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Leaching study of spent Li-ion batteries

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Abstract

In order to investigate the characteristics of spent Li-ion batteries in acid leaching, the alkaline leaching residue was act as raw material. The effect of leaching rate was examined by XRD, SEM and ICP-AES. At last, the enlarged experiment was conducted. The results indicated that, in this experimental research scope, the best condition is 3 mol·L⁻¹ H₂SO₄, 15: 1 of liquid/solid, 0.25 mol · L⁻¹ [Na₂S₂O₃], 90 °C, 3 h. According to the enlarged experiment, conducted at the best conditions, the main phase of raw materials is LiCoO₂ and C, and the main phase of pickling residues is C. Co recycling rate was up to 99.95%, and Li leaching rate was up to 99.71%.

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Keywords: WEEE; spent li-ion batteries; pickling; Co; recycle

1. Introduction

With the development of technology, electronic products have penetrated every corner of people's life. The Li-ion battery (LIBs) has become power sources dominant in these products, like cellular phones, laptop computers, video-cameras and other modern-life appliances[1,2] and [3] due to its good performance compared with nickel-cadmium (NiCd) or nickel-metal hydride (NiMH) batteries, for example smaller, lighter, high energy density, high working voltage, long cycle life, low self-discharge rate and have no memory effect[2] and[3]. Thus the production of spent LIBs is increasing dramatically, a large number of production brings lot of waste. For example, the worldwide production of LIBs is 2044 million in 2007[4], and the number of spent LIBs was up to 4.6 billion around worldwide in 2010[3].

Spent Li-ion batteries as a kind of WEEE (Waste Electrical and Electronic Equipment), is defined as hazardous waste by every country. If not be handled properly, it will cause serious harm to the environment and human's health [5]. But on the other hand, there are also so much valued metals in the

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spent LIBs, like Co (5-20 wt. %), Li (5-7 wt. %) etc. [6] Therefore, recycling Li-ion batteries can bring huge economic benefits[8]. Then spent LIBs resource recycle is necessary both from the viewpoints of environmental conservation and the recovery of value metals [8], but it is still necessary to develop an efficient collection system in order to receive the spent batteries consumed around the world[7].

At present, the mainly techniques of recovery treatments for spent LIBs contain pyrometallurgical process, hydrometallurgical process or the combination of both and microbial metallurgy[9]. Although there are some problems [9] (e.g. serious equipment corrosion, etc.) existed in hydrometallurgical process, it is undoubtedly the most suitable method for industrial production at present. The original route of hydrometallurgical process comprises the following steps[3, 7]: (1) discharging pretreatment to remove the excess capability, (2) dismantling of spent LIBs to remove the plastic and metallic shells or size reduction, (3) leaching with strong acid solutions or leaching with alkaline liquor first to remove Al then leaching with strong acid solutions and (4) metals separation. This work focused on pickling. The leaching of Li-ion batteries has been investigated using H_2SO_4 , HCl and HNO_3 as leaching agents by some researchers [3, 10-13]. It was found that the leaching rate of cobalt is higher when the existence of $Na_2S_2O_3$ compared with H_2O_2 and the absence of reducing agent [2, 17].

In this paper, recovery of Co and Li, the leaching rate of Al, Ni and Cu and the characteristics of Co which recycled by pickling, were discussed.

2. Experiments

2.1. Materials

In this study, the spent LIBs were provided by Sichuan Changhong Electric Co., Ltd. The preparation of raw material for this experiment contains three steps: discharging, size reduction and alkaline leaching. The spent LIBs were firstly discharged with dilute NaCl solution to remove the excess capability. Secondly shear crusher (SM2000 smf / UpM, Retsch, Germany) was used for size reduction of spent LIBs. After size reduction, the materials were screened by a series of sieves with holes of 0.5, 2 and 5 mm. Then the materials which fraction ≤ 0.5 mm were handled by alkaline leaching, and the alkaline residues were dried at $80^\circ C$ for 24 h.

2.2. Experiment Methods

For a typical experiment, 5 g powder was taken to a 250 mL conical flask, leaching at a constant temperature water bath shock box (SHA-CA, Changzhou aohua instrument co., Ltd, China). After leaching, it was filtrated. And the experiment conditions investigated were shown in table 1. Leaching rates were calculated according to formula (1).

$$X_B = \frac{m_1}{m_2} \times 100\% \quad (1)$$

where X_B is leaching rate, %. m_1 is actual quality of metal leaching, g. m_2 is metal quality of raw material, g.

