

Article

Recovery of Valuable Metals from Cathode—Anode Mixed Materials of Spent Lithium-Ion Batteries Using Organic Acids

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Abstract: Spent lithium-ion batteries (LIBs) contain a large number of valuable metals and will be an important strategic resource in the future. Therefore, recycling is extremely important. In this work, acetic acid and hydrogen peroxide were used as leaching agents to recover valuable metals (lithium, cobalt, nickel, manganese, and aluminum) from cathode and anode materials (LiCoO_2 , $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$, and C) of spent LIBs. The leaching solution and leaching residue were analyzed by inductive plasma optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The optimum experimental conditions were obtained by changing the concentration of acetic acid, solid–liquid ratio, reaction temperature, time, and the concentration of hydrogen peroxide reducing agent. Under the experimental conditions of 2 M acetic acid, 4.0 vol.% H_2O_2 , 20 g/L, and 70 °C for 40 min, the leaching rates of lithium, cobalt, nickel, manganese, and aluminum reached 98.56%, 94.61%, 96.39%, 97.97%, and 94.7%, respectively. This hydrometallurgical process is simple and environmentally friendly and maximizes the recovery of valuable metals from spent LIBs.

Keywords: acetic acid; leaching; spent lithium-ion batteries; metal recovery



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1. Introduction

LIBs have the advantages of long service life, small size, light weight, and no memory effect, and are widely used in electronic equipment and electric vehicles [1,2]. In the past decade, due to the significant reduction in manufacturing costs, LIBs now occupy a dominant position in the electric vehicle (EV) market, which not only reduces environmental pollution but also reduces energy consumption [3–5]. However, the use of LIBs in vehicles shows an explosive growth, and a large number of spent LIBs have been produced in recent years [6,7]. According to statistics, China will produce nearly 2.5 billion spent LIBs in 2020, with a mass of about 500,000 tons [8]. Every 4000 tons of spent lithium-ion batteries contain 1100 tons of heavy metals and more than 200 tons of toxic electrolytes [9]. If spent LIBs were directly landfilled, heavy metals may infiltrate into soil and groundwater, causing serious environmental pollution [10]. The recycling of spent LIBs has become very urgent for environmental protection and social needs. Spent LIBs typically contain 5~20% cobalt, 5~10% nickel, 5~7% lithium, 15% organic compounds, and 7% plastic [8,11]. The metal composition is very similar to the composition of natural ores, and the grade is even higher. If the valuable metals could be recycled, there would be significant economic benefits [12–15].

To deal with spent LIBs, pyrometallurgy, hydrometallurgy, and biometallurgy processes have been proposed one after another. The traditional pyrometallurgical process removes all acetylene black, organic electrolytes and binders, and generates large amounts of SO_2 , CO, HF, and other gases [16]. The biometallurgical process takes too long to treat the spent LIBs, so it is difficult for the bacteria to grow, and the efficiency is not high. Due to the advantages of high recovery efficiency, low cost, and low energy consumption, the hydrometallurgy process was considered to be an effective method to recover spent LIBs. To recover the metal from spent LIBs by the hydrometallurgical process, it is necessary to

transfer as many of the metal elements in the electrode material to the solution as possible. In the past, treatment of cathode materials mainly used hydrochloric acid [17], nitric acid [18], sulfuric acid [19], and other inorganic acids as leaching agents, so that metal elements existed in the respective solutions in the form of metal ions. Table 1 summarizes some of the experiments on the leaching of spent lithium-ion battery cathode materials with inorganic and organic acids [20,21].

Table 1. Leaching of spent LIBs using different leaching reagents.

