Review

A review of processes and technologies for the recycling of lithium-ion secondary batteries

Jinqiu Xu [a,*], H.R. Thomas [b], Rob W. Francis [b], Ken R. Lum [b],
Jingwei Wang [a], Bo Liang [a]

[a] *School of Urban Construction and Environmental Engineering, Shanghai Second Polytechnic University,
201209 Shanghai, People's Republic of China*
[b] *Geoenvironmental Research Centre, Cardiff School of Engineering, Cardiff University, United Kingdom*

Abstract

The purpose of this paper is to review the current status of the recycling technologies of spent lithium-ion secondary batteries. It introduced the structure and components of the lithium-ion secondary batteries, summarized all kinds of single recycling processes from spent lithium-ion secondary batteries and presented some examples of typical combined recycling processes. Also, the problems and prospect of the studies of their recycling technologies have been put forward.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Review; Lithium-ion secondary batteries; Recycling processes

Contents

* Corresponding author. Tel.: +86 21 50211231; fax: +86 21 50216301.
E-mail addresses: jqxu@eed.sspu.cn, jqxu9802601@163.com (J. Xu).

1. Introduction

The increasing public concern about the environment in the last decade has resulted in stricter regulations worldwide on those related to the adequate destination of hazardous residues containing heavy metals such as spent portable batteries. These regulations have prompted society to look for technical alternatives in order to treat these types of residues since the consumption of batteries is considerable around the world [1]. For instance, in the USA and Europe, the consumption of batteries is estimated to be 8 billion units per year [2]. In Japan, around 6 billion batteries were produced in 2004, while almost 1 billion units are consumed every year in Brazil [3].

High power lithium-containing batteries are extensively used as electrochemical power sources in modern-life equipments. They are often preferred to conventional systems with aqueous electrolytes such as the nickel–cadmium (Ni–Cd) rechargeable batteries [4]. In 2003, primary lithium batteries, and lithium-ion secondary rechargeable batteries (LIBs) represent about 28% of the rechargeable battery world market [5]. There is an important difference between the primary lithium batteries and lithium-ion secondary rechargeable batteries (LIBs) [2]. Primary lithium batteries use metallic lithium as cathode and contain no toxic metals; however, there is the possibility of fire if metallic lithium is exposed to moisture while the cells are corroding. Lithium-ion secondary rechargeable batteries (LIBs), on the other hand, do not contain metallic lithium. Most lithium-ion systems use a material like $LiXMA_2$ at the positive electrode and graphite at the negative electrode. Some materials used at the cathode include $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. LIBs contain toxic and flammable electrolyte, an organic liquid with dissolved substances like $LiClO_4$, $LiBF_4$ and $LiPF_6$ [2,6–8]. They consist of heavy metals, organic chemicals and plastics in the proportion of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers [9]. The chemical composition of a typical LIB is shown in Table 1 [5]. According to Mantuano et al. [1],

LIBs contain 36 ± 9% (w/w) of cobalt, excluding the plastic and metallic shells. The cathode $LiCoO_2$ is usually linked together with aluminum foil through adhesive agent such as polyvinylidene fluoride (PVDF) binder, which is chemically stable and has very good mechanical performance. PVDF binder could not react with most of strong acid and base, most of strong oxidant and halogen, and could not be dissolved in such organic reagents as fatty hydrocarbon, aromatic hydrocarbon, aldehyde and alcohol at room temperature and could only partly be dissolved in oleum, some special ketones and ethers [10]. Some metals in LIBs could be normally found at very high concentration levels, sometimes even higher than those found in processing concentrates of natural ores or natural ores themselves [11,12].

The usage of LIBs has rapidly increased because nowadays, they are widely used as electrochemical power sources in mobile telephones, personal computers, video-cameras and other modern-life appliances [13,14]. They not only dominate the cellular phones and laptop computer areas, but also will be the first category of dynamic batteries to be chosen to provide power for electronic automobile in the future time. Due to their characteristics of light weight, high energy and good performance [15–17], LIBs are increasingly substituting for other batteries. In 2000, the worldwide production of LIBs reached about 500 millions cells. From this consumption, LIB waste is annually estimated at 200–500 MT, with a metal content of 5–15 wt.% Co and 2–7 wt.% Li [18].

Recycling of LIBs has increasingly become important because their safe disposal may become a serious problem due to the presence of flammable and toxic elements or compounds although spent LIBs are not generally classified as dangerous waste [4,19], and at the same time, some economic benefits could be achieved in recovery of major components from LIBs [20,21]. Unlike other batteries, LIBs often blow up during the recycling process due to radical oxidation of lithium metal produced from battery metals. There are two problems to be solved; disposal of harmful waste and prevention of explosion during recycling of LIB waste [5]. Since spent LIBs represent a valuable waste material for the recovery of metals present (Co, Li, Mn and Ni) or their compounds [22], recycling of spent batteries may result in economic benefits [20,21]. Recovery of cobalt and lithium is one of the primary objectives in the recycling of spent LIBs [17,22–26], since cobalt is a rare and precious metal, and is a relatively expensive material compared with the other constituents of LIBs, and lithium is also vitally important in many industrial applications. Data from London Metal Exchange from January to October 2004 have shown that the price of cobalt is about two times more expensive than nickel, 24 times more expensive

Table 1
Chemical composition of a typical lithium-ion secondary rechargeable battery

Component	wt.%
$LiCoO_2$	27.5
Steel/Ni	24.5
Cu/Al	14.5
Carbon	16
Electrolyte	3.5
Polymer	14

than aluminium and 15 times more expensive than copper [1]. It is still necessary to develop an efficient collection system in order to receive the spent LIBs consumed around the world and recycle the spent LIBs [11].

From the viewpoints of environmental preservation, recovery of major components or valuable resources, and provision of raw materials, the recycling of spent LIBs is highly desirable in either the present time or the future [9,14,27]. In fact, for the battery industries it could be very interesting to recover battery materials to recycle in the production of new ones [28].

The recycling process should reduce scrap volume, separates battery components and enriches valuable metals and eliminate or reduce danger of waste of LIBs to environment. Two basic classes of recycling processes, including physical processes and chemical processes, have been applied for separation or the recovery of cobalt, lithium and other components from the spent LIBs.

