cathode material from the aluminum plate when recycling waste lithium-ion batteries. In this study, the peeling effect and mechanism of Fenton’s reagent on the cathode material and aluminum plate of spent lithium-ion batteries under the action of ultrasound has been researched. The results showed that when the ratio of Fe²⁺/H₂O₂ was 1:40, temperature was 45 °C, time was 35 min, and liquid-solid ratio was 50:1, the removal rate of cathode material was 98.52%. The combined action of Fenton’s reagent and ultrasonic cavitation oxidized or promoted PVDF to combine with lithium cobalt oxide to form COF₃, thereby separating the cathode material from the aluminum foil without changing the structure of lithium cobalt oxide cathode material. Nevertheless, this study may provide a processing method to separate the cathode material from the aluminum plate effectively.

1. Introduction

In 1990, lithium-ion battery was first identified as a new source of portable energy[1,2]. Lithium-ion batteries are widely used in consumer electronic products and considered to be the most suitable battery power for electric cars, because of its high-energy density, high-voltage, long life, no memory effect, light weight, and safety[3-5]. However, the life cycle of lithium-ion batteries is too short (1-3 years), which results in a high consumption of lithium-ion batteries. For instance, the quantity and weight of spent lithium-ion batteries in China will grow exponentially to 1.36 million tons in the world by 2025 [6]. The lithium-ion battery is composed of heavy metals, organic chemicals, and plastics. Generally, the cobalt content is 5 – 20 %, nickel content is 5 – 10 %, lithium content is 5 – 7 %, organic chemical content is 15 %, and plastic content is 7 %. Furthermore, batteries produced by different manufacturers will be slightly different in composition. However, the metal grade of spent lithium-ion batteries is usually higher than that of natural ores [7-9]. On the other hand, hazardous materials in spent lithium-ion batteries, such as electrolytes, can be potentially harmful to the ecosystem and human health [10-12]. Therefore, to alleviate the shortage of metal resources and protect the environment, it is necessary to realize the recycling or environmental treatment of spent lithium-ion batteries. Currently, there are several ways to recycle spent lithium-ion batteries, such as mechanical process [7,13], thermal treatment [14], mechanochemical process [15], acid leaching [1,16-18], alkali leaching [19], bioleaching [6,20], cryogenic grinding [21], and high-temperature activation [22]. However, owing to the presence of polyvinylidene fluoride (PVDF) adhesive, it is difficult to separate the cathode material from the aluminum plate effectively [23-25]. The adhesive can be removed via four main methods i.e.: solvent dissolution [26,27], ultrasonic action with N-methyl-2-pyrrolidone [28], heat treatment [29,30], and Fenton’s reagent treatment [31]. However, the organic solvent is poisonous,
N-methyl-2-pyrrolidone is expensive, and harmful gases are generated during thermal treatment, thereby limiting their applications. Fenton reagent is effective in cathode materials treatment and does not produce pollutants. Previous studies usually used Fenton’s reagent to dissolve PVDF in cathode materials and paid less attention to the removal effect of PVDF using Fenton’s reagent and ultrasonic action although the purity of aluminum foil recovered by ultrasonic action was higher than that achieved by the mechanical separation method. Therefore, this study analyzes the peel-off of cathode materials under the combined action of Fenton’s reagent and ultrasonic action [31].

2. Experimental method

2.1 Materials and methods

The main components of spent lithium-ion batteries are shown in Table 1. The spent lithium-ion batteries were first discharged in an NaCl solution (5 wt%) for 24 h and air dried before being taken apart manually to obtain the casing, cathode, anode, and separator. The Fenton’s reagent (Fe$^{2+}$/H$_2$O$_2$) was prepared by mixing FeSO$_4$·7H$_2$O solution (0.1 mol/L), H$_2$O$_2$ solution (0.1 mol/L), and deionized water in a certain proportion. Approximately 100 g/L of sodium hydroxide solution was used to dissolve the Al foil. For this study, analytically pure NaCl, FeSO$_4$, H$_2$O$_2$, and NaOH were obtained from the Tianjin Fuchen chemical reagent factory, Taishan chemical plant, Guoyao chemical reagent Co., Ltd., and Tianjin Damao chemical reagent factory, respectively.