Electrode Materials	Conditions	Leaching Efficiency (%)	Reductant	Ref.
Inorganic Acid Leaching				
LiCoO ₂	0.7 M H ₃ PO ₄ ; 1% vol H ₂ O ₂ ; 1 h; 40 °C; 50 g/L	>99% Li, >99% Co	H ₂ O ₂	[22]
LiCoO ₂	1 M HNO ₃ ; 1% vol H ₂ O ₂ ; 1 h; 80 °C; 20 g/L	~100% Li, ~100% Co	H ₂ O ₂	[23]
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	1 M H ₂ SO ₄ ; 4 h; 95 °C; 50 g/L	93.4% Li, 66.2% Co, 96.3% Ni, 50.2% Mn		[24]
LiCo _x Mn _{1-x} O ₂	1.75 M HCl; 2 h; 50 °C; 200 g/L	99.2% Li, 98% Co, 99% Mn		[25]
LiCoO ₂	2 vol.% H ₃ PO ₄ ; 60 min, 90 °C; 8 g/L	99% Li, 99% Co	H ₂ O ₂	[3]
Organic Acid Leaching				
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	1.5 M citric acid; 120 min; 80 °C; 20 g/L	99% Li, 91% Ni, 92% Co, 94% Mn	D-glucose	[26]
LiCoO ₂	1.5 M DL-malic acid, 40 min; 80 °C; 20 g/L	94% Li, 93% Co	H ₂ O ₂	[9]
LiCoO ₂	1.5 M succinic acid, 40 min; 60 °C; 15 g/L	96% Li, 100% Co	H ₂ O ₂	[27]
LiNi _{1/3} Co _{1/3} Mn _{1/3} O ₂	3 M trichloroacetic acid, 30 min, 64 °C; 50 g/L	93.0% Ni, 91.8% Co, 89.8% Mn, 99.7% Li	H ₂ O ₂	[28]

Nan et al. [19] used 3 M H₂SO₄ as a leaching agent, and the leaching rates of Co and Li in LiCoO₂ were more than 98% under the condition of S/L = 5 g/L and a temperature of 70 °C for 6 h. Lee and Ree [18] mixed HNO₃ with H₂O₂ as a leaching agent, in which H₂O₂ played a reducing role and could reduce Co³⁺ to Co²⁺, carried out reactions for 30 min under the conditions of 1 M HNO₃, 1.7 vol.% H₂O₂, S/L = 20 g/L, and a temperature of 75 °C, and the LiCoO₂ powder was almost completely dissolved. Granata [17], under optimum leaching conditions (1.75 M HCl, 2 h, 50 °C, S/L = 200 g/L), achieved leaching rates for the metals in LiCo_xMn_{1-x}O₂ of 99.2% (Li), 98% (Co), and 99% (Mn), respectively. It can be found that inorganic strong acids have very good leaching effects on metals in the cathode material, but harmful fumes and gases, such as Cl₂, SO₃, and NO_x, will be generated during the leaching process, and the spent liquid is also difficult to treat.

In order to overcome the pollution caused by inorganic acid leaching, the method of recycling spent LIBs using organic acids (ascorbic acid [29], citric acid [30], DL-malic acid [31], succinic acid [32], oxalic acid [28], etc.) as leaching agents has been studied. Chen et al. [33] treated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ with a mixed solution of citric acid and D-glucose as a leaching agent. Under conditions of 1.5 M citric acid, 120 min, 80 °C, and 20 g/L, the leaching rates for lithium, nickel, cobalt, and manganese reached the maximum rates, i.e., 99%, 91%, 92%, and 94%, respectively. Ning et al. [34], under optimum conditions (solid–liquid ratio of 1 M DL-malic acid, 4 vol.% and 5 g/L, 80 °C, 30 min), used ultrasonic-assisted leaching to greatly improve the leaching efficiency of metals. Nayaka et al. [32] leached cobalt at 80 °C for 6 h with 0.5 M glycine (leaching agent) and 0.02 M ascorbic acid (reducing agent), and the leaching rate for cobalt reached 95%. Although many technologies have been introduced to recover valuable metals from spent LIBs, their economic and environmental compatibilities were not satisfactory. In addition, the leaching rates for valuable metals, such as cobalt and lithium, need to be further improved. Therefore, our goal was to develop an economical and environmentally friendly recovery process that

avoids the use of inorganic acid leaching and improves leaching efficiency. Acetic acid is an organic monobasic weak acid, which is often used as a raw material in the manufacturing industry. It has the advantages of being easily soluble in water and relatively cheap.

In this work, the technological conditions for recovering lithium, cobalt, nickel, manganese, and aluminum from the cathode–anode mixture of spent LIBs using a mixed solution of acetic acid (leaching agent) and hydrogen peroxide (reducing agent) were studied. The effects of acid concentration, solid–liquid ratio, temperature, hydrogen peroxide concentration, and leaching time on metal recovery were investigated. A novel approach was proposed to develop an environmentally friendly and economical recycling process.