Table 1 Factors and its levels of acid leaching experiments

Factors	Levels
H ⁺ concentration (mol·L ⁻¹)	1, 2, 3, 3.5, 4
L/S ratio (mL·g ⁻¹)	6:1, 10:1, 15:1, 20:1
Temperature (°C)	70, 80, 85, 90, 100
Na ₂ S ₂ O ₃ (mol·L ⁻¹)	0, 0.1, 0.2, 0.25, 0.3
Time (h)	0.5, 1, 1.5, 2, 2.5, 3

In order to examine the contents of Co, Li, Al, Ni and Cu in both raw materials and pickling residues, “HNO₃-HF-H₂O₂” [15] system was used. After digestion, Co, Li, Al, Ni and Cu were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-OES, Thermo Scientific, iCAP 6500, U.S.A.). The surface topography and phase analysis were investigated by scanning electron microscope (SEM, S440, Leica, Germany) and X-ray diffraction (X' pert MPD Pro, PANalytical, Netherlands) respectively.

3. Experiments

3.1. Chemical Characterization of Raw Material

The chemical composition of raw material is shown in Table 2. It shows that the Co is the highest, 35.40 wt. %. It indicates that 5 g sample needs at least 0.06 mol H⁺. And all the examined conditions were higher than several times of this, indicating that H⁺ were more than the needed value. In Table 2, it can be found that Co/Li is 9.57, which is much higher than 8.49 of LiCoO₂. Thus Li is lower in this raw material than that spent LIBs. This could be attributed to the loss of Li in alkaline leaching. Fe is mainly from the iron shells. The contents of Al, Cu and Ni are up to 1.30 wt. %, 9.10 wt. % and 0.20 wt. % respectively, and all of them will make many troubles in the process of purification of cobalt if they can't be removed completely. And Li is also a kind of valuable metals. Therefore, it is necessary to examine the leaching characteristics of Li, Al, Cu and Ni.

Table 2 Chemical composition of raw material

Sample	Al	Co	Cu	Fe	Li	Mg	Mn	Ni
Sample 1 (wt. %)	1.30	35.30	8.80	0.40	3.70	4.30	0.30	0.10
Sample 2 (wt. %)	1.30	35.50	9.40	0.70	3.70	3.80	0.30	0.30
Average 1 (wt. %)	1.30	35.40	9.10	0.55	3.70	4.05	0.30	0.20

3.2. H⁺ concentration

Fig. 1 showed the leaching behavior of metals cobalt, copper, aluminum, lithium and nickel from alkaline residue of spent LIBs by sulfuric acid with the exist of Na₂S₂O₃. It can be seen that the recycling rate of Co and Li increased when H⁺ concentration increased from 1 M to 3 M, then it reached to a plateau. Cu leaching rate increased firstly, and decreases afterwards while H⁺ concentration increased from 1 M to 4 M, it reaches its maximum of 65.00% when H⁺ concentration was 3 M. Ni and Al leaching rate were not significantly influenced by H⁺ concentration, they remained at about 35% and 43% when H⁺ concentration was increased from 1 M to 4 M. Therefore, 3 M is the best condition for H⁺ concentration in this study scope.