Physical processes mainly involve mechanical processes, thermal treatment, mechanochemical process and dissolution process, and chemical processes mainly involve acid leaching or base leaching, bioleaching, solvent extraction, chemical precipitation and electrochemical process. A single recycling process can only achieve the destination of recovering a part of components or can only be one step of a whole procedure for recycling spent LIBs. Therefore, combination of several single recycling processes is necessary to recycle or recover the main components from spent LIBs. Re-synthesis of electrode materials or synthesis of other reactive materials from the recycled spent LIBs is also studied through many investigations. Because metallic lithium in the used LIBs can be formed on graphite anode by overcharging and abnormal deposition, and vigorous oxidation of metallic lithium with moisture or air can be dangerous during the mechanical treatment of spent LIBs, safety in mechanical treatment, and waste minimization are considered to be the most important for successful recovery of cobalt and lithium from spent LIBs.

Although there are a lot of research achievements developed on the recycling technologies of LIBs, most of them are still in pilot or laboratory scale. Most of the proposed processes are based on hydrometallurgical chemistry and are developed at a laboratory scale [26,29–32]. Because of high reactivity of lithium in air or moisture, primary lithium batteries are industrially processed only in a few places (Canada and USA) by Toxco Inc. and BDC Inc. using low-temperature process recycling plants [33]. LIBs are reprocessed in France (SNAM) or in UK (AEA technology batteries) [34] mainly with the aim to recover electrolyte and valuable metals from the positive electrode.

This paper mainly introduced the composition, electrochemical working principle of LIBs and the current status of their recycling technologies as well.

2. Structure of lithium-ion rechargeable battery

A LIB comprises a cathode, an anode, organic electrolyte, and a separator. The lamination of a cathode, an anode, and a separator by a pressing makes those electric contacts. The anode is a copper plate coated with a mixture of carbon graphite, conductor, PVDF binder, and additives. Similarly, the cathode is an aluminum plate coated with a mixture of active cathode material, electric conductor, PVDF binder, and additives. $LiCoO_2$ is commonly used as an active cathodic material for almost all commercialized LIBs due to its suitable performances such as high energy density, ease of manufacture, etc. However, it also has several unfavorable points such as high cost, limited cobalt resources, toxicity, etc. The chemical reactions in the two electrodes can be simply expressed as follows [26]:

The cathodic reaction:

$$6\,C + x Li^+ + x e^- \Leftrightarrow C_6 Li_x \tag{1}$$

The anodic reaction:

$$LiCoO_2 \Leftrightarrow Li_{(1-x)}CoO_2 + x Li^+ + x e^- \tag{2}$$

where the forward direction is the charge reaction and the reverse is the discharge reaction.

The energy is stored in these batteries through the movement of lithium ions from the cathode to the anode (charge process of the battery) or vice versa (discharge process) according to Eq. (3):

$$LiCoO_2 + 6C \Leftrightarrow Li_{(1-x)}CoO_2 + C_6 Li_x \tag{3}$$
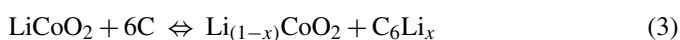
3. Recycling processes

Metallic scraps can be subject to different recycling processes, including the basic two classes of recycling processes: physical processes and chemical processes. The principal flowsheet shown in Fig. 1 was mainly adopted in hydrometallurgical recycling processes of spent lithium-ion batteries. Firstly, the spent LIBs should be experienced to some types of physical processes as pre-treatment processes such as skinning, removing of crust, crushing, sieving and separation of materials in order to separate the cathode materials from other materials. Secondly, the separated cathode materials will be used to recovered cobalt and other metals through a series of chemical processes.
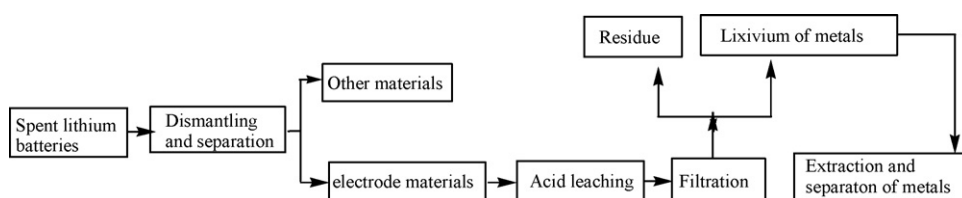

Fig. 1. Flow-sheet of the hydrometallurgical recycling process of lithium-ion secondary rechargeable batteries.

Safety precaution should be paid attention and be emphasized when LIBs are manually dismantled [11,35]. Dorella and Mansur [11] reported the related safety precautions as the following steps when lithium-ion batteries were dismantled using a manual procedure. First, the plastic cases of the batteries were removed using a small knife and a screwdriver. Second, in order to remove the metallic shell that covers the battery, it was immersed into liquid nitrogen for 4 min and fixed in a lathe. Such a cryogenic method was adopted for safety precautions. Third, the metallic shell was then cut using a saw; the ends of the metallic shell were removed firstly and a longitudinal cut was done aiming to access the internal material of the battery which was removed using pliers. Fourth, anode and cathode were uncurled manually, separated and dried for 24 h at 60 °C. All steps in the experimental procedure were carried out using glasses, gloves and gas masks for safe operation.

3.1. Physical processes

Among physical processes for recycling spent LIBs, mechanical separation techniques intend to separate materials according to different properties like density, conductivity, magnetic behavior, etc. [36]. Thermal processes are usually associated with the production of steel, ferromanganese alloys or other metallic alloys. Mechanochemical (MC) process is to use a grinding technique that makes the crystal structure of the $LiCoO_2$, the positive electrode in the LIB, into disordered system, enabling useful substances such as Co and Li easily extracted by acid leaching at room temperature from the LIBs scraps wastes [37–40]. Dissolution process is to use special organic reagents to dissolve the adhesive substance (PVDF), which adheres the anode and cathode electrodes, and therefore this process can make $LiCoO_2$ get separated from their support substrate easily and recovered effectively [31].