2. Experimental

2.1. Materials

The experimental raw materials used in this experiment were obtained from a chemical company. When recycling spent lithium-ion batteries, they directly crushed and calcined the materials of spent lithium-ion batteries, such as positive electrodes, negative electrodes, and metal plates, and ground them into mixed powders to reduce costs, as shown in Figure 1a. Acetic acid (AR) was obtained from Chengdu Kelong Chemical Co., Ltd. (Chengdu, China). Hydrogen peroxide (30%) was provided by the Chengdu Changlian Chemical Reagent Co., Ltd. Single-element standard solutions of lithium, cobalt, nickel, manganese, and aluminum were obtained from the China National Nonferrous Metals and Electronic Materials Analysis and Testing Center, and all solutions of specific concentrations were prepared or diluted with deionized water.

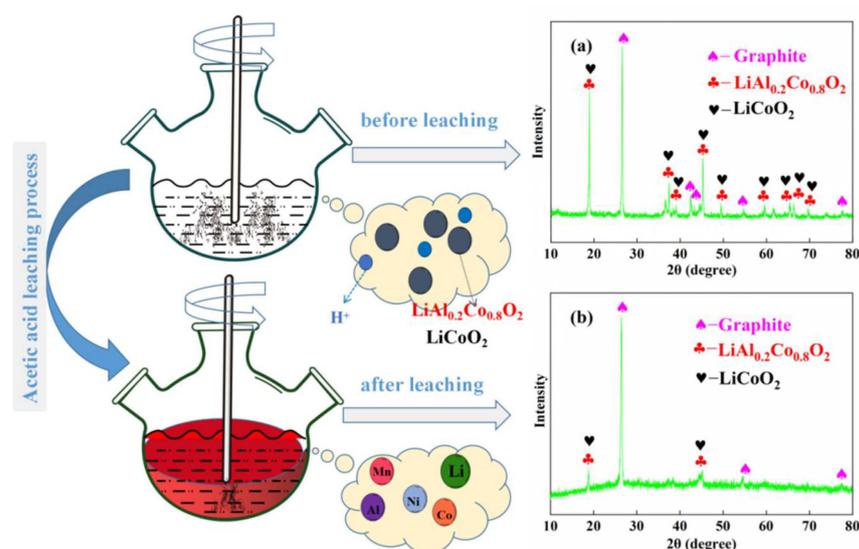


Figure 1. XRD patterns for:(a) electrode materials after calcination and grinding but before leaching and (b) black residues after leaching.

2.2. Metal Leaching

All leaching experiments were carried out in 250 mL three-neck round-bottom flasks and thermostatic water baths with temperature control facilities. The temperature was adjusted via the thermometer, controller, and sensor connected to the heater to improve temperature accuracy. The reaction device used a magnetic stirrer for stirring so that the leaching solution and the electrode material powder were in full contact, and the connected reflux condenser was able to reduce the loss caused by the evaporation of water at high temperatures. The optimum value for each factor was determined by the method of controlling variables. The ranges for each variable were as follows: 0.5–3.0 M leaching agent (acetic acid), 1.0–6.0 vol.% reductant (H_2O_2), solid–liquid ratio 5–30 g/L, time 10–60 min, temperature 30–80 °C (precision: ± 1 °C). After the reaction was completed, the product was filtered and washed to obtain a pink filtrate and a black residue.

2.3. Analytical Method

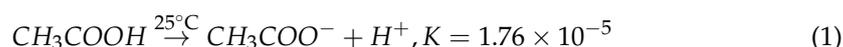
To determine the total amounts of lithium, cobalt, nickel, manganese, and aluminum in the samples, three groups of alkali fusion experiments were carried out and analyzed using an inductively coupled plasma atomic emission spectrometer (ICP-OES; ICAP7400, Thermo Scientific, Waltham, MA, USA). The results were averaged, and the chemical composition is shown in Table 2. The concentrations of various metal ions in the leaching solution were determined by ICP-OES to calculate the leaching efficiency, which was defined as the ratio of the number of components in the leaching solution to the total amount of metals in the sample. The leached residue was filtered, dried, weighed, and analyzed by X-ray diffraction (XRD6100, Shimadzu, Beijing, China, $\lambda = 1.5406 \text{ \AA}$) and scanning electron microscopy (SEM; Hitachi SU3500).

Table 2. Li, Co, Mn, Ni, and Al contents in the cathodic active material of the spent LIBs.

