Innovative leaching of cobalt and lithium from spent lithium-ion batteries and simultaneous dechlorination of polyvinyl chloride in subcritical water

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HIGHLIGHTS

- A co-treatment process for recovery of Co and Li and simultaneous detoxification of PVC in subcritical water was proposed.
- PVC was used as a hydrochloric acid source.
- More than 95% Co and nearly 98% Li were leached under the optimum conditions.
- Neither corrosive acid nor reducing agent was used.
- The co-treatment process has technical, economic and environmental benefits over the traditional recovery processes.

ARTICLE INFO

Article history:

Received 29 January 2016

Received in revised form 22 April 2016

Accepted 28 April 2016

Available online 6 May 2016

Keywords:

Spent lithium-ion battery

Dechlorination

Polyvinyl chloride

Metal leaching

Subcritical water

ABSTRACT

In this work, an effective and environmentally friendly process for the recovery of cobalt (Co) and lithium (Li) from spent lithium-ion batteries (LIBs) and simultaneously detoxification of polyvinyl chloride (PVC) in subcritical water was developed. Lithium cobalt oxide (LiCoO₂) powder from spent LIBs and PVC were co-treated by subcritical water oxidation, in which PVC served as a hydrochloric acid source to promote metal leaching. The dechlorination of PVC and metal leaching was achieved simultaneously under subcritical water oxidation. More than 95% Co and nearly 98% Li were recovered under the optimum conditions: temperature 350 °C, PVC/LiCoO₂ ratio 3:1, time 30 min, and a solid/liquid ratio 16:1 (g/L), respectively. Moreover, PVC was completely dechlorinated at temperatures above 350 °C without any release of toxic chlorinated organic compounds. Assessment on economical and environmental impacts revealed that the PVC and LiCoO₂ subcritical co-treatment process had significant technical, economic and environmental benefits over the traditional hydrometallurgy and pyrometallurgy processes. This innovative co-treatment process is efficient, environmentally friendly and adequate for Co and Li recovery from spent LIBs and simultaneous dechlorination of PVC in subcritical water.

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1. Introduction

Spent lithium-ion batteries (LIBs) contain large quantities of valuable metals such as cobalt (Co) and lithium (Li) and thus are an attractive secondary mineral resource [1–3]. Interest in recycling Co and Li from spent LIBs has recently increased for environmental and economic purposes [4–7]. Hydrometallurgy is preferred over pyrometallurgy for metal recovery from spent LIBs due to its low dust generation, simple working conditions, low energy consump-

tion, and high recovery rate [8]. However, acids used during the hydrometallurgical process pose serious threats to human health and to the environment. Organic acids provide a possible environmentally friendly alternative for the recovery of Co and Li from spent LIBs [9–11]. These mild reactants give satisfactory results, but consume large quantities of chemical reagents, thus increasing recycling cost [12,13]. Therefore, if a suitable waste could be employed as the leaching agent for metal recovery, it would greatly reduce recycling costs by utilizing the strategy of waste treatment by waste.

Polyvinyl chloride (PVC) is widely used in the plastics industry due to its chemical stability and hardness, which can be tuned using chemical additives [14]. However, enormous PVC is disposed after

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Fig. 1. Effects of (a) temperature (b) PVC/LiCoO₂ mass ratio (c) time (d) solid/liquid ratio on the leaching efficiencies of Co and Li. (Experimental conditions: (a) PVC/LiCoO₂ mass ratio = 2:1, time = 60 min, solid/liquid ratio = 16 g/L; (b) temperature = 350 °C, time = 60 min, solid/liquid ratio = 16 g/L; (c) temperature = 350 °C, PVC:LiCoO₂ mass ratio = 3:1, solid/liquid ratio = 16 g/L; (d) temperature = 350 °C, PVC:LiCoO₂ mass ratio = 3:1, time = 30 min).

the usage and is destined to be wasted. Proper disposal of this Cl-containing polymer is a serious challenge since high-temperature incineration and thermal pyrolysis result in the formation of highly corrosive HCl and extremely toxic dioxins [15,16]. Therefore, there is a need to develop a reliable, safe and environmentally friendly way to treat these compounds that does not result in the release of chlorinated compounds into the environment.

