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Reductive acid leaching of valuable metals from spent lithium-ion batteries using hydrazine sulfate as reductant

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Abstract: Hydrazine sulfate was used as a reducing agent for the leaching of Li, Ni, Co and Mn from spent lithium-ion batteries. The effects of the reaction conditions on the leaching mechanism and kinetics were characterized and examined. 97% of the available Li, 96% of the available Ni, 95% of the available Co, and 86% of the available Mn are extracted under the following optimized conditions: sulfuric acid concentration of 2.0 mol/L, hydrazine sulfate dosage of 30 g/L, solid-to-liquid ratio of 50 g/L, temperature of 80 °C, and leaching time of 60 min. The activation energies of the leaching are determined to be 44.32, 59.37 and 55.62 kJ/mol for Li, Ni and Co, respectively. By performing X-ray diffraction and scanning electron microscopy in conjunction with energy dispersive X-ray spectroscopy, it is confirmed that the main phase in the leaching residue is MnO₂. The results show that hydrazine sulfate is an effective reducing agent in the acid leaching process for spent lithium-ion batteries.

Key words: spent lithium-ion batteries; reductive acid leaching; hydrazine sulfate; leaching mechanism; kinetics

1 Introduction

Over the past decade, the development of electronic products, particularly electric vehicles, has resulted in a rapid increase in the use of lithium-ion batteries (LiMnO₄, LiCoO₂, LiNi_xCo_v- $Mn_{1-x-y}O_2$, and LiFePO₄; hereafter referred to as LIBs) [1]. Consequently, the amount of spent LIBs has increased dramatically. LIBs typically consist of metals (5-20 wt.% Co, 5-10 wt.% Ni, and 5-7 wt.% Li), electrolytes (15 wt.%), and plastics (7 wt.%), with the exact composition varying slightly for different manufacturers [2,3]. While the inappropriate management of spent LIBs poses significant biological and environmental risks, spent LIBs are considered as valuable resources, with the potential for significant economic benefits through the efficient recovery of major components.

Currently, main methods for recycling LIBs include pyrometallurgy and hydrometallurgy [4]. The pyrometallurgical process involves the crushing of spent batteries, reduction roasting, and the smelting and refining of metals. Two of the numerous disadvantages of the pyrometallurgical process are the high energy consumption and the transfer of lithium from the spent LIBs into the slag, from which it is not easily extractible [5]. Compared with the pyrometallurgical recovery process, the hydrometallurgical recovery offers significant advantages, owing to its low energy consumption and environmental friendliness [6]. The leaching process is one of the key steps in hydrometallurgical recovery, and the main technologies employed include inorganic [7-9] and organic acid leaching, e.g., by citric, oxalic, or lactic acid [10,11], ammonia leaching [12], and biological leaching [13]. However, commercial LIB

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recycling enterprises currently employ only sulfuric acid leaching.

Reducing agents have also been proposed to enhance metal leaching [14]. Many studies have proposed the use of various substances as reducing agents in the leaching process, including H₂O₂, sodium sulfite, sodium hydrogen sulfite, and iron powder [15-17]. Owing to the high reduction activity of hydrazine sulfate, in the present study, it was selected as a reducing agent in order to increase the leaching rate of metals. The effects of the sulfuric acid concentration, solid-to-liquid ratio, reducing agent dosage, leaching temperature, and leaching time for metal leaching were investigated. In addition, the mechanism of the leaching process was examined by performing X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analyses and kinetic modeling.

2 Experimental

2.1 Spent LIBs pretreatment

The spent LIBs with LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ as the cathode material used in the present study were provided by Hunan Ye Xiang Technology Co., Ltd. (Changsha, China). The spent LIBs were first discharged in 5% NaCl solution to prevent spontaneous combustion and short circuiting, and they were then dismantled manually with appropriate safety precautions to obtain different components. The cathode materials were cut into small fixed-sized pieces that were placed in a muffle furnace and heated at 400 °C for 2 h. Thereafter, the samples were naturally cooled to room temperature, and the active materials were removed from the current collector (aluminum foil).

2.2 Leaching process

Leaching experiments were performed in three-necked round-bottom flasks (250 mL in capacity) fitted with reflux condensers to prevent solution loss due to evaporation. Powdered cathode materials were measured and added to a designated volume of dilute H_2SO_4 solution at a fixed temperature, and the slurry was agitated with a magnetic stirrer for certain time, after which it was filtered. Previous studies [18] have shown that the agitation speed has little effect on the leaching rate for metals; hence, we selected an agitation speed of 400 r/min for all experiments. The progress of the leaching process was monitored by sampling the leachate at various time intervals and analyzing its elemental composition. The leaching rate of metals can be expressed as follows:

$$\eta = \frac{C_{\rm Me} V_{\rm liq}}{mM_e} \tag{1}$$

where C_{Me} is the concentration of the metal ions in the leachate, V_{liq} is the volume of the leachate, *m* represents the mass of the cathode powder, and M_{e} represents the mass fraction of a particular element in the active material of the cathode.