3.1.1. Mechanical separation processes

Mechanical separation processes are usually applied as a pretreatment to treat the outer cases and shells and to concentrate the metallic fraction, which will be conducted to a hydrometallurgical or a pyrometallurgical recycling process in recycling of spent LIBs [9,26,41,42].

Shin et al. [9] presented a process for the recovery of metal from spent LIBs for possible application to a commercial scale plant, including mechanical separation of lithium cobalt oxide particles and a hydrometallurgical procedure for lithium and cobalt recovery. The experimental procedure is illustrated in Fig. 2. A series of mechanical processes involving crushing, sieving, magnetic separation, fine crushing and classification were carried out to yield enriched particles of lithium cobalt oxide in sequence. Two stages of crushing and sieving resulted in satisfactory separation of the metal-bearing particles from the waste. A magnetic separator was used to remove pieces of steel casing. In order to eliminate small pieces of aluminum foil attaching to the particles of lithium cobalt oxide, a fine crushing followed. The reason why mechanical separation is emphasized before the metal leaching process here is that it improves the recovery efficiency of target metals and eliminates the need for
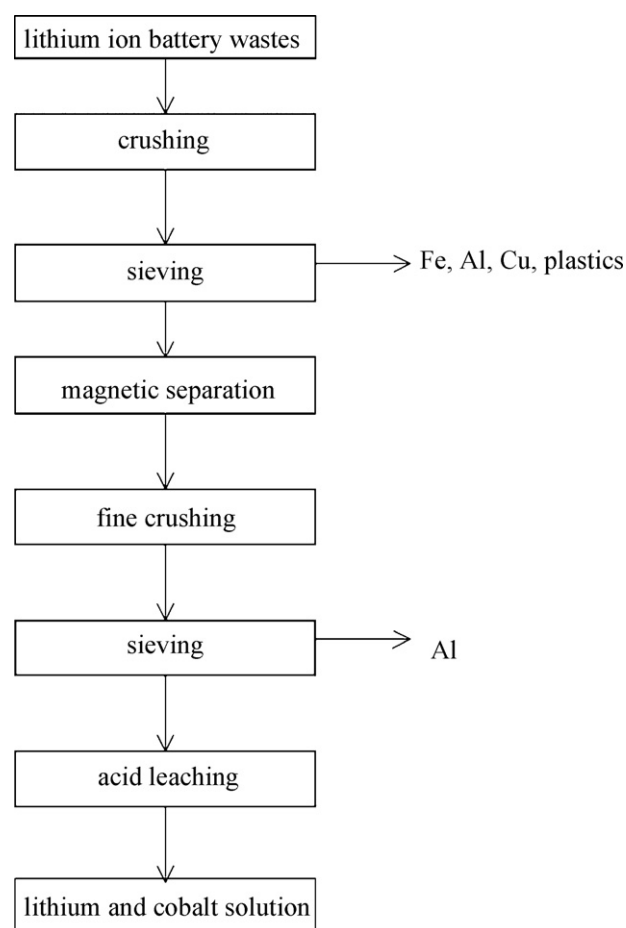

Fig. 2. Flow-sheet of the metal recovery process.

a purification process of the leachate. Because PVDF binder does not dissolve in acid solution, it remains in the cake after filtration. Also, carbon does not dissolve in acid solution, and instead it floats on the solution; from filtration it is separated in the cake. The electrolyte lithium exafluorophosphate ($LiPF_6$) decomposes into lithium fluoride and phosphor pentafluoride in the crushing process, and the lithium dissolves in the acid solution during leaching. The organic solvents propylene carbonate (PC) and diethyl carbonate (DEC) were evaporated in the crushing process.

Mechanical separation processes have a disadvantage of not completely making all kinds of components in spent LIBs get separated from each other since LIB is composed of several metals, organic substances, inorganic substances which penetrate into each other, and has a small volume and a very accurate, fine and complicated structure, therefore these components are difficult to get separated from each other by mechanical separation processes.

3.1.2. Thermal treatment

Castillo et al. [4] reported that the solid residue coming from the operational step of the dilute HNO_3 acid leaching of spent LIBs and consisting of iron, cobalt and nickel hydroxides mixture and some traces of $Mn(OH)_3$, were introduced into a muffle furnace at 500 °C during 2 h to eliminate carbon and organic

compounds. The alloy can then directly undergo beneficiation in metallurgical applications.

Lee and Rhee [5] applied a recycling process involving mechanical, thermal, hydrometallurgical and sol–gel steps to recover cobalt and lithium from spent LIBs and to synthesize $LiCoO_2$ from leach liquor as cathodic active materials. Electrode materials containing lithium and cobalt can be concentrated with a two-step thermal treatment. First, LIB samples were thermally treated in a muffle furnace at 100–150 °C for 1 h. The samples were disassembled with a high-speed shredder. Second, a two-step thermal treatment was performed in a furnace, and electrode materials were liberated from the current-collectors by a vibrating screening. Next, the cathodic active material, $LiCoO_2$, was obtained by burning off carbon and binder in the temperature range 500–900 °C for 0.5–2 h. Third, after $LiCoO_2$ in a nitric acid solution was leached in a reactor, the gel was placed inside a stainless-steel crucible and calcined into powder in air for 2 h in the temperature range 500–1000 °C.

It was reported that the cathodic active materials $LiCoO_2$ were separated from spent LIBs by shredding followed by thermal treatment at a moderately high temperature in a sequence of steps. This thermal treatment was carried out at 150–500 °C for 1 h to burn binder and organic additives [27].

Thermal treatment has the advantage of having simple and convenient operations, and at the same time the disadvantages of being unable to recovering organic compounds so that it needs to install equipments for purifying the smoke and gas resulting from combustion of carbon and organic compounds.