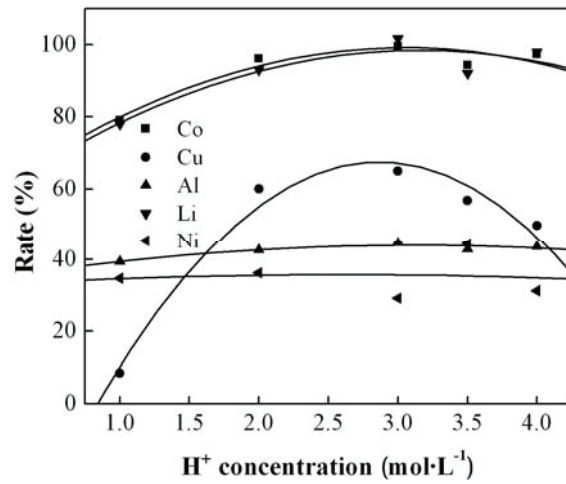


Fig. 1 Effect of H⁺ concentration on leaching rate of Co and other metals

3.3. L/S Ratio

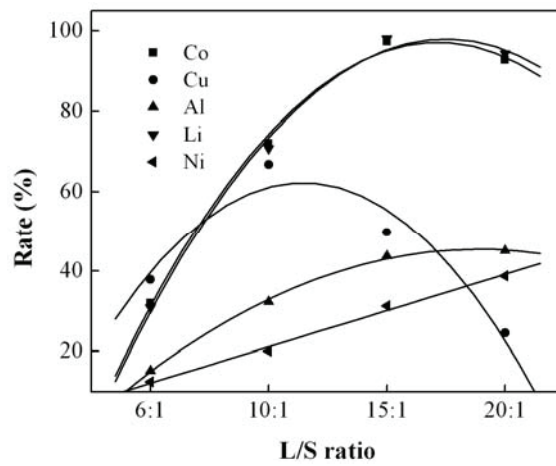


Fig. 2 Effect of L/S ratio on leaching rate of Co and other metals

The effects of L/S ratio on leaching rate of Co, Cu, Al, Li and Ni were shown in Fig. 2. The leaching rates of Co and Li firstly increased and then decreased, from 31.99% and 30.84% to 97.33% and 97.97% when L/S ratio increased from 6: 1 to 15:1; continuing increase L/S ratio to 20: 1, the leaching rates of Co and Li decreased to 92.74% and 94.32%. Cu leaching rate also increased firstly and then decreased, it increased from 37.86% to 66.81% while L/S ratio increased from 6:1 to 10:1, and then decreased to 49.86% and 24.51% when the L/S ratio was increased to 15: 1 and 20: 1. The influence of L/S ratio on leaching rate of Ni and Al was not obvious, which were in the range of 12.50% ~ 38.75% and 28.75%~45.00%, respectively. Thus the best condition of L/S ratio was 15: 1.

3.4. Temperature

The effects of temperature on leaching rates of Co and other metals were shown in Fig. 3. When temperature was higher than 80 °C, it hindered the reaction. While temperature increased from 70 °C to 80 °C, the leaching rates of Co, Li, Cu, Ni and Al decrease from 99.52%, 97.43%, 71.26%, 42.50% and 50.77% to 47.23%, 45.35%, 23.65%, 22.50% and 20.19% respectively. Continuing increasing it to 90 °C, the leaching rates of Co, Li, Al, Cu and Ni increased to 97.33%, 97.97%, 49.86%, 31.25% and 43.65%. At 70 °C, Co and Li were leached completely, while the content of impurity elements, Al, Cu and Ni, were relative lower at 90 °C. Thus the best condition of temperature was 90 °C.

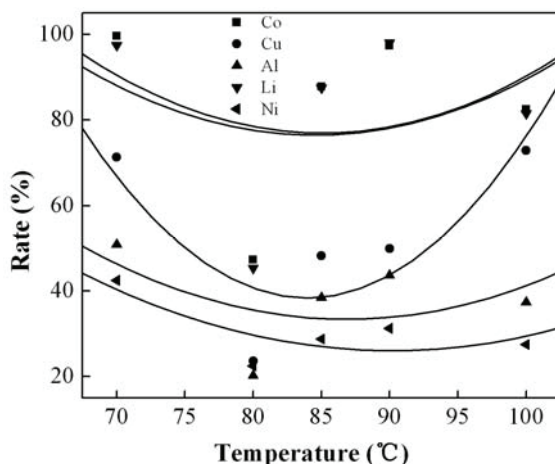


Fig. 3 Effect of temperature on leaching rate of Co and other metals

3.5. $\text{Na}_2\text{S}_2\text{O}_3$ Concentration

The effect of $\text{Na}_2\text{S}_2\text{O}_3$ concentration on leaching rate of Co and other metals were shown in Fig. 4. Co and Li recycling rates increased firstly and then decreased. When $\text{Na}_2\text{S}_2\text{O}_3$ concentration increased from 0 to 0.25 M, Co and Li recycling rates increase from 71.12% and 88.11% to 97.33% and 97.97% respectively, almost leaching completely; continuing increasing $\text{Na}_2\text{S}_2\text{O}_3$ concentration to 0.3 M, the leaching rates of Co and Li decreased to 77.58% and 74.86%, respectively. Cu leaching rate decreased dramatically from 99.31% to 34.86% when $\text{Na}_2\text{S}_2\text{O}_3$ increased from 0 to 0.3 M. However, no obvious impact of $\text{Na}_2\text{S}_2\text{O}_3$ concentration on Al and Ni leaching rates was found in this study, about 35% and 43%, respectively. Thus the best condition of $\text{Na}_2\text{S}_2\text{O}_3$ concentration was 0.25 mol·L⁻¹.