Table 1. Main components of spent lithium-ion batteries

| Components     | Mass (g) | Wt%  |
|----------------|----------|------|
| Casing         | 7.714    | 22.56|
| Cathode$^1$    | 13.246   | 38.73|
| Anode$^2$      | 8.503    | 24.86|
| Separator      | 0.718    | 2.10 |
| Electrolyte    | 4.019    | 11.75|
| Total          | 34.200   | 100.00|

1 Including positive active material, conductive agent, binder, and aluminum foil
2 Including graphite, conductive agent, binder, and copper foil

The cathode materials, before and after ultrasonic action using Fenton’s reagent, were subjected to various investigations, such as mineralogy, morphology, and surface modification level. The phase analysis of cathode materials were performed on powder using an X-ray diffractometer (TTR-III, Rigaku Corporation, Japan) with Cu Kα radiation ($\lambda = 1.5406$ Å). The Fourier transform infrared spectroscopy (FTIR) spectra of the samples were recorded on a Nicolet 6700 (Thermofisher, USA) spectrophotometer in the range 400 – 4000 cm$^{-1}$. Additionally, X-ray photoelectron spectroscopy (XPS, Thermo Scientific Co., USA) was applied to observe the surface modification level. Furthermore, surface microscopic morphology and micro-area composition analyses were conducted by SEM (JSM-6360LV, JEOL, Japan) and EDX (GENSIS60S, EDAX, USA), respectively.

2.2 Fenton’s reagent and ultrasonic wave action

To study the effect of Fenton’s reagent and ultrasonic wave on the peel-off efficiency of cathode materials, a certain quality of Fenton’s reagent was treated with 50 ml of Fenton’s reagent (FeSO$_4$·7H$_2$O concentration of $2 \times 10^{-4}$ mol/L) with different Fe$^{2+}$/H$_2$O$_2$ molar ratios in a 250 ml beaker placed in an ultrasonic cleaner (KQ300E). When the reaction was completed, cathode materials and Al foil substrates were separated via sieving using a 400 mesh screen and dried at 55 ℃ for 2 h. The peel-off efficiency of cathode materials is given by Eq. (1):

\[
\text{Peel-off efficiency} = \left( \frac{m_1}{m_1 + m_2} \right) \times 100 \%
\]  

(1)
where \( m_1 \) represents the collected cathode materials, and \( m_2 \) indicates the cathode material attached to the Al foil obtained by dissolving the foil in 10% NaOH solution.

2.3 Synergistic mechanism of Fenton’s reagent and ultrasonic action

To verify the synergistic effect of the combined method further, ultrasonic action, Fenton’s reagent treatment, and combination of Fenton’s reagent and ultrasonic action were performed. Add Fenton reagent with \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio of 1:40 into the beaker with solid-liquid ratio of 1:50, and then stir with magnetic stirrer for 20 min while maintaining the temperature at 35°C. In the other two beakers with a solid-liquid ratio of 1:50, one is added with Fenton reagent with the ratio of \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) of 1:40, and the other is not added. Finally, the two beakers were placed in an ultrasonic cleaning machine for 20 min and the temperature was controlled at 35°C.

3. Results and discussion

3.1 Ultrasonic action with Fenton’s reagent

The effects of \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio, temperature, ultrasonic time, liquid-solid ratio, and treatment methods on the peel-off efficiency of cathode materials were studied. In all experiments, the ultrasonic frequency and ultrasonic power were fixed at 40 kHz and 200 W, respectively. The oxidation ability of Fenton’s reagent is closely related to the \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio in the solution. Hence, the effects of \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio on the peel-off efficiency of cathode materials were studied initially. Figure 1(a) shows the results. When the \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio increased from 1:20 to 1:40, the matching peel-off efficiency of cathode materials was enhanced from 42.56% to 76.87%. Additionally, with the increase in \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio, the peel-off efficiency of cathode materials decreased significantly. Therefore, the optimal \( \text{Fe}^{2+}/\text{H}_2\text{O}_2 \) ratio was determined to be 1:40.