3.1.3. Mechanochemical process

Saeki et al. [39] developed an effective process for recovering Co and Li from LIB wastes by using mechanochemical method. The process consists of co-grinding $LiCoO_2$ with polyvinyl chloride (PVC) in planetary ball mill in air to form Li and Co-chlorides, and subsequent leaching with water of the ground product, to extract Co and Li. In the grinding stage, mechanochemical (MC) reaction between $LiCoO_2$ and PVC takes place to form chlorides which are soluble in water. Therefore, grinding stage is important to improve the yield. PVC plays an important role as a chloride source for the MC reaction. The grinding facilitates mechanochemical (MC) reaction, and the extraction yields of both Co and Li are improved as the grinding progresses. The 30 min grinding makes the recoveries of Co and Li to reach over 90% and nearly 100%, respectively. Accordingly, about 90% of chlorine in the PVC sample has been transformed into the inorganic chlorides by the time. The concept of this process is to recycle useful materials from the both wastes of battery and PVC.

It was reported that room temperature extraction of valuable substances from $LiCo_{0.2}Ni_{0.8}O_2$ scrap containing the PVDF has been carried out using 1N HNO_3 solution after mechanochemical (MC) treatment by a planetary mill with and without Al_2O_3 powder [40]. Crystalline $LiCo_{0.2}Ni_{0.8}O_2$ in the scrap was pulverized and became amorphous by MC treatment for 60 and 240 min, respectively, with and without Al_2O_3 power. This shows that the addition of Al_2O_3 is very effective for MC treatment. Accordingly, Co as well as Ni and Li were extracted at

a high yield of more than 90% from the amorphous scrap sample. About 1% of fluorine in PVDF was dissolved in the filtrate when the Al_2O_3 powder was added to the scrap during the MC treatment, while no fluorine was detected in the filtrate obtained from the ground scrap sample without Al_2O_3 powder.

3.1.4. Dissolution process

Contestabile et al. [31] presented a laboratory-scale spent LIBs recycling process without the separation of anode and cathode electrodes. The battery rolls were treated with N-methylpyrrolidone (NMP) at 100 °C for 1 h and $LiCoO_2$ was effectively separated from their support substrate and recovered. The recovery of both copper and aluminium in their metallic form was also achieved. Although this process was very convenient, the recovery effects of $LiCoO_2$ were demonstrated to be influenced by the used adhesive agent and rolling method of electrodes.

This process has the advantage of making $LiCoO_2$ get separated from their support substrate and recovered easily, and therefore this process greatly simplifies the separation procedures of cobalt and aluminium. It still has the disadvantage that the solvent for dissolving PVDF, N-methylpyrrolidone (NMP), is too expensive and consequently is not very suitable for scale-up operation. The further work to do in this respect is to develop much cheaper solvent and make it recycled and reused in order that this treatment cost could be decreased.

3.2. Chemical processes

Chemical processes are connected to leaching steps in acid or alkaline medium and purification processes in order to dissolve the metallic fraction and to recover metal solutions that could be used by the chemical industry. Recycling through chemical processes basically consists of acid leaching or base leaching, chemical precipitation, filtration, extraction or other processes. The function of the acid or base leaching of scrap is to put the metals in a solution. Once in a solution, metals can be recovered by chemical precipitation through altering the pH of the solution or adding some reaction agent, or by electrolysis. The solution can also be separated by solvent extraction through using an organic solvent, which binds to the metallic ion, separating the metal from the solution. The metal separated by solvent extraction can then be recovered by electrolysis or by chemical precipitation. The following will present these technologies in detail.

3.2.1. Acid leaching

The dust, which has been separated from plastic, iron scraps and paper residues in the sorting and dismantling preliminary treatment step, is leached by an acidic solution in order to transfer the metals of interest from it to the aqueous liquor.

The leaching of $LiCoO_2$ from spent LIBs is usually carried out by using inorganic acids such as H_2SO_4 [1], HCl [31] and HNO_3 [4,5] as leaching agents. Zhang et al. [26] studied the leaching of $LiCoO_2$ by the use of H_2SO_3, $NH_4OH·HCl$ and HCl as leaching agents. The experimental results indicated that the leaching efficiency of Co is highest in hydrochloric acid among

Table 2
Summary of some of the best operational conditions for the leaching of spent lithium-ion secondary rechargeable batteries by different acidic media

References	Leaching agent	Temperature (°C)	Time (h)	S/L ratio (g mL^{-1})	Reduction agent	Results
[26]	4.0 mol l^{-1} HCl	80	1	1/10	No agent	Around 100% Li, Co
[4]	2.0 mol l^{-1} HNO$_3$	80	2	–	No agent	Around 100% Li
[5]	1.0 mol l^{-1} HNO$_3$	75	1	1/50	1.7% (v/v) H$_2$O$_2$	Around 85% Li, Co

these three leaching agents and higher the temperature, higher the leaching efficiency of Co. The leaching reaction of LiCoO$_2$ of LIBs in HCl is as following:

$$2LiCoO_2 + 8HCl \Leftrightarrow 2CoCl_2 + Cl_2 + 2LiCl + 4H_2O \quad (4)$$
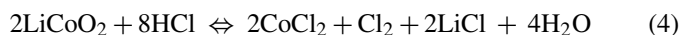
However, this process need to install special antisepticising equipments to treat with chlorine (Cl$_2$) resulting from HCl, which will result in much more recycling cost, and maybe result in serious environmental problem if this kind of equipments are not available. In order to solve this problem, Mantuano et al. [1] and Lee and Rhee [18] studied the leaching of LiCoO$_2$ by the use of H$_2$SO$_4$ and HNO$_3$ to substitute HCl with the addition of hydrogen peroxide as a reducing agent respectively. The leaching reaction of LiCoO$_2$ of LIBs in H$_2$SO$_4$ or HNO$_3$ with the addition of hydrogen peroxide is as following:

$$2LiCoO_2 + 6H^+ + H_2O_2 \Leftrightarrow 2Co^{2+} + O_2 + 2Li^+ + 4H_2O$$
$$(5)$$
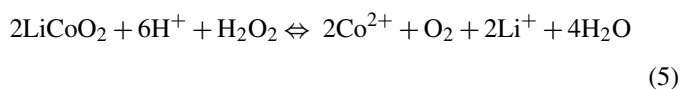
The experimental experiments carried out by Lee and Rhee [18] indicated that in the process of reductive leaching with the addition of hydrogen peroxide as a reducing agent, the leaching efficiency increased by 45% for Co and 10% for Li compared with that in only nitric acid leaching. This behavior seems to be due to the reduction of Co^{3+} to Co^{2+}, which is readily dissolved. The leaching efficiency of Co and Li increased with increasing HNO$_3$ concentration, temperature, and hydrogen peroxide concentration and with decreasing S/L ratio. An effective condition for the leaching would be 1 M HNO$_3$, 10–20 g L^{-1} initial S/L ratio, 75 °C temperature, and 1.7 vol.% H$_2$O$_2$ addition. From the kinetic study, the dissolution rates of Co and Li were found to be inversely proportional to their respective ionic concentrations. The apparent activation energy was obtained as 12.5 and 11.4 kcal mol^{-1} for Co and Li, respectively. This indicates that the dissolution of LiCoO$_2$ is controlled by surface chemical reaction.