In recent years, supercritical fluid (SCF) has been investigated as an environmentally friendly technology to solve environmental problems related with waste electrical and electronic equipment [17–19]. SCFs such as water [20], methanol [21] and acetone [22] have extraordinary properties (e.g. low viscosity, high mass transport coefficient, high diffusivity, and high solubility etc.) and are used as green solvents to decompose hazardous organic polymers. In SCF, hazardous organic polymers can be decomposed into small molecules, leading to environmental protection [23,24]. SCF is becoming an increasingly popular technique for the disposal of waste electronic equipment, however there is little research on its ability to recover metals from spent LIBs.

In this work, an effective and environmentally friendly process for the recovery of Co and Li from spent LIBs was developed. In this process, waste PVC was introduced into the subcritical/supercritical water system as an acid source to leach Co and Li from spent LIBs. Thus, dechlorination of waste PVC and the metal leaching could be achieved simultaneously. The effects of various parameters on leaching efficiencies of Co and Li were investigated and the mechanism underlying the co-treatment of the two wastes in subcritical water was discussed in detail.

2. Experimental

2.1. Materials and reagents

Spent LIBs were supplied by HuaXing Environmental Protection Company (Beijing, China). A commercially available PVC powder (Sinopharm Chemical Reagent Company of Beijing) was used in this study. The diameters of PVC particles were around 50–100 μm.

2.2. Dismantling, anode/cathode separation and LiCoO₂ collection

The spent LIBs were first discharged to discard any remaining capacity and then dismantled to remove the plastic and steel cases. During the dismantling, the anode and cathode materials were collected from the cells after the removal of plastic films. *N*-methyl-2-pyrrolidone was used to effectively dissolve the polyvinylidene fluoride binder between the cathode materials and aluminum foil, while aluminum foil was recovered in its metallic form. The cathode materials containing LiCoO₂ were washed and dried at 100 °C for 1 h and then cooled to room temperature. After aqua regia digestion, Co and Li contents in cathode materials were measured using an inductively-coupled plasma optical emission spectrometer (ICP-OES, Prodigy, Leeman, USA) and determined to be 51.8% and 6.5%, respectively. The remaining weight in cathode materials is graphite.

2.3. Metal leaching in subcritical/supercritical water

The co-treating experiments in subcritical/supercritical water were carried out in 100 ml high-pressure reactors, which were placed in an electric jacket to control the reaction temperature within a deviation of ±2.0 °C. The cathode materials, PVC and deionized water were then introduced into the high-pressure reactors. The temperature varied from 150 to 400 °C. The reaction times and PVC/LiCoO₂ mass ratios were changed separately as required. After each reaction, the gas phase was passed through a NaHCO₃ solution and the resulting liquid-solid mixture was separated by vacuum filtration.

2.4. Analysis methods

After co-treatment, Co and Li contents in solution were measured by ICP-OES. The metal leaching efficiency is determined as follows:

$$\text{Metal leaching efficiency(\%)} = W_1 \times 100 / W_2$$

Table 1
Effect of mass ratio of PVC to LiCoO₂ on solution pH.

m _{PVC} :LiCoO ₂	1:1	2:1	3:1	4:1	5:1
PH	5.22	3.86	3.36	3.07	2.97

Fig. 2. Effects of (a) temperature and (b) time on PVC dechlorination. (Experimental conditions: (a) PVC/LiCoO₂ mass ratio = 2:1, time = 60 min, solid/liquid ratio = 16 g/L; (b) temperature = 350 °C, PVC: LiCoO₂ mass ratio = 2:1, solid/liquid ratio = 16 g/L).

where W_1 is the leached metal content and W_2 is the initial metal content in the LiCoO₂.