Element	Li	Co	Ni	Mn	Al
Wt.%	3.55	24.9	1.21	2.4	2.73

3. Results and Discussion

Acetic acid is a common weak organic acid. One carboxyl is contained in one CH_3COOH molecule, and upon dissociation of 1 mol acetic acid in distilled water 1 mol H^+ is theoretically produced. In fact, not all the H^+ is released into the solution. The dissociation reaction of acetic acid can be expressed as follows:



After the mixed cathode and anode powder reacts with the leaching solution, the metal enters the solution, and the unreacted metal oxides and graphite remain in the leaching residue.

The XRD spectrum for the leaching residue is shown in Figure 1b. It can be seen that the spectral peaks for LiCoO_2 and $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$ in the leaching residue obviously weakened and disappeared, and there were almost only the spectral peaks for graphite. We attributed this difference to the spent LiCoO_2 and $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$ samples reacting with the acetic acid.

3.1. Effect of H_2O_2 on Leaching

We studied the effect of H_2O_2 dosage (1~6 vol.%) on metal leaching efficiency under the following conditions: solid–liquid ratio (S/L) of 20 g/L, temperature of 70 °C, and acetic acid concentration of 2 M for 40 min. The results in Figure 2 indicated that the amount of H_2O_2 plays an important role in the process of leaching spent LIBs with acetic acid. When the concentration of H_2O_2 in the leaching solution was 1 vol.%, the reaction efficiencies of aluminum, cobalt, lithium, manganese, and nickel were 62.43%, 56.31%, 73.92%, 58.18%, and 66.59%, respectively. This shows that the leaching efficiency for Ni, Co, Mn, and Al was relatively low, while the leaching of Li was relatively easy. When 4 vol.% H_2O_2 was added, the leaching rates for aluminum, cobalt, lithium, manganese, and nickel increased by 32.27%, 38.3%, 24.64%, 29.79%, and 29.8%, respectively, and the leaching rates were all close to 95% and above.

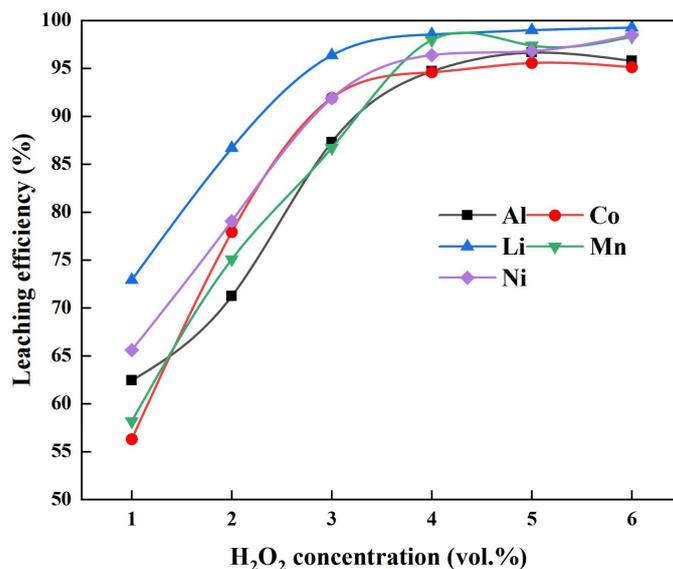
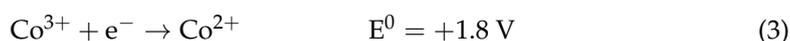


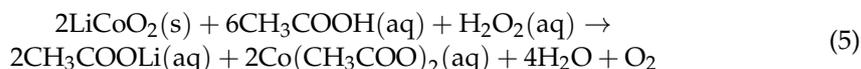
Figure 2. Effect of H₂O₂ concentration on metal leaching rates.

According to the research presented in [34], it was found that H₂O₂ may be related to change in the leaching kinetics of LiCoO₂. In essence, H₂O₂ undergoes a redox reaction with metal compounds in the electrode material, and the reduction of Co from a high-valence state to a low-valence state is more conducive to leaching. When the addition of H₂O₂ was further increased to 6 vol.%, the metal leaching rate did not increase obviously. Therefore, 4 vol.% H₂O₂ was the optimum reducing agent concentration.