2.3 Characterization

The concentrations of Li, Ni, Co and Mn metal ions were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (iCAP 7400, Series). The elemental composition of the cathode material is given in Table 1. The materials primarily consist of 29.6% Ni, 7.03% Li, 16.7% Mn and 11.5% Co, while the content of other metals, such as Cu, Al, and Fe, is extremely low (<0.2%). The XRD pattern analyses were performed using a Bruker X-ray diffractometer with Cu K_{α} radiation at 30 mA and 30 kV over a 2 θ range of 5°–70°. SEM images and EDS spectra were obtained using a FEI-TESCAN microscope.

 Table 1 Elemental composition of primary elements in cathode material (wt.%)

Li	Ni	Co	Mn	Al	Cu	Fe	Р
7.03	29.6	11.5	16.7	0.17	0.02	0.04	0.35

3 Results and discussion

3.1 Optimization of leaching process

3.1.1 H₂SO₄ concentration

Figure 1 shows the leaching rates of Li, Ni, Co and Mn with respect to the H_2SO_4 concentration (0.5–3.0 mol/L). The leaching rate tends to increase with increasing H_2SO_4 concentration because a larger H_2SO_4 concentration increases the collision frequency between the leaching agent and the cathode material powders, which in turn increases the leaching rate [19]. The leaching rate of Mn is noticeably lower than that of Li, Ni and Co, maybe because Mn^{2+} is readily oxidized to MnO_2 by the dissolved gaseous oxygen in the leachate. At an H_2SO_4 concentration of 2.0 mol/L, the leaching rates of Li, Ni, Co and Mn reach 97%, 96%, 95% and 86%, respectively, and there are no significant changes at acid concentrations exceeding 2.0 mol/L. Therefore, sulfuric acid concentration of 2.0 mol/L is sufficient.



Fig. 1 Effect of H_2SO_4 concentration on leaching rate of metals (hydrazine sulfate 30 g/L, solid-to-liquid ratio 50 g/L, temperature 80 °C, and leaching time 60 min)

3.1.2 Hydrazine sulfate concentration

Figure 2 shows the leaching rate with respect to the hydrazine sulfate concentration. The lithium leaching rate is extremely high, regardless of the hydrazine sulfate concentration, and this is because the free lithium ions in the layered structure provide enhanced reactivity with the leaching agent relative to the other metals [20]. In contrast, the Ni, Co and Mn leaching rates increase with increasing hydrazine sulfate concentration (from 10 to 30 g/L), confirming that hydrazine sulfate acts as a reducing



Fig. 2 Effect of hydrazine sulfate concentration on leaching rate of metals ($H_2SO_4 2.0 \text{ mol/L}$, solid-to-liquid ratio 50 g/L, temperature 80 °C, and leaching time 60 min)

agent (Eq. (2)), and promoting leaching through the reduction of solid-phase Co³⁺ and Mn⁴⁺ to Co²⁺ and Mn²⁺, which are more readily dissolved in solution [21]. Because the cathode materials of $LiNi_xCo_yMn_{1-x-y}O_2$ batteries have layered structures of α -NaFeO₂, increasing the cobalt and manganese leaching rate promotes an increase in the nickel leaching rate [22]. At a hydrazine sulfate concentration of 30 g/L, the leaching rates of Li, Ni, Co and Mn reach 97%, 96%, 95% and 86%, respectively. There are no obvious changes when the hydrazine sulfate concentration is further increased to 40 g/L, indicating that the leaching reaction proceeds to completion. Therefore, 30 g/L hydrazine sulfate concentration is sufficient for the leaching process.

$$10\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_{2}+2\text{N}_{2}\text{H}_{5}^{+}+30\text{H}^{+}=$$

$$10\text{Li}^{+}+2\text{Co}^{2+}+5\text{Ni}^{2+}+3\text{Mn}^{2+}+2\text{NH}_{4}^{+}+$$

$$16\text{H}_{2}\text{O}+\text{N}_{2}\uparrow+2\text{O}_{2}\uparrow$$
(2)

3.1.3 Temperature

Figure 3 shows the leaching rate with respect to the solution temperature. The leaching rate increases with increasing temperature for all the metals, which can be attributed to the endothermicity of the leaching reaction, wherein the dissociation constant and ion transfer rate of H_2SO_4 are enhanced when the temperature increases [23]. In addition, the average kinetic energy of the molecules increases with increasing temperature, causing more frequent and energetic collisions, and hence accelerating the leaching [24]. The leaching rates for Li, Ni, Co and Mn are increased from 80%, 61%, 65% and 63% to 97%, 96%, 95% and 86%,