The leaching of LIBs has been investigated using H$_2$SO$_4$ [1], HCl [31] and HNO$_3$ [4,5] as leaching agents. Metals were leached according to the following sequence for sulphuric media: aluminium > lithium > cobalt » copper. The leaching of cobalt was found to be very low for economical purposes (around 30%) and it was attributed to the absence of an reductive agent like H$_2$O$_2$ in the leaching solution. For hydrochloric and nitric media, however, extractions of cobalt and lithium higher than 85% were obtained even at the absence of an oxidizing agent. Table 2 summarises some of the best operational conditions found for the leaching of LIBs including different acidic media such as sulphuric acid, hydrochloride acid and nitric acid.

3.2.2. Bioleaching

It has been reported that bio-hydrometallurgical processes have been gradually replacing the hydrometallurgical one due to their higher efficiency, lower costs and few industrial requirements [43–45]. Bio-hydrometallurgical processing of solid waste is similar to natural biogeochemical metal cycles and reduces the demand of resources, such as ores, energy and landfill space [46–49].

The study was carried out on bioleaching method for the extraction of cobalt and lithium from spent LIBs containing LiCoO$_2$, using chemolithotrophic and acidophilic bacteria, acidithiobacillus ferrooxidans, which utilized elemental sulfur and ferrous ion as the energy source to produce metabolites like sulfuric acids and ferric ion in the leaching medium [23]. These metabolites helped dissolve metals from spent batteries. Results of research work indicated that it is possible to dissolve metals from spent cathode material of LIBs by the use of acidophilic bacteria. These cells are able to grow in the medium containing elemental sulfur and iron as their energy source. Results revealed that a culture of ferrooxidans can produce sulfuric acid to leach metals indirectly from the LIBs. Cobalt was leached faster than lithium. The EDXA mapping demonstrated a slower dissolution rate of lithium than that of cobalt. The use of Fe(II) ion in the leaching experiments was to proliferate the cell growths in the lixiviant: the higher the Fe(II) ion concentration, the slower the metal dissolution. The Fe(III) ion formed during the course of the investigation was found to be precipitated with the metals in the leach residues. Higher solid/liquid ratios prevented bacterial activity in the process as higher metal concentrations are considered to be toxic for cells.

The current technologies of bio-hydrometallurgical processes have not gotten mature in their applications for recycling LIBs and are still in the research stage until now.

3.2.3. Solvent extraction

Such extractants as di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex 272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) were usually used as extractants to separate the metals in some hydrometallurgical process, in which Co, Li and Cu are usually recovered from spent LIBs [26,43,50–53].

A hydrometallurgical plant involving metal purification/separation by liquid–liquid extraction with Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) as extractant, was found to be technically viable to separate base metals from NiCd, NiMH and LIBs of spent mobile phone [1]. The route comprises the main steps schematically shown in Fig. 3: preliminary
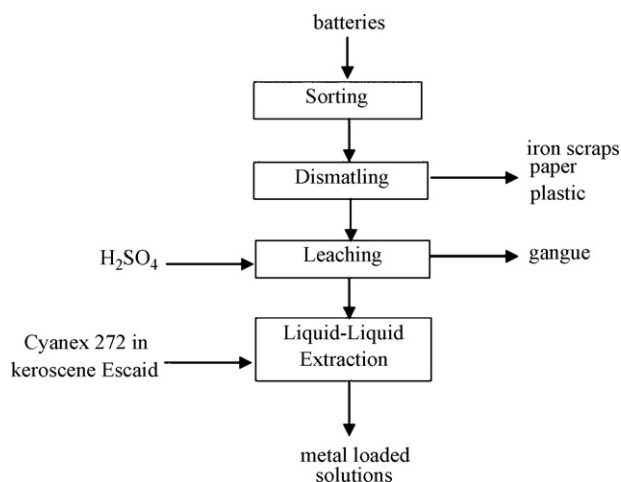
Fig. 3. Scheme of the hydrometallurgical route evaluated in this paper to treat NiCd, NiMH and lithium-ion secondary rechargeable batteries.

treatment of batteries, followed by leaching with sulphuric acid and metal purification/separation by liquid–liquid extraction with Cyanex 272 (bis-2,4,4-trimethylpentyl phosphinic acid) as extractant. Metal separation by liquid–liquid extraction with Cyanex 272 must be carried out in two sequential steps: firstly to extract aluminium at pH 2.5–3.0 and secondly to remove cobalt at pH 4.5, thus leaving lithium in solution. As shown in Fig. 4, only one experiment was performed at pH 4.5 so aluminium was in practice fully extracted. It has been pointed out that the metals, nickel and cobalt, are economically attractive enough to be

recovered from spent mobile batteries because of their price and grade. Cyanex 272 can separate cobalt from lithium ($pH_{1/2} \approx 3$) in LIBs.

This process has the advantages of easy operational conditions, low energy consumption and good separation effect. High recoveries of recycled metals such as cobalt, nickel, copper and lithium could be achieved and the recovered products have high purities. At the same time, it still has the disadvantage that some solvent extractants are very expensive and consequently it might result in too high treatment cost when it is scaled-up in industry. Therefore choosing appropriate and cheap solvent extractants would become the most important in application of this process in order to decrease the treatment cost.