The half reactions for hydrogen peroxide in acidic solutions and for the reduction of Co³⁺ to Co²⁺ are as follows [35]:



The leaching reaction of spent LiCoO₂ and LiAl_{0.2}Co_{0.8}O₂ with a CH₃COOH solution may be represented as follows:



It can be seen from Formulas (4) and (5) that H₂O₂ can reduce Co(III) in the reactant to Co(II). Therefore, in the acid leaching process of LiCoO₂ and LiAl_{0.2}Co_{0.8}O₂, the leaching efficiency of high-valent metals was improved by adding a reducing agent H₂O₂ solution.

3.2. Effect of Acetic Acid Concentration

Under the conditions of a solid–liquid ratio of 20 g/L, temperature of 70 °C, H₂O₂ concentration of 4.0%, and reaction time of 40 min, the effect of acetic acid concentration in the range of 0.5–3.0 M on the leaching efficiency of electrode materials was investigated. As shown in Figure 3, the leaching efficiency of metals increased sharply with the increase in acetic acid concentration. With 0.5 M acetic acid solution, the reaction efficiencies for aluminum, cobalt, lithium, manganese, and nickel were only 46.45%, 55.93%, 67.89%, 52.33%, and 59.56%. As the acetic acid concentration increased to 2.0 M, the reaction efficiencies increased to 94.7%, 94.61%, 98.56%, 97.47%, and 96.39%. When the acid concentration was further increased from 2.0 M to 3.0 M, the metal leaching rate did not

change significantly. From these results, we concluded that 2.0 M acetic acid was the optimal initial acid concentration.

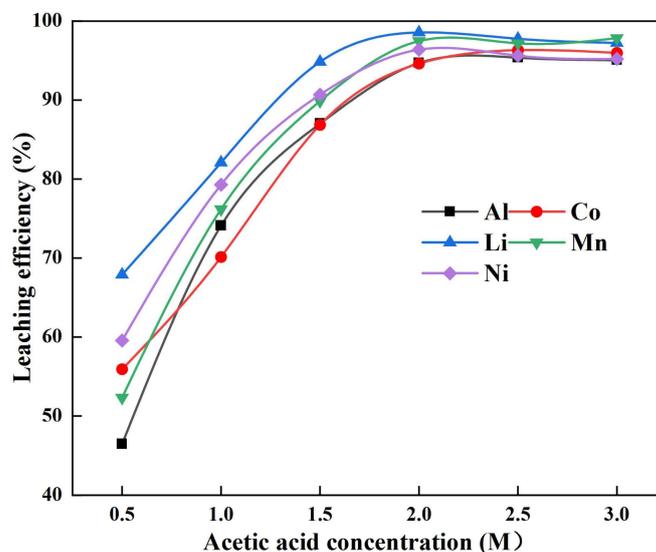


Figure 3. Effect of acetic acid concentration on the leaching of metals from electrode materials.

3.3. Metal Dissolution at Different Solid–Liquid Ratios

Figure 4 shows the change in metal leaching rate when the solid–liquid ratio was increased from 5 to 30 g/L. It was observed that the leaching rates of the five metals decreased with the increase in the solid–liquid ratio under the experimental conditions of 70 °C, 4 vol.% H₂O₂, 2 M acetic acid, and 40 min reaction time. When the solid–liquid ratio was 30 g/L, the reaction efficiencies for aluminum, cobalt, lithium, manganese, and nickel were 79.38%, 80.11%, and 89.91%, 85.73%, and 82.17%, respectively, between 80% and 90%. The leaching rate reached the maximum when the solid–liquid ratio was 5 g/L because the amount of H⁺ was enough to react almost completely with the metal compounds at a low solid–liquid ratio. A high solid–liquid ratio was more acceptable because more electrode materials were treated, and a solid–liquid ratio of 5 g/L handles less electrode material. Considering the lower chemical consumption and relatively good leaching efficiency, the best condition for leaching nickel, aluminum, cobalt, manganese, and lithium from the material was 20 g/L.