Fig. 3 Effect of leaching temperature on leaching rate of metals (H_2SO_4 2.0 mol/L, solid-to-liquid ratio 50 g/L, hydrazine sulfate 30 g/L, and leaching time 60 min)

respectively, as the temperature increases from 50 to 80 °C. The leaching rates of Li, Ni and Co essentially remain unchanged upon a further increase in temperature to 90 °C. It should be noted that the leaching rate of Mn decreases slightly at temperatures exceeding 80 °C, which can be attributed to the simple oxidation of Mn^{2+} to MnO_2 by the dissolved oxygen in the leachate, causing a loss of Mn to the leaching residue; increasing the temperature exacerbates this trend. Based on these comprehensive considerations, 80 °C is selected as the best leaching temperature.

3.1.4 Solid-to-liquid ratio

Figure 4 shows the effects of the solid-toliquid (S/L) ratio on Li, Ni, Co and Mn leaching rates. It can be seen that increasing the S/L ratio has an adverse impact on the leaching rate of the metals. As the S/L ratio increases, the leaching rate of Mn shows a gradual decreasing trend, while the leaching rates of Li, Ni and Co remain basically unchanged when the S/L ratio is lower than 50 g/L. When the S/L ratio is 50 g/L, the leaching rates of Li, Ni, Co and Mn are 97%, 96%, 95% and 86%, respectively.



Fig. 4 Effect of S/L ratio on leaching rate of metals $(H_2SO_42.0 \text{ mol/L}, \text{hydrazine sulfate 30 g/L}, \text{temperature 80 °C}, and leaching time 60 min)$

As the S/L ratio is increased beyond 50 g/L, the leaching rates of all the metals tend to decrease. This may be because an increased S/L ratio reduces the effective surface area available to participate in the reaction for each particle in the unit volume [25]. In general, high acid concentrations and low solid-to-liquid ratios result in an increased metal leaching rate. High S/L ratios can lead to a high process throughput, but high ratios result in decreases in the metal leaching rate. Therefore, to obtain high metal leaching rates while simultaneously maintaining a high process throughput, a 50 g/L S/L ratio is selected as the optimum value in the subsequent leaching experiments.

3.1.5 Leaching time

Figure 5 shows the leaching rate with respect to time. Prolonging the leaching time from 5 to 60 min slightly increases the leaching rate of all the metals. When the reaction time reaches 60 min, approximately 97% of the available Li, 96% of the available Ni, 95% of the available Co, and 86% of the available Mn are leached. After further prolonging the leaching time from 60 to 90 min, there is no substantial change in the leaching rates of Li, Ni and Co, indicating that the leaching reaction basically proceeds to completion. However, the leaching rate of Mn shows a decreasing trend after the leaching time exceeds 40 min. This is because manganese ions are readily oxidized to MnO_2 by the oxygen dissolved in the leachate [26], and the hydrazine sulfate reducing agent is almost completely consumed after the leaching time exceeds 40 min. This results in the generation of MnO₂, which enters the leaching residue as the manganese ions cannot be reduced. After comprehensive consideration, we choose 60 min as the best leaching time.



Fig. 5 Effect of leaching time on leaching rates of metals $(H_2SO_4 2.0 \text{ mol/L}, \text{ hydrazine sulfate } 30 \text{ g/L}, \text{ S/L ratio } 50 \text{ g/L}, \text{ and temperature } 80 \text{ }^{\circ}\text{C})$

3.2 Characterization of raw materials and leaching residue

To illustrate the compositions of different samples, XRD measurements were obtained. As

shown in Fig. 6, the characteristic peak of the leaching residue after different leaching time remains close to the same location as in the original sample, but the peak intensity gradually decreases. This decrease may be attributed to the gradual corrosion of cathode material particles by the leaching agent as the leaching time is prolonged, causing the layered structure of the cathode material to gradually collapse. In addition, the characteristic peak position of the leaching residue is slightly displaced from that of the raw sample, which may be related to the replacement of lithium ions by hydrogen ions in the layered structure of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$. As can be seen from the XRD pattern of the leaching residue at 60 min, the peak intensity of the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ characteristic peak is sharply decreased relative to the raw sample, and many heterogeneous peaks are present. These heterogeneous peaks are characteristics of MnO₂, and are consistent with the lower leaching rate of Mn described previously.