3.2.4. Chemical precipitation

Chemical precipitation method for recycling spent LIBs is to use precipitation agents to precipitate precious metals such as cobalt from spent LIBs [4,31]. Contestabile et al. [31] studied a laboratory process aiming to the treatment and recycling of spent LIBs and being composed of sorting, crushing and riddling, selective separation of the active materials, lithium cobalt dissolution and cobalt hydroxide precipitation. The flow-sheet of the recycling process is shown in Fig. 5. The cobalt dissolved in the hydrochloric solution was recovered as cobalt hydroxide $Co(OH)_2$ by addition of one equivalent volume of a 4 M NaOH solution. The precipitation of cobalt hydroxide begins at a pH value of 6 and can be considered to be completed at pH 8. Ideally, $Co(OH)_2$ precipitation could be obtained by using an ammonia solution, a weak base, which forms a buffer solu-
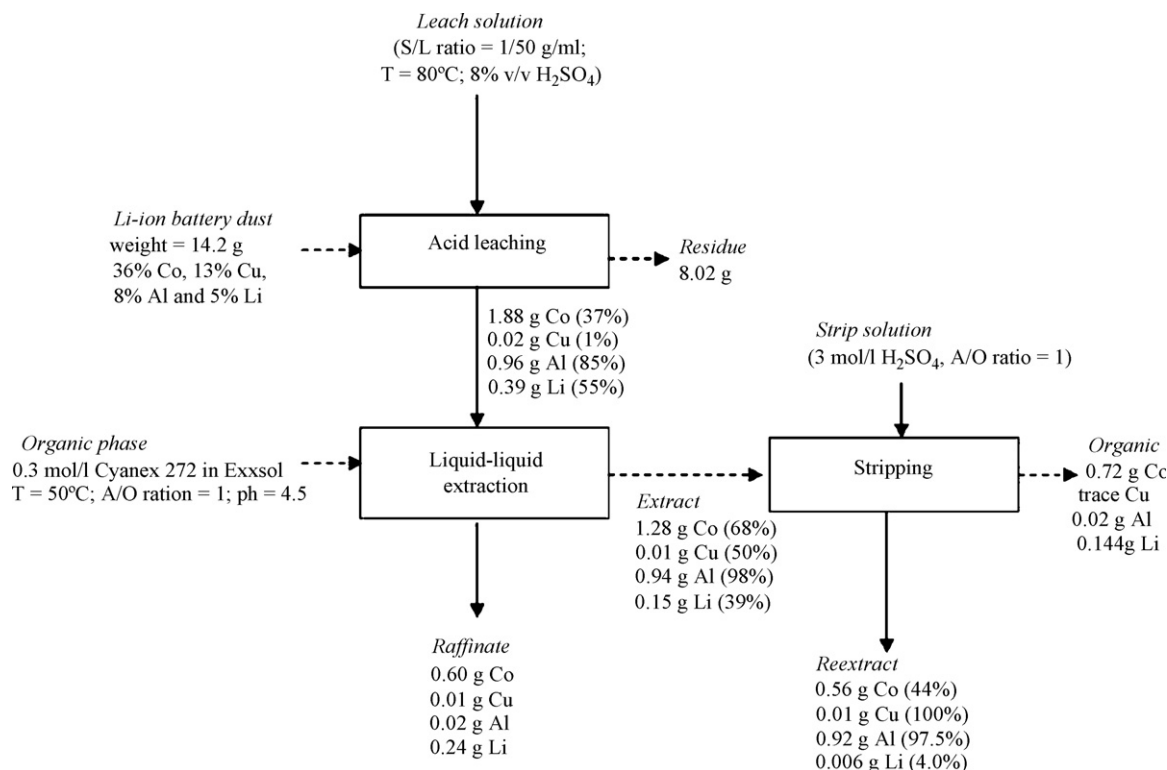

Fig. 4. Illustrative application of hydrometallurgical route to treat lithium-ion secondary rechargeable.
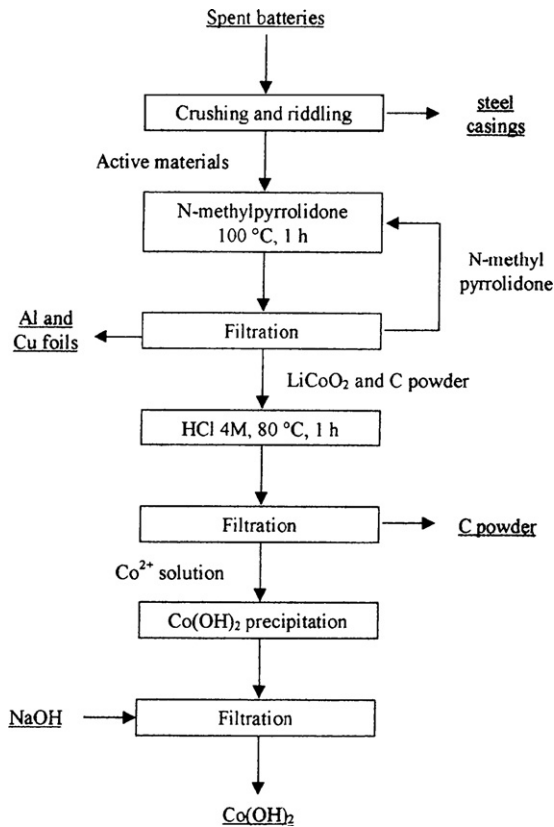
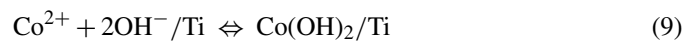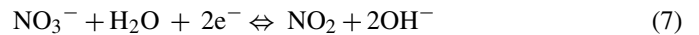Fig. 5. Flow-sheet of the recycling process for spent lithium-ion batteries.

tion at pH 9. Unfortunately, ammonia forms stable complexes with cobalt causing the partial dissolution of the hydroxide and thus, preventing from a quantitative recovery. Therefore, NaOH, which is a strong base and allows to work with small volumes of solution, remains the best choice. On an industrial scale, this step can be controlled by using an adequate pH sensor. The $Co(OH)_2$ precipitate can be easily separated from the solution by filtration, to be then recycled.

This process has simpler operation and relatively higher recoveries of metals from spent LIBs than solvent extraction method. It can get the product of high purity meeting with the general requirements of chemical products and its recycling cost will be low if it is chosen to remove impurity or purify recovered products in the process of recycling spent LIBs. The key is to choose appropriate chemical precipitation agents [54].