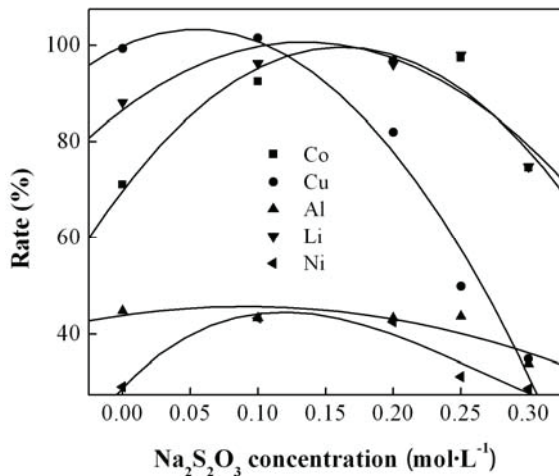


Fig. 4 Effect of Na₂S₂O₃ concentration on leaching rate of Co and other metals

3.6. Time

The effects of time on leaching rate of Co and other metals were shown in Fig. 5. According to Fig. 5, the leaching of Co, Li, Cu, Al and Ni was favoured as the time extension. The leaching rates of Co, Li, Cu, Al and Ni increased from 84.22%, 92.70%, 48.93%, 22.15% and 40.96% to 97.33%, 98.58%, 53.90%, 48.75% and 45.19% when time increased from 0.5 h to 3 h. Therefore, the best condition of time is 3 h.

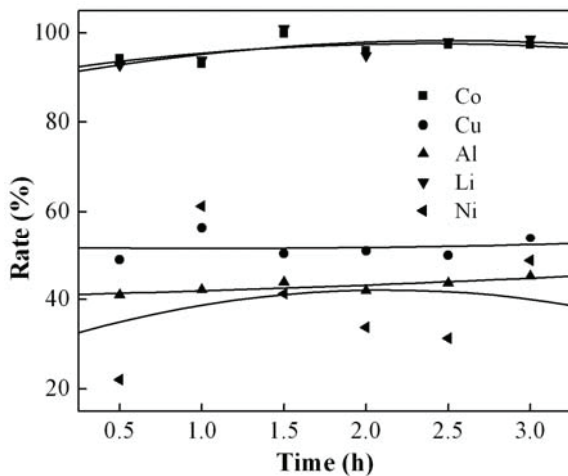


Fig. 5 Effect of Time concentration on leaching rate of Co and other metals

3.7. Enlarged Experiment

300 g alkaline residues were used in this enlarged experiment, and 159.6 g pickling residue was obtained. H^+ concentration, L/S ratio, temperature, $Na_2S_2O_3$ concentration and time were set at 3 M, 15:1, 90 °C, 0.25 M and 3 h. The chemical composition of pickling residue was shown in Table 3. Scanning electron microscope and X-ray diffraction of raw material and pickling residue were shown in Fig. 6 and Fig. 7.

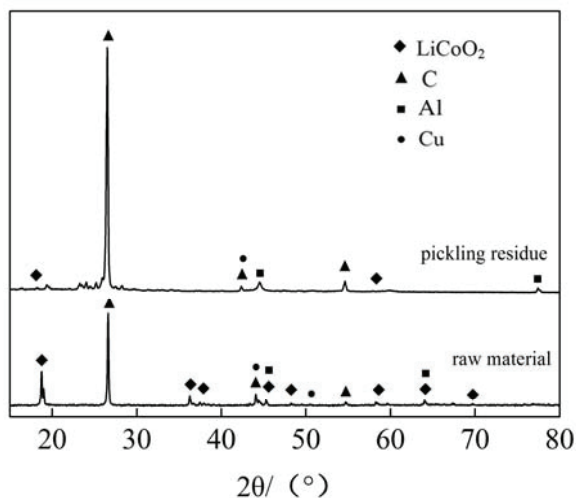


Fig. 6 X-ray diffraction patterns of raw material and pickling residue

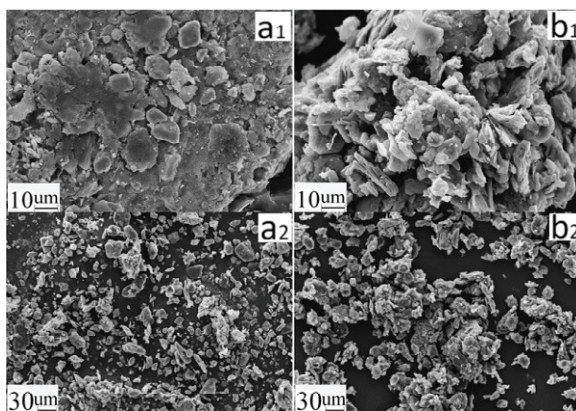


Fig. 7 Scanning electron microscope of raw material and pickling residue (a1, a2 - raw material; b1, b2 - pickling residue)

For understanding the effect of pickling on leaching $LiCoO_2$, phase properties of both the raw material and pickling residue were studied by X-ray diffraction spectroscopy. Fig. 6 shows clearly that the main phase of raw material is $LiCoO_2$, C and part of Al, Cu. Compared with raw material, $LiCoO_2$ decreases dramatically, C is the main phase in the pickling residue, the peaks of $LiCoO_2$ decreases dramatically, which indicates that the amount of $LiCoO_2$ is very little in the pickling residue, basically leached completely after pickling. The peaks of Cu and Al basically remain unchanged.