This is because, in the aforementioned phenomenon of the Fenton’s reagent system, the hydroxyl radical (\( \cdot \text{OH} \)) is produced by hydrogen peroxide, and the proportion of hydrogen peroxide in Fenton’s reagent will directly affect the yield of \( \cdot \text{OH} \) and affect the removal rate. When the amount of hydrogen peroxide is low, the amount of hydroxyl radicals is less, which results in a low removal rate. However, when the amount of hydrogen peroxide is high, the excess hydrogen peroxide will react with hydroxyl radicals in the system to form \( \text{HO}_2^- \), thereby resulting in the decrease in removal rate [32-36]. Moreover, in the Fenton’s reagent system, ferrous ion acts as a catalyst. When the ferrous ion content is not high, it cannot catalyze hydrogen peroxide in time, and the amount of hydroxyl radicals in the system is low, which affects the removal effect. If the ferrous ion content is high, the content of hydroxyl radical will increase rapidly, and the excess hydroxyl radicals will have other reactions, see (3), (5), and (10). Finally, the hydroxyl radical affects the experimental results. The specific reactions are as follows.

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} + \cdot \text{OH} \quad (2)
\]

\[
\text{OH} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH} \quad (3)
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^- \quad (4)
\]

\[
\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (5)
\]

\[
\text{HO}_2^- + \text{Fe}^{2+} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}_2 \quad (6)
\]

\[
\text{HO}_2^- + \text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad (7)
\]

\[
\text{HO}_2^- \rightarrow \text{O}_2^- + \text{H}^+ \quad (8)
\]

\[
\text{RH} + \cdot \text{OH} \rightarrow \text{R} + \text{H}_2\text{O} \quad (9)
\]
The effect of temperature on the peel-off efficiency of cathode materials is shown in Figure 1(b). The peel-off efficiency of cathode materials was significantly affected by temperature, i.e., the increased temperature strengthened the separation between cathode materials and Al foil substrates by promoting the diffusion process and chemical reaction rate to accelerate the liquid-solid reaction rate from the perspective of kinetics. Furthermore, the peel-off efficiency increased significantly from 65.32 % to 92.56 % with the increase in temperature from 25 ℃ to 45 ℃. However, with a further increase to 65 ℃, the peel-off efficiency increased by only 2.4 %. Therefore, the selected optimal temperature was 45 ℃.

The effect of ultrasonic time on the peel-off efficiency of cathode materials is presented in Figure 1(c). The peel-off efficiency of cathode materials increased with increased time. When the time was increased to 35 min, the peel-off efficiency reached 98.52 %. Thus, it needed a certain reaction time to separate the cathode material from Al foil substrates effectively. However, when the ultrasonic time was further increased to 45 min, the peel-off efficiency did not have a remarkable increase. Thus, cathode materials and Al foil substrates were separated efficiently, and the optimal ultrasonic time was selected to be 35 min.

The effect of liquid-solid ratio on the peel-off efficiency of cathode material is shown in Figure 1(d). The result showed that the peel-off efficiency of cathode materials can be improved by increasing the liquid-solid ratio. When the liquid-solid ratio was increased to 50:1, the peel-off efficiency was 98.52 %, which suggested that a high liquid-solid ratio was beneficial to improve the effective contact between cathode materials and Fenton’s reagent and conducive to the oxidation of PVDF. When the liquid-solid ratio reached 100:1, the peel-off efficiency of cathode material did not improve significantly. However, the economic cost and energy consumption increased significantly. Furthermore, the results suggested that the optimum liquid-solid ratio was 50:1 at 45 ℃.

When the ratio of Fe²⁺/H₂O₂ was 1:40, temperature was 45 ℃, ultrasonic time was 35 min, and the liquid-solid ratio was 50:1, the peel-off efficiency of the cathode material was 98.52 %.

The effect of various methods on the peel-off efficiency of cathode materials is shown in Table 2 and Figure 2. It can be observed from Table 2 that the peel-off efficiency of cathode materials was 64.26 % when only Fenton’s reagent was used. Figure 2(1) shows that some cathode materials were present on aluminum foil. However, when only ultrasonic action was used, the removal rate of cathode materials was 45.34 %. Figure 2(2) shows that most cathode materials were present on the aluminum foil. When Fenton’s reagent and ultrasonic action were used together, the removal rate of cathode materials was 88.7 %. Figure 2(3) shows that a small quantity of cathode material was on the aluminum foil. The combination of Fenton’s reagent and ultrasonic action had a synergistic effect.
Figure 1. Factors affecting the separation efficiency of cathode materials:

(a) Fe^{2+}/H_2O_2 ratio; (b) temperature; (c) time; (d) liquid-solid ratio

Table 2. Effect of different methods on the peel-off efficiency of cathode materials

| Methods                  | Fenton   | Ultrasonic | Fenton-ultrasonic |
|--------------------------|----------|------------|-------------------|
| Removal rate (%)         | 64.26    | 45.34      | 88.72             |

Figure 2. Pictures of Al foil treated with different methods. (1) Treated with Fenton’s reagent; (2) treated with ultrasonic waves; (3) treated with Fenton’s reagent and ultrasonic waves
3.2 Characterization of ultrasonic-treated LiCoO₂

The ultrasonic-treated samples were analyzed by X-ray diffraction (XRD), FTIR, XPS, and scanning electron microscope coupled with an energy dispersive X-ray spectroscopy (SEM-EDS) to compare and ascertain the changes before and after ultrasonic wave treatment using the Fenton’s reagent. The ultrasonic-treated cathode materials were washed thoroughly using distilled water and dried at 55 °C for 2 h before being characterized using physical and mineralogical properties.

3.2.1. XRD analysis. To verify the changes in the cathode materials after ultrasonic action with Fenton’s reagent, the cathode materials were analyzed using XRD before and after the ultrasonic action. The XRD analysis results are shown in Figure 3. Figure 3(a) shows the diffraction peak of lithium cobalt oxide along with the diffraction peak of acetylene black at 2θ of 26.554 (acetylene black was added to the cathode material in the battery manufacturing process). After ultrasonic action with the Fenton’s reagent, the diffraction peak of graphite disappeared (Figure 3(b)), whereas the diffraction peak of lithium cobalt oxide increased. This finding can be explained by the removal of acetylene black from untreated cathode materials.

![XRD pattern of cathode materials: (a) untreated cathode materials; (b) after ultrasonic action with Fenton’s reagent](https://example.com/xrd-pattern.png)

**Figure 3.** XRD pattern of cathode materials: (a) untreated cathode materials; (b) after ultrasonic action with Fenton’s reagent (▽ – lithium cobalt oxide; ▲ – acetylene black)

3.2.2. FTIR spectral analysis. The XRD analysis results indicated the changes in acetylene black. The diffraction apex of PVDF was undetected because of low content or poor crystallization. Therefore, FTIR was used to further examine the changes in PVDF, and the results are presented in Figure 4. The absorption peak at 3448.62 cm⁻¹ was attributed to the remaining structural water. The evident characteristic absorption peaks of PVDF at 1403, 1186, and 877 cm⁻¹ were also observed in the treated cathode materials. These peaks indicated that the adhesive contained in the cathode was PVDF. However, the characteristic absorption peaks of PVDF in the cathode materials separated from the Al foil disappeared because most of the PVDF was dissolved in the ultrasonic action using Fenton’s reagent.
3.2.3. X-ray photoelectron spectroscopy. XPS was applied to analyze the surface modification level. The C1s spectra of the cathode materials before and after ultrasonic action with Fenton’s reagent are shown in Figure 5(a) and (b). The percentage of each chemical state is listed in Table 2. It can be observed that C existed on the surface of lithium cobaltite in various forms of the combined state. The comparison of Figure 5(a) and (b) revealed that −[CF₂CH₂]-n(PVDF), −[CF₂CH₂]-n(PVDF)/C–O, and carbon black decreased significantly, whereas C–C/C–H and C–COOR increased remarkably. Therefore, majority of PVDF present on the surface of lithium cobaltite was oxidized and decomposed into carbon dioxide and water with the action of ·OH generated from Fenton’s reagent and cavitation caused by ultrasonic waves [29,32]. This result is also supported by the change in −[CF₂CH₂]-N content in cathode materials from 22.64 % to 11.60 % after ultrasonic action.