3.2.5. Electrochemical process

Myoung et al. [55] reported that cobalt ions, extracted from waste $LiCoO_2$ by using a nitric acid leaching solution, are potentiostatically transformed into cobalt hydroxide on a titanium electrode and cobalt oxide is then obtained via a dehydration procedure. In linear sweep voltammetry, distinct cathodic current peak is observed and indicates that hydroxide ions are formed near the electrode via the electroreduction of dissolved oxygen and nitrate ions give rise to an increase in the local surface pH of the titanium. Under appropriate pH conditions, island-shaped cobalt hydroxide is precipitated on the titanium substrate and heat treatment of the cobalt hydroxide results in the formation of

cobalt oxide. The detailed reaction mechanisms are considered to be:

$$2H_2O + O_2 + 4e^- \Leftrightarrow 4OH^- \tag{6}$$

$$NO_3^- + H_2O + 2e^- \Leftrightarrow NO_2 + 2OH^- \tag{7}$$

$$Co^{3+} + e^- \Leftrightarrow Co^{2+} \tag{8}$$

$$Co^{2+} + 2OH^-/Ti \Leftrightarrow Co(OH)_2/Ti \tag{9}$$

The reduction of dissolved O_2 and nitrate ion, i.e. reactions (6) and (7), could increase the local pH of the electrode. Thus, the precipitation of hydroxide films of $Co(OH)_2$ (see Eq. (9)) under appropriate pH condition could be possible. Therefore, this process provides a good way for recovering cobalt oxide from $LiCoO_2$.

Shen [56] investigated the cobalt recovery process from spent LIBs by sulfuric acid leaching and electrowinning. In the condition of 70 °C temperature, 10 mol L^{-1} sulphuric acid concentration and 1 h retention time, almost 100% of cobalt in the spent LIBs is dissolved. The leach liquor is purified by hydrolyzed deposition in the range of pH 2.0–3.0 and 90 °C. The cathode cobalt is produced by electrowinning in current density 235 A m^{-2}. The quality of cathode cobalt is accorded with the China's 1A# cobalt standard of GB6517–86. The net recovery of cobalt is more than 93%. This process was thought to be feasible for scale-up application in industry.

Compared with other hydrometallurgical processes for recycling metals from spent LIBs, the electrolysis process can achieve the cobalt compound of very high purity from spent LIBs since it does not introduce other substances and therefore avoid introduction of impurities [57]. However, this process has a disadvantage of consuming too much electricity.

4. Synthesis or renovation of $LiCoO_2$ cathode material

$LiCoO_2$, which is used as the cathode material for almost all commercialized LIBs due to its excellent performances, still has several unfavorable points such as high cost, limited cobalt resources, toxicity, etc. Considering these unfavorable points of $LiCoO_2$, the recycling of spent $LiCoO_2$ electrodes has many advantages such as an alternative cobalt resource, mitigation of environmental pollution, etc. At present time, since $LiCoO_2$ recycling is considered to be the most important target of the spent LIBs, most of research work is concentrated on the recycling of cobalt and other metals from the cathode, or separation and renovation of $LiCoO_2$ cathode material from spent LIBs.

Contestabile et al. [31] studied a laboratory process, in which the recycled cobalt hydroxide was used to synthesize lithium cobalt oxide to be tested as a cathode in a common LIBs configuration. The galvanostatic intercalation and deintercalation cycles demonstrated the good working capabilities of the electrode, which can undergo various cycles with a good capacity retention. This favorable electrochemical response is confirmed by the cycling voltammogram which clearly shows the reversibility of the electrode within the expected voltage limits.

It is reported that $LiCoO_2$ phase can be obtained by the hydrothermal reaction [42,58–63]. For instance, Kim et al. [42]

reported that $LiCoO_2$ cathode material was renovated and simultaneously separated from spent $LiCoO_2$ electrodes containing $LiCoO_2$, electron-conducting carbon, binder, Al current collector, and separator in a single synthetic step using hydrothermal method in a concentrated LiOH solution at $200\,°C$ without any scraping procedures. The estimated properties show the renovated $LiCoO_2$ phase to be encouraging as a cathode material for LIBs. The renovated $LiCoO_2$ phase exhibits the first discharge capacity of $144.0\,mAh\,g^{-1}$ and the discharge capacity retention of 92.2% after 40 cycles. This technology can be expected to serve as an effective route for the recycling of spent LIBs. The reaction mechanism is fully based on "dissolution–precipitation" mechanism [60–63].

Lundblad and Bergman [64] studied synthesis of $LiCoO_2$ through the calcination of a mixed precursor of Li_2CO_3 and Co_3O_4 mixture, and investigated the factors affecting it (initial Li/Co ratio, calcination atmosphere, temperature, leaching media (H_2O or acetic acid), final Li/Co ratio, primary particle size and conductivity).

Suresh et al. [65] investigated the synthesis of $LiCoO_2$ by heating a mixed solution of $Co(NO_3)_2$, Li_2CO_3 and di-formyl hydrazine fuel at $350\,°C$ followed by annealing at $850\,°C$ for 6 h to obtain an ordered crystalline layer compound.

In addition, Gummow and Thackeray [66] made a study of preparation of $LiCo_{1-x}Ni_xO_2$ cathode material for LIBs by reacting of Li_2CO_3, $CoCO_3$ and $Ni(NO_3)_2\cdot6H_2O$ in air at $400\,°C$ for 2–5 days, and Hu et al. [67] made a study of synthesis of $LiMn_2O_4$ spinel by heating a mixture of Li_2CO_3 and $MnCO_3$.

It is concluded that this process may indeed provide good quality grade recycled materials which can be directly rerouted to the manufacturers for the production of new batteries since this process has an advantage of saving some operational steps of

metal separation in other hydrometallurgical processes and this process can provide its ultimate recycling product, i.e. $LiCoO_2$, or $LiCo_{1-x}Ni_xO_2$, or $LiMn_2O_4$, as the renewed cathode materials, which can be put into production in manufacturing new LIBs [54].