SEM images of the leaching residue after different leaching times are shown in Fig. 7. It can be seen that the original cathode material is composed of spherical particles with clear outlines, surrounded by finer aggregates. As the leaching time is prolonged, these spherical particles break up to form many finer particles with irregular shapes, and corrosion pits appear on the surfaces of these fine particles. When the leaching time exceeds 30 min, many fine strip grains can be observed on



Fig. 6 XRD patterns of leaching residue after different leaching time

the particle surface, and when the leaching time exceeds 60 min, the leaching residue consists almost entirely of fine strip grains. EDS analysis (Fig. 8) shows that Mn is the main compositional element of the leaching residue after 60 min of leaching. It is believed that the primary species in the leaching residue is MnO_2 , which is consistent with the results of the XRD analysis.

3.3 Leaching kinetics

Figure 9 shows the leaching kinetics at various temperatures and leaching durations under the optimized conditions detailed above. Following the methods of previous studies [27,28], surface chemical reaction, external diffusion control, and



Fig. 7 SEM images of leaching residue after different leaching time (t_L): (a) Raw sample; (b) t_L =10 min; (c) t_L =20 min; (d) t_L =30 min; (e) t_L =45 min; (f) t_L =60 min



Fig. 8 EDS spectrum of leaching residue after 60 min of leaching



Fig. 9 Effect of temperature and leaching time on leaching rate of metals from spent LIBs: (a) Li; (b) Ni; (c) Co; (d) Mn

internal diffusion control models are employed to analyze the leaching mechanisms. However, the fitting results from these three models all have low correlation coefficients ($R^2 < 0.95$). This may be attributed to the oxidation-reduction reaction during the leaching process, which is accompanied by a large amount of gas production [29].

Because the concentration of the leaching agent varies with time, and gas is generated during the leaching reaction, the leaching reaction is actually a heterogeneous liquid-solid reaction involving gas production. Based on this observation, a revised kinetic model is introduced (Eq. (3)), which has been successfully applied to the leaching kinetics of different heterogeneous reactions in many cases [30,31]:

$$1-3(1-x)^{2/3}+2(1-x)=kt$$
(3)

where x is the reaction fraction and k represents the reaction rate constant.

Figures 10(a–c) show that the leaching process agrees well with the revised shrinking core model.



Fig. 10 Kinetic models fit for Li (a), Ni (b) and Co (c), and Arrhenius plots (d)

Because Mn^{2+} is easily oxidized to MnO_2 in the leachate, and the theoretical model does not account for this effect on the leaching rate of Mn, the kinetic model is not fitted to the Mn leaching behavior. The relationship between the specific rate constant and temperature can be expressed by the Arrhenius equation:

$$k = A \exp[-E_a/(RT)] \tag{4}$$

where A is the frequency factor (\min^{-1}) , E_a is the apparent activation energy (J/mol), T is the temperature (K), and R is the universal gas constant (8.314 J/(mol·K)).

Using this equation, the activation energy of leaching can be estimated, as shown in Fig. 10(d). The leaching activation energies are equal to 44.32, 59.37 and 55.62 kJ/mol for Li, Ni and Co, respectively. These values of activation energy are all higher than 40 kJ/mol, which is the typical value for a chemical-reaction-controlled process [32].

4 Conclusions

(1) Hydrazine sulfate is used as an alternative

reducing agent to hydrogen peroxide for the recovery of Li, Ni, Co and Mn from spent LIBs. The optimum conditions of the leaching process are as follows: H_2SO_4 concentration 2.0 mol/L, hydrazine sulfate dosage 30 g/L, solid-to-liquid ratio 50 g/L, leaching time 60 min, and leaching temperature 80 °C. 97%, 96%, 95% and 86% of the available Li, Ni, Co and Mn, respectively, are extracted by reductive acid leaching under these optimized conditions.

(2) The morphologies of the leaching residue confirm the leaching kinetics model in the temperature range of 60–85 °C, and the leaching process of Li, Ni and Co agree well with the revised shrinking core model, with activation energy of 44.32, 59.37 and 55.62 kJ/mol for Li, Ni and Co, respectively.

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硫酸肼还原酸浸出废旧锂离子电池中的有价金属

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摘 要:采用硫酸肼作为锂、镍、钴和锰从废锂离子电池中浸出时的还原剂,结合条件实验对浸出机理和浸出动 力学进行研究。在最优条件:硫酸 2.0 mol/L、硫酸肼 30 g/L、固液比 50 g/L、温度 80 ℃ 和浸出时间 60 min 下, 97%的 Li、96%的 Ni、95%的 Co 以及 86%的 Mn 被浸出。通过浸出动力学分析得出 Li、Ni 以及 Co 的浸出活化 能分别为 44.32、59.37 和 55.62 kJ/mol,表明浸出过程受化学反应控制。XRD 和 SEM-EDS 分析结果表明,浸出 渣的主要组成为 MnO₂。上述研究结果表明,硫酸肼可作为废锂离子电池中有价金属浸出的有效还原剂。 关键词:废旧锂离子电池;还原酸浸;硫酸肼;浸出机理;动力学

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