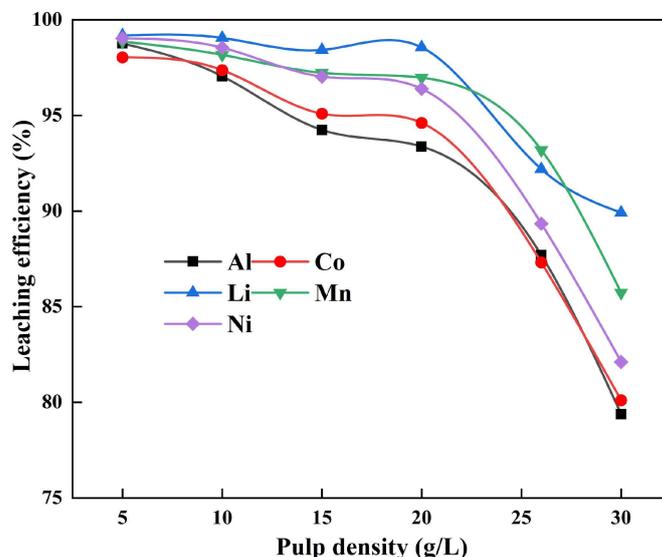


Figure 4. Effect of solid–liquid ratio on the leaching of metals from electrode materials.

3.4. Effects of Temperature and Time on Leaching

The effects of temperature and time on metal leaching efficiency were studied using 2 M acetic acid. During the leaching process, the solid–liquid ratio was maintained at 20 g/L and the H₂O₂ concentration was 4.0 vol.%. The results are shown in Figure 5a,b. In the experiment at 30 °C, a leaching rate of more than 71% was achieved. With an increase in temperature, metal leaching efficiency also increased. When the temperature was raised to 70 °C, the metal recovery rates were all close to or higher than 95%. When the temperature of the solution increases, H₂O₂ becomes unstable and easily decomposes, as shown in Formula (6).

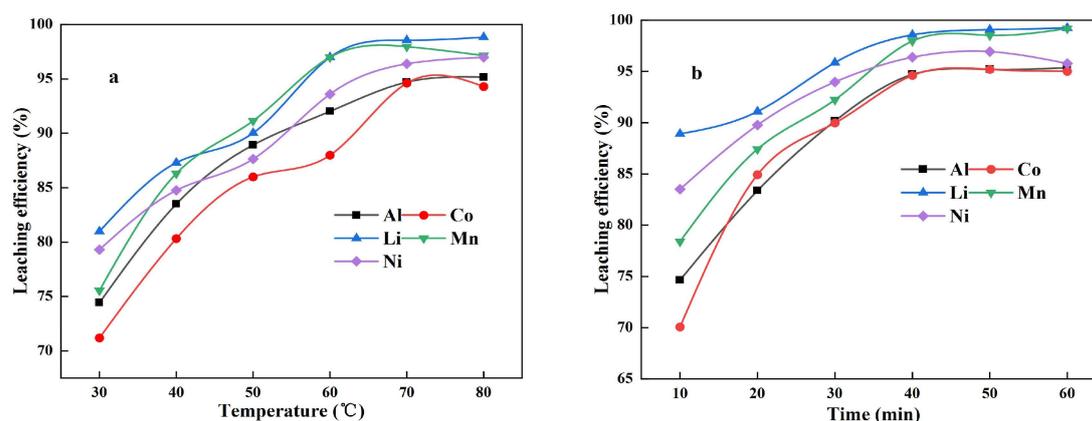


Figure 5. Effects of (a) temperature and (b) time on the leaching of metals from electrode materials.

It was confirmed that the leaching process for the metals in the electrode material was an endothermic reaction and that increasing the temperature to 80 °C did not significantly improve the leaching efficiency of the metals.

Figure 5b shows that metal leaching efficiency was also greatly affected by time, and it was obvious that increasing the reaction time was beneficial for metal leaching. The leaching rate was fastest before 30 min, slowed down at 30~40 min, and decreased after 40 min. When the reaction time was increased to 50 min or 60 min, the leaching efficiencies for aluminum, cobalt, lithium, manganese, and nickel hardly improved.

3.5. Material Characterization

XRD analysis: The metals in the electrode materials of spent lithium-ion batteries usually exist as oxides, which can only be leached by acid or alkali solutions without the introduction of a reducing agent. The recovery of metals has been found to be extremely unsatisfactory, because the binding abilities of various elements in oxides are very strong. With the addition of a reductant, the valence states of metal ions are changed, which can destroy the bonds between metal ions and oxygen, thereby increasing leaching rates [17].