Chlorine contents in PVC and residue were analyzed by oxygen combustion bomb-ion chromatography (IC). Organic products after co-treatment were analyzed on a gas chromatography mass spectrometry system (GC/MS, Agilent 7890A/5975C, Agilent Technologies, USA) using hexane as an extraction agent. Solid products were characterized on a Bruker D8 X-ray powder diffractometer (XRD) under 50 kV, 100 mA and Cu K α radiation ($k = 1.5418 \text{ \AA}$). The morphological properties of the products were examined using a scanning electron microscopy and energy disperse X-ray system (SEM-EDX, S-3000 N, Hitachi, Japan).

3. Results and discussion

3.1. Metal leaching

3.1.1. Effect of temperature

LiCoO₂ powder with PVC was treated by subcritical/supercritical water from 150 to 400 °C to test the recovery of Co and Li from spent LIBs. As shown in Fig. 1a, the leaching efficiencies of Co and Li were negligible at co-treatment temperatures below 200 °C due to inefficient PVC dechlorination below 200 °C. As the temperature rose, the leaching efficiencies of Co and Li increased significantly up to 61.4% and 93.9%, respectively, at 250 °C. This phenomenon can be explained by the release of Cl in PVC by dehydrochlorination and its subsequent dissolution in water to form HCl [25]. Co and Li in

LiCoO₂ can react with HCl to form stable CoCl₂ and LiCl compounds, respectively. At 350 °C, the Co and Li leaching efficiencies further increased, which could be attributed to the complete dechlorination of PVC. The metal leaching efficiencies were also maximized. About 86.9% of Co and 98.6% of Li were leached at 350 °C. Any further rises in temperature did not improve the Co leaching efficiency. Conversely, CoCl₂ became unstable in the supercritical water system at high temperatures and pressures. At 400 °C, the leaching efficiencies of Co and Li both decreased. The supercritical point of water was 374.2 °C, 22.1 MPa, and the physicochemical properties of supercritical water were significantly different from that of subcritical water. When the reaction temperature was 350 °C, the physicochemical properties of subcritical water (e.g., density, ion product and dielectric constant) approached normal water, with relatively mild conditions in the system. When the reaction temperature was 400 °C, a large number of H⁺ and OH⁻ could be produced, accelerating the hydrolysis of LiCl and CoCl₂ [26]. The following reactions could occur:

When the temperature reaches 400 °C, Li and Co have been leached from LiCoO₂, but the contents detected in the solution decrease compared to that at 350 °C. Therefore, the optimal reaction temperature for Co and Li leaching is 350 °C.

3.1.2. Effect of the PVC/LiCoO₂ mass ratio

During the co-treatment of PVC and LiCoO₂, the PVC/LiCoO₂ mass ratio plays a critical role in the efficiencies of metal leaching. As shown in Fig. 1b, the Co content in the resulting solution is negligible because of the low HCl content in solution. In addition, Li is efficiently leached from LiCoO₂ at a PVC/LiCoO₂ ratio of 1:1. One explanation for this observation is that the small atomic radius, strong polarizability and high activity of Li in the LiCoO₂ crystals promotes its initial reaction with Cl to form LiCl, while the less active Co was not involved in the solution phase. The leaching efficiencies of Co and Li were improved at a mass ratio of 2:1 due to sufficient generation of HCl from the dechlorination of PVC. Furthermore, nearly 97.8% of Co and 98.3% of Li were leached into the subcritical water when the PVC-LiCoO₂ ratio was 3:1 after reacting at 350 °C for 60 min. In this case, any further increase in the PVC/LiCoO₂ ratio did not improve the leaching efficiency of Co or Li. We can therefore infer that increasing the PVC mass ratio in the mixture is conducive for the generation of excess HCl, which promotes the leaching of Li and Co metals into the subcritical water system. This conclusion was also confirmed by the changing of the pH of system after co-treatment at different mass ratios. As shown in Table 1, the pH of the system decreased from 5.22 to 2.97 as the PVC/LiCoO₂ ratio increased from 1:1 to 5:1. Therefore, a ratio of 3:1 was suitable for the leaching of Co and Li.