![Figure 4. FTIR spectral analysis in PVDF](image)

### Table 3. Chemical states of graphite carbon on the surface of cathode materials before and after ultrasonic action

| Chemical State       | Peak BE/eV | At.% (untreated) | At.% (ultrasonic-action) |
|----------------------|------------|------------------|--------------------------|
| Carbon black         | 284.480    | 30.12            | 20.11                    |
| C–C/C–H             | 284.951    | 9.85             | 25.85                    |
| C–COOR               | 285.520    | 14.68            | 18.49                    |
| −[CF₂CH₂]-n/C–O     | 286.445    | 23.13            | 19.19                    |
| C=O                 | 288.005    | 6.63             | 7.30                     |
| O–C=O               | 290.035    | 4.23             | 3.24                     |
| −[CF₂CH₂]-n         | 290.672    | 11.32            | 5.80                     |

The F1s spectra of cathode materials before and after ultrasonic action with Fenton’s reagent are shown in Figure 5(c) and (d). The percentage of each chemical state is listed in Table 4. By observing the XPS spectra of F1s, it was found that there were four main forms of F on the surface of the treated positive electrode material, i.e., LiF at 685.1 eV, CoF₃ at 686.44 eV, C–F at 685.1 eV, P–F at 686.44 eV. The latter two belonged to the organic structure.

It can be observed from Figure 5(c), Figure 5(d), and Table 3 that the peak intensity of C–F decreased significantly, and the peak area decreased from 28.87 % to 21.94 %. While the peak intensity of CoF₃ increased significantly, the peak area increased from 12.37 % to 28.54 %. This indicated that during oxidation, part of F in PVDF combined with lithium cobaltite to form CoF₃, which reduced the surface binding energy, thereby demonstrating hydrophilic properties.

Therefore, the removal of PVDF includes two aspects, i.e., the direct oxidation and decomposition of PVDF to remove it from the surface of cathode materials, and the C–F bond of a part of PVDF opened, and F combined with lithium cobalt oxide to form a lower binding energy structure.
Table 4. Chemical states of carbon on the surface of cathode materials before and after ultrasonic action with Fenton’s reagent

| Chemical State | Peak BE/eV | At.% (untreated) | At.% (ultrasonic-treated) |
|---------------|------------|-----------------|--------------------------|
| LiF           | 685.1      | 40.24           | 29.13                    |
| CoF₃          | 686.44     | 12.37           | 30.54                    |
| C-F           | 687.85     | 28.87           | 18.38                    |
| P-F           | 688.44     | 18.52           | 20.94                    |

3.2.4. SEM-EDS analysis. SEM-EDS was used to identify the modified surface of lithium cobalt oxide particles, as shown in Figure 6. Figure 7 presents the results of cathode, which shows that the lithium cobaltite particles were irregular and uneven in shape. Additionally, flake-like adhesive, which may be PVDF compounds, electrolytes, and acetylene black from the EDS results of Point 1 in Figure 6, can also be observed between the lithium cobaltite particles. Additionally, PVDF or electrolyte may also adhere to the surface of lithium cobaltite particles due to the presence of C (Point 2 in Figure 4). After ultrasonic action with Fenton’s reagent, the coarse lithium cobaltite particles existed independently, whereas the fine particles reunited, as shown in Figure 7. The partial enlargement showed that the surface of lithium cobaltite particles was smooth, and no C was observed at Point 1 in Figure 7. Therefore, the PVDF or electrolyte on the surface of lithium cobaltite particles was removed. Nonetheless, the presence of C (Point 2 of Figure 5) suggested that the remaining PVDF agglomerated
the fine lithium cobaltite particles. This finding is consistent with the analysis results shown in Table 3.

Figure 6. SEM-EDS of untreated cathode materials

Figure 7. SEM-EDS of ultrasonic-treated cathode materials

Therefore, the PVDF in cathode materials can be oxidized and removed by ultrasonic action with Fenton’s reagent. Consequently, cathode materials and Al foil substrates were separated efficiently.

4. Conclusion
(1) When the ratio of Fe\(^{2+}/\text{H}_2\text{O}_2\) was 1:40, temperature was 45 °C, time was 35 min, and liquid-solid ratio was 50:1, the removal rate of cathode material was 98.52%.

(2) Fenton’s reagent and ultrasonic action have a synergistic effect, and the mechanism of PVDF modified by oxidation may result from two aspects, i.e., strong oxidant hydroxyl radical produced by Fenton’s reagent and cavitation effect produced by ultrasonic waves.

5. References
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Acknowledgments
We sincerely appreciate the Department of mineral engineering, School of minerals processing and Bioengineering, Central South University for providing laboratory and equipment for this experiment.