In all leaching processes (acid leaching or alkali leaching), the choice and amounts of reducing agents have extremely important influences on metal leaching rates. On the basis of the experimental results, it was found that the leaching rates of metals significantly improved after the addition of the reducing agent hydrogen peroxide. Figure 6 shows that after leaching in the leaching solution with different H₂O₂ concentrations, the XRD patterns of the leaching residue changed obviously, and most of the spectral peaks belonging to LiCoO₂ and LiAl_{0.2}Co_{0.8}O₂ disappeared. The strongest spectral peak for LiCoO₂ and LiAl_{0.2}Co_{0.8}O₂ is located at 18.77°. After treatment with a leaching solution containing 2 vol.%, 4 vol.%, and 6 vol.% H₂O₂, the intensity of the spectral peak gradually weakened until it disappeared. Only the spectral peaks of graphite remained in the leaching residue, indicating that the metal oxide was almost completely reacted, and the leaching rate of the metal also reached the maximum at this time, which was mutually confirmed by the results

in Figure 2. Under optimal experimental conditions, the metal leaching rate is shown in Figure 6c.

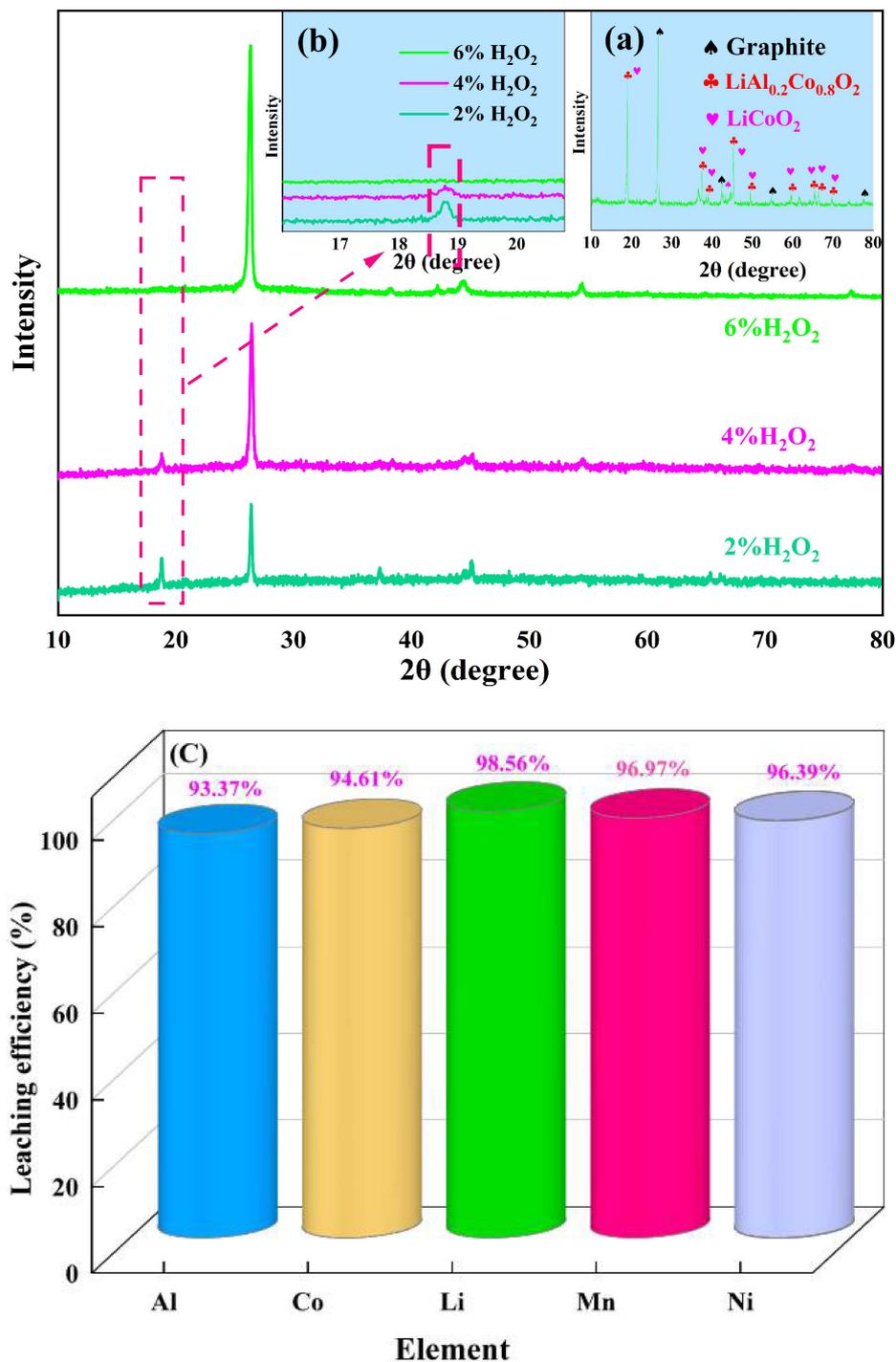


Figure 6. XRD patterns of leaching residues with different H_2O_2 concentrations. (a) XRD patterns of powder before leaching. (b) Enlarged image of the strongest spectral peak for LiCoO_2 and $\text{LiAl}_{0.2}\text{Co}_{0.8}\text{O}_2$. (c) Leaching rates for metal elements.

SEM analysis: Figure 7a–d show scanning electron micrographs (SEMs) of the electrode material before and after leaching. Figure 7a,b show that the surface of the electrode material is extremely smooth; it is formed by the stacking of sheet-like substances. When the acetic acid and hydrogen peroxide in the leaching solution come into contact with the metal oxide and react, this process destroys the original structure of the metal oxide.