3.1.3. Effect of time

The effect of reaction time shown in Fig. 1c demonstrates that, at the start of the reaction at 350 °C, over 86.2% Co and 92.1% Li were leached, indicating that subcritical co-treatment of PVC and LiCoO₂ is an efficient process for leaching of Co and Li from LiCoO₂. Even during the process of raising the temperature, along with the PVC dechlorination, the majority of the metals were already leached from the LiCoO₂ powder. The leaching efficiencies of Co

Fig. 3. XRD patterns of solid products before and after co-treatment.

and Li increased with longer reaction times. After 30 min, the Co and Li leaching efficiencies were improved to 96.8% and 96.1%, respectively. However, after a reaction time of 60 min, the leaching efficiencies of Co and Li both decreased significantly. With the extension of reaction time, etching reaction may occur slowly between the metallic inwall of hydrothermal reactor and $\text{Li}^+/\text{Co}^{2+}$ in the solution. Therefore, the optimum time for Co and Li leaching is 30 min.

3.1.4. Effect of solid/liquid ratio

As the solid/liquid ratio increased, the Co leaching efficiency was improved (Fig. 1d), while the Li leaching efficiency was reduced slightly. The leaching efficiencies of both Co and Li peaked at a solid/liquid ratio of 16:1 g/L. Therefore, the most suitable solid/liquid ratio for both Co and Li leaching was 16:1 g/L. Based on the experimental results above, the optimum co-treatment conditions for Co and Li leaching were determined to be: temperature

of 350 °C, PVC/LiCoO₂ ratio of 3:1, time of 30 min and solid/liquid ratio of 16:1 g/L. Under these conditions, the maximum leaching efficiency is 98.4% Co and 96.6% Li.

3.2. Dechlorination behavior of PVC in subcritical/supercritical water

3.2.1. Effect of temperature

Temperature can dramatically affect dechlorination of PVC in subcritical/supercritical water oxidation. High reaction temperatures provide enough energy to break down the chemical bonds of PVC and improve the dechlorination efficiency [27]. Fig. 2a illustrates the effects of temperature on the dechlorination behavior of PVC in subcritical/supercritical water oxidation. PVC dechlorination was negligible at lower temperatures below 200 °C. Dechlorination was improved at higher temperatures and exceeded 96.6% above 300 °C. The percentage of dechlorinated PVC increases with temperature, gradually approaching a saturated level at 97.6% after a 1 h treatment above 350 °C. At 350 °C, all of the HCl released from PVC is captured by LiCoO₂.

3.2.2. Effect of time

Fig. 2b illustrates the effects of time on PVC dechlorination at 350 °C. The initial extent of PVC dechlorination measured was 96.5%, and then stabilized around 97.0% for all residence time durations studied. This result indicated that PVC dechlorination in subcritical water proceeded continuously as the temperature increased. When the initial temperature was reached, the majority of Cl in PVC was already released into the subcritical water system. The dechlorination of PVC was not dependent on the residence time after 30 min. Therefore, we infer that 30 min is sufficient enough time for the release of all Cl from PVC into the subcritical water at 350 °C. These findings are consistent with the observed leaching trends of Co and Li in the subcritical/supercritical water system,

Fig. 4. SEM-EDX analysis of LiCoO₂ and PVC. SEM images (a) before and (b) after co-treatment; EDX analysis (c) before and (d) after co-treatment.

Table 2
GC–MS analysis of oil products.

Ret. time (min)	Components	Structure	Areas (%)
7.849	C ₇ H ₆ O		66.43%
10.483	C ₁₃ H ₁₈ O		11.54%
14.399	C ₁₄ H ₂₂ O ₂		2.68%
15.764	C ₁₆ H ₁₂ O ₃		19.44

Table 3
Comparison of economic evaluations and environmental impacts on different methods.