4. Conclusions

(1) The recycling rates of Co and Li increase while H^+ concentration increased. Cu leaching rate increases first and decreases afterwards. The leaching rates of Co, Cu and Li are also increase first and decrease afterwards while $Na_2S_2O_3$ concentration increased. The effects of H^+ and $Na_2S_2O_3$ concentration on leaching rates of Ni and Al are not significant. The impact of temperature on leaching rates of Co, Li, Al, Cu and Ni are basically similar, they all decrease first and increase afterwards.

(2) The enlarged experiment which conducted at the best condition in this study scope ($3 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$, 15: 1 of liquid/solid, $0.25 \text{ mol}\cdot\text{L}^{-1} [Na_2S_2O_3]$, $90 \text{ }^\circ\text{C}$, 3 h), indicates that the recycling rates of Co and Li are 99.95% and 99.71% respectively.

References

- [1] Kang JG, Senanayake G, Sohn J, Shin SM. Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272. *Hydrometallurgy*, 2010, 100: 168-171.
- [2] Chen L, Tang XC, Zhang Y, Li LX, Zeng ZW, Zhang Y. Process for the recovery of cobalt oxalate from spent lithium-ion batteries. *Hydrometallurgy*, 2011, 108: 80-86.
- [3] Zeng GS, Deng XR, Luo SL, Luo XB, Zou JP. A copper-catalyzed bioleaching process for enhancement of cobalt dissolution from spent lithium-ion batteries. *Journal of Hazardous Materials*, 2012, 199-200: 164-169.
- [4] Scrosati B, Krebs A, Beck M, Bartels J. An update of the portable battery market and the rechargeable battery collection in Japan. *Proceedings of 12th international Congress for Battery Recycling ICBR, Budapest, Hungary, June 20-22, 2007: 27-34.*
- [5] SPENCER CM, HOUP T. Dynamics of c-fos and ICER mRNA expression in rat forebrain following lithium chloride injection[J]. *Molecular Brain Research*, 2001, 93: 113-126.
- [6] Shin SM, Kim NH, Sohn JS, Yang DH, Kim YH. Development of a metal recovery process from Li-ion battery wastes. *Hydrometallurgy*, 2005, 79: 172-181.
- [7] Dorella G, Mansur MB. A study of separation of cobalt from spent Li-ion battery residues. *Journal of Power Sources*, 2007, 170: 210-215.
- [8] Kang J, Sohn, G, Chang H, Senanayake G, Shin SM. Preparation of cobalt oxide from concentrated cathode material of spent lithium ion batteries by hydrometallurgical method. *Advanced Power technology*, 2010, 21: 175-179.
- [9] Xin BP, Zhang D, Zhang X, Xia YT, Wu F, Chen S et al. Bioleaching mechanism of Co and Li from spent lithium-ion battery by the mixed culture of acidophilic sulfur-oxidizing and iron-oxidizing bacteria. *Bioresource Technology*, 2009, 100: 6163-6169.
- [10] Mantuano DP, Dorella G, Elias TCA, Mansur MB. Analysis of a hydrometallurgical route to recover base metals from spent rechargeable batteries by liquid-liquid extraction with Cyanex 272. *Journal of Power Sources*, 2006, 159:1510-1518.
- [11] Zhang PW, Yokoyama T, Itabashi O, Suzuki TM, Inoue K. Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. *Hydrometallurgy*, 1998, 47: 259-271.
- [12] Castillo S, Ansart F, Laberty-Robert C, Portal J. Advances in the recovering of spent lithium battery compounds. *Journal of Power Sources*, 2002, 112: 247-254.
- [13] Lee CK, Rhee KI. Preparation of $LiCoO_2$ from spent lithium-ion batteries. *Journal of Power Sources*, 2002, 109: 17-21.
- [14] Guo LP, Fang W, Du XD, Lei JH. Study on reducing lithium cobalt oxide by sodium thiosulfate instead of hydrogen peroxide. *Inorganic Chemicals Industry*, 2006, 28: 49-50.
- [15] YAMASAKI S. Digestion method for total element analysis[M], In: Hakuyusya editors. *Method of Soil Environmental Analysis*. Tokyo: Japanese Society of Science and Plant Nutrition; 1997, p. 278.