Eventually, the metal ions enter the solution. It can be clearly seen in Figure 7c,d that there are more holes and defects in the surface of the leaching residue, indicating that acetic acid has an etching effect on the substance.

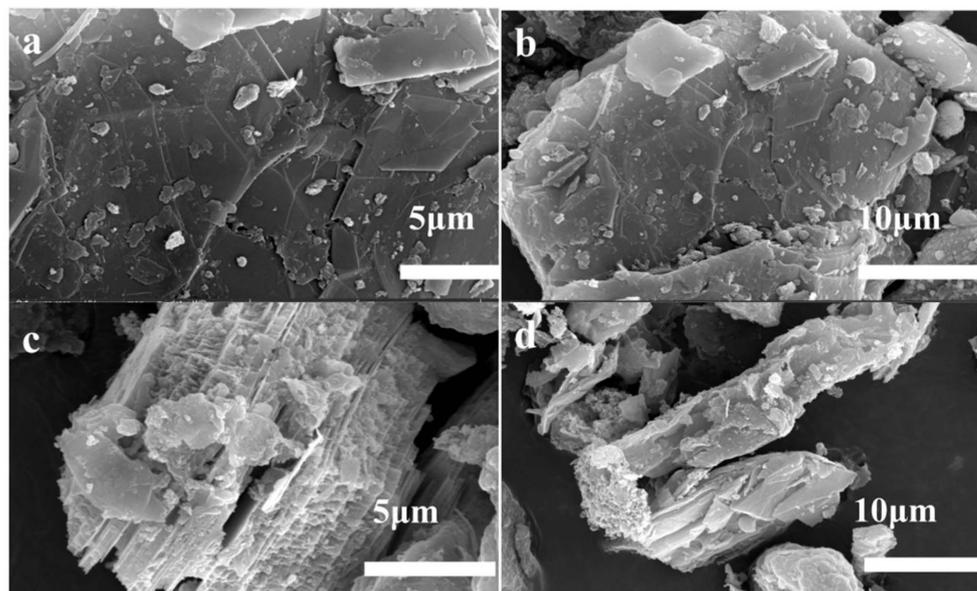


Figure 7. SEM images of (a,b) mixed material before leaching and (c,d) black leaching residues.

4. Conclusions

Spent lithium-ion battery electrode materials are one source of metal raw materials, such as lithium, nickel, manganese, cobalt, and aluminum. Reusing metals after recycling can not only reduce the global consumption of metal resources but also improve the living environment. In this paper, a hydrometallurgical route for metal recovery from spent Li-ion battery positive and negative electrode materials was investigated, especially from materials mixed with high contents of aluminum. Using acetic acid and hydrogen peroxide as leaching solutions, metals were transferred from electrode active materials into aqueous solutions. Considering the need to reduce energy consumption and chemical reagent usage while maintaining better metal leaching efficiency, the optimal conditions for leaching were determined. Using 2 M acetic acid, 4.0 vol.% H₂O₂, a leaching temperature of 70 °C, an S/L ratio of 20 g/L, and a time of 30 min, the leaching rates for aluminum, cobalt, lithium, manganese, and nickel reached 94.7%, 94.61%, 98.56%, 97.47%, and 96.39%, respectively.

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Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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