Method	Pyrometallurgy	Hydrometallurgy	Co-treatment
Spent LIBs cost (\$/kg)	10	10	10
Reagent cost (\$/kg)	0	H ₂ O ₂ and acid	0
Metals recovery rate (%)	<95%	<95%	<95%
Equipment cost (K\$)	600	–	100
Power (kW)	4	None	2
Temperature (°C)	1000	60–80	350
Extraneous earnings	None	None	Benzene derivative
Environmental effects	Waste gas	Waste water	None

suggesting that the dechlorination of PVC is synchronized with the leaching of Co and Li.

3.2.3. Effect of PVC particle size

Fig. S1 shows the comparison picture of PVC with different particle sizes before and after co-treatment in subcritical water. PVC with larger particle size (1000–2000 μm) maintains original shape after co-treatment in subcritical water. However, the granule interior have been carbonized—black and round particles can be smashed by extrusion. Fig. S2 shows dechlorination efficiency of PVC with different particle sizes and metal leaching efficiency in subcritical water. With the increase of PVC particle size, dechlorination and metal leaching efficiency slightly decrease. There is a large contact area between PVC (with small particle size ≈ 100 μm) and water. HCl generated by hydrothermal decomposition can be quickly spread and dissolved in subcritical water. In contrast, there is a small contact area between PVC (with large particle size ≈ 1000 and 2000 μm) and water. Dechlorination occurs from the outside to inside, leading to inadequate PVC degradation. The limited dechlorination cannot provide sufficient H⁺ and Cl[–] for the leaching of Li and Co. Therefore, we infer that PVC with the smaller particle size will lead to more full degradation reaction in subcritical water, with higher metal leaching efficiency.

In the conventional PVC chemical treatment, pyrolysis is easy to produce toxic dioxins as well as coke and pyrolysis oil adhering to the pipe inner wall (which is difficult to be cleaned) [14]. Furthermore, dechlorination reagents such as CaO and La₂O₃ are needed to dispose waste PVC by mechanochemical method. It is difficult to separate dechlorination reagents from degradation product [28,29]. Using subcritical water to dispose waste PVC has the following advantages—fast dechlorination speed, no additional additives, without volatile organics containing chlorine, and the recycling of HCl and chemical products. Therefore, it has significant

Fig. 5. Interaction route of PVC and LiCoO₂ during co-treatment in subcritical water.

technical advantages by using subcritical water to dispose waste PVC compared with other conventional chemical methods.

3.3. Product characterization

3.3.1. XRD, SEM-EDX analysis of solid products

Fig. 3 shows XRD spectra of the LiCoO₂ and PVC products before and after co-treatment. The XRD patterns of the solid products before co-treatment clearly show the crystalline LiCoO₂ phase (Fig. 3). The XRD patterns of the solid products after co-treatment at 350 °C show the appearance of an amorphous diffraction peak at 10°–30° due to PVC dechlorination at high temperatures and the complete disappearance of the diffraction peak of the LiCoO₂ phase due to dissolution of the metal. Amorphous peaks can therefore be attributed to the residue of graphite from cathode material.

In addition, the SEM image of solid products before co-treatment shows regular round particles, with graphite and LiCoO₂ attached on the surface (Fig. S3 and Fig. 4a). When dechlorination occurred, the PVC was degraded into HCl and. Only the graphite from LiCoO₂ can be detected in the microscopic view (Fig. 4b). EDX shows that the Cl content in solid products after co-treatment was reduced to almost zero (Fig. 4c and d). Based on the statistical analyses, quantitative analyses, XRD, and SEM, it can be generally concluded that subcritical water oxidation is able to synchronize the Co/Li leaching from LiCoO₂ and the Cl removal from PVC.

3.3.2. GC–MS analysis of oil products

The main organic products formed after PVC dechlorination in subcritical water are benzene derivatives (Table 2). Based on the identified organic products, the mechanism of PVC and LiCoO₂ co-treatment in subcritical water was investigated (Fig. 5). Takeshita et al. [30] reported that PVC was dehydrochlorinated by the zipper mechanism, in which the loss of HCl from a given two-carbon segment is facilitated by dehydrochlorination of an adjacent monomer unit. In the subcritical co-treatment process, HCl dissolved in water to become hydrochloric acid, inducing the rapid leaching of metals from the LiCoO₂ crystals. The resulting polyenes underwent chain rupture to form small-molecule compounds. In addition, these polyenes undergo intermolecular and intramolecular Diels-

Fig. 6. Schematic diagram of the proposed co-treatment process.

Alder reactions to form benzene rings. The cyclization, hydrolysis, pyrolysis and oxidation interactions in the subcritical water result in further formation of benzene derivatives. Based on the above results, the following reaction equation can be given:

Therefore, the proposed co-treatment process is safe and environmentally friendly, and avoids the release of toxic chlorinated organic compounds.

3.4. Economic feasibility and environmental impact evaluation

Fig. 6 shows the flow chart describing steps towards recovering metals from spent LIBs via the co-treatment process in subcritical water. Based on the flow chart and product analysis discussed above, we evaluated the economic feasibility and environmental impacts of the laboratory-scale PVC and LiCoO_2 subcritical water co-treatment process and compared it with the traditional hydrometallurgy and pyrometallurgy processes. Table 3 shows the process flows, recovery effects and operation energy consump-

tions of the three processes. The subcritical co-treatment process has essentially the same lithium battery dismantling process and metal recovery efficiency as the hydrometallurgy and pyrometallurgy processes. In comparison, hydrometallurgy requires the use of an acid source, such as strong acids (HNO_3 , H_2SO_4 and HCl) or inorganic acids [9,10,31]. In addition, in order to accelerate the leaching of Co^{3+} from LiCoO_2 , hydrometallurgy requires the addition of a reductant (e.g. H_2O_2) to convert Co^{3+} to Co^{2+} [9,10,32]. Moreover, the pyrometallurgy equipment is highly expensive, with reaction temperatures generally above 700–1000 °C, resulting in a large consumption of energy [6,33]. In comparison, the subcritical co-treatment did not require other reagents other than the waste PVC, and used a temperature of only 350 °C. Furthermore, the waste PVC has the extra benefit of being simultaneously converted to chemical raw materials. We believe that this work has the potential commercial applications. Further commercial production needs to consider many factors such as equipment, work space and separation costs. The commercial cost of this work is mainly determined by the price of hydrothermal equipment (100 K\$) and the power consumption (0.07735\$ for each test in our city).

Comparison with environmental impacts of different LIB recovery processes revealed that the subcritical water co-treatment process did not have any environmental impacts. After the reaction, the Cl present in PVC bound with the metals to form nontoxic inorganic chlorine, avoiding the generation of any environmentally destructive organic chlorine compounds. The resulting metal chlorides can be separated and recovered via subsequent precipitation, allowing the waste liquids to be converted into highly pure hydrosolvents, which were recycled into the high-pressure reactor [34]. In comparison, the pyrometallurgy process generates toxic waste gas and thus causes secondary pollution to the environment. Therefore, the PVC and LiCoO_2 subcritical co-treatment process has significant technical, economic and environmental benefits over the traditional recovery processes, and thus has wide development prospects in metal recovery from spent LIBs.

4. Conclusions

This work innovatively performed the co-treatment of cathode material (C/LiCoO_2) from spent LIBs and PVC in subcritical water. Using hydrochloric acid produced by dechlorination of PVC in subcritical water as acid source, Li and Co were leached from LiCoO_2 . Characterizations of XRD, SEM-EDX and GC-MS showed the organochlorine in PVC has been converted into inorganic Cl ligand of Li and Co after co-treatment in subcritical water. PVC was synchronously converted into useful chemical materials, without organics containing Cl in the co-treatment process. The proposed process provides a new recycling method and technology for harmless and resourceful treatment of spent LIBs and waste PVC.

Acknowledgments

This research was financially supported by the National Natural Science Foundation of China (21477151, 51278485), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB05050200) and the Science Promotion Program of Research Center for Eco-Environmental Sciences, CAS (YSW2013B05).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.04.080>.

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