5. Examples of typical combined recycling processes

Characterization of the metal content of LIBs has shown [4,11,14,26] that copper, aluminium, cobalt, manganese and lithium are the main metal species to be separated and the recoveries of cobalt and lithium are more attractive due to their comparatively high price. Usually, several kinds of recycling processes should be combined together in order to recover the main targeted metal species from spent LIBs since just a single kind of recycling process such as dismantling, thermal treatment, acid leaching, solvent extraction, chemical precipitation and electrochemical process cannot complete the recycling tasks of spent LIBs. The following introduces examples of typical combined recycling processes.

5.1. Combination of crushing, acid leaching, heat treatment and chemical precipitation

Castillo et al. [4] developed a combined process based on simple and environmentally compatible operations, aimed to the treatment and recycling of spent LIBs. It operates mainly in a selective dissolution in dilute acid, a chemical treatment of the filtrate and a thermal treatment of the solid residue. The follow-sheet of the combined processes for recycling components from spent LIBs is shown in Fig. 6. First, a representative sample of the "material" heterogeneity to treat is prepared by
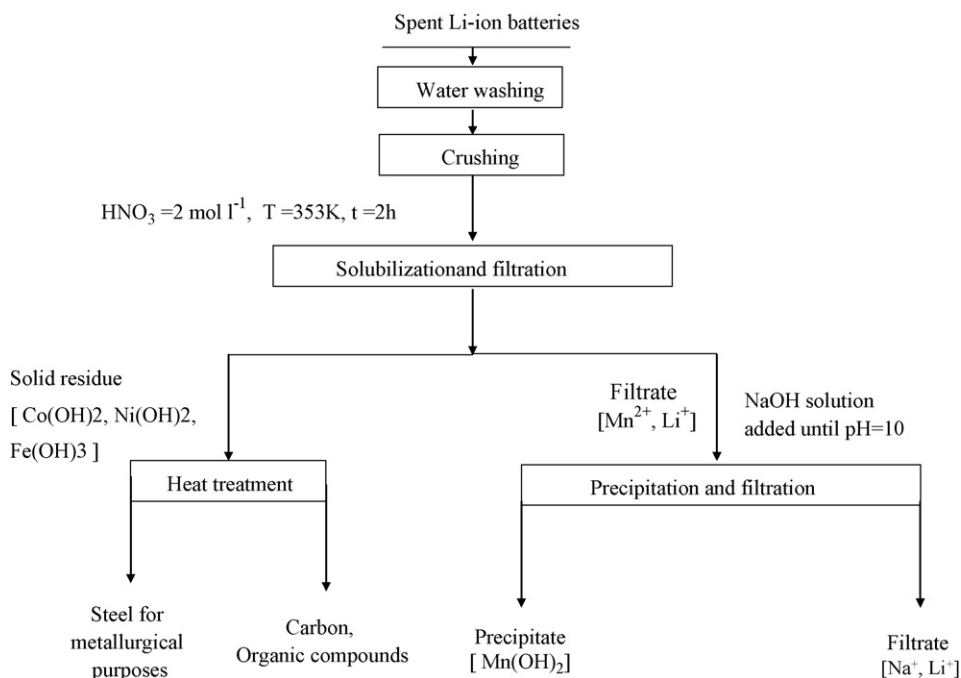

Fig. 6. The follow-sheet of the combined processes for recycling components from spent lithium-ion batteries.

mixing 15 spent lithium-ion batteries of different mark and composition. After the first filtration, 100% lithium and 95% manganese in the filtrate were recover. Second, the precipitation of the manganese hydroxides at pH 10 with addition of NaOH solution then makes possible a good separation between lithium and manganese. $Mn(OH)_2$ precipitate can be easily separated from the solution by filtration. The alkaline ions, Na^+, coming from NaOH, are recovered, mixed with the alkaline ions, Li^+ at the last step. Third, the solid residue, consisting of a iron, cobalt and nickel hydroxides mixture and some traces of $Mn(OH)_2$, is introduced into a muffle furnace at 500 °C during 2 h to eliminate carbon and organic compounds. The alloy can then directly undergo beneficiation in metallurgical applications. Furthermore, it is also possible to consider a thermal valorization by recovery of combustion gases of organic and plastic compounds at the calcination furnace output.

This method involves very simple equipment and can be scaled-up for commercial production. This process is safe, economic, and can recover as much of the battery materials as possible. Based on the projected quantities of LIBs available for recycling in the next few years, it was considered to have a significant market opportunity for a successful technology.

5.2. Combination of mechanical, thermal, hydrometallurgical and sol–gel steps

Lee and Rhee [5] presented a flow-sheet for recycling spent LIBs shown in Fig. 7 to recover cobalt and lithium from spent LIBs and to synthesize $LiCoO_2$ from leach liquor as cathodic active materials. Of the many possible processes to produce $LiCoO_2$, the amorphous citrate precursor process (ACP) has been applied to synthesize powders with a large specific surface area and an exact stoichiometry. After leaching used $LiCoO_2$ with nitric acid, the molar ratio of Li to Co in the leach liquor is adjusted to 1.1 by adding a fresh $LiNO_3$ solution. Then, 1 M citric acid solution at a 100% stoichiometry is added to prepare a gelatinous precursor. When the precursor is calcined at 950 °C for 24 h, purely crystalline $LiCoO_2$ is successfully obtained. The particle size and specific surface-area of the resulting crystalline powders are 20 μm and 30 $cm^2\,g^{-1}$, respectively. The $LiCoO_2$ powder is found to have good characteristics as a cathode active material in terms of charge–discharge capacity and cycling performance.

5.3. Combination of dismantling, acid leaching, chemical precipitation and solvent extraction

Dorella and Mansur [11] investigated a hydrometallurgical route consisting of the following steps for focusing on the recovery of cobalt from spent LIBs and for separation of the main metal species such as aluminium, cobalt, lead and lithium contained in spent LIBs: (a) manual dismantling, in order to separate iron scraps, plastics and battery dust containing cobalt and other metals, (b) anode/cathode manual separation, aiming to separate lead from the residue, (c) acid leaching with H_2SO_4 and H_2O_2, to transfer metals from the residue to the aqueous solution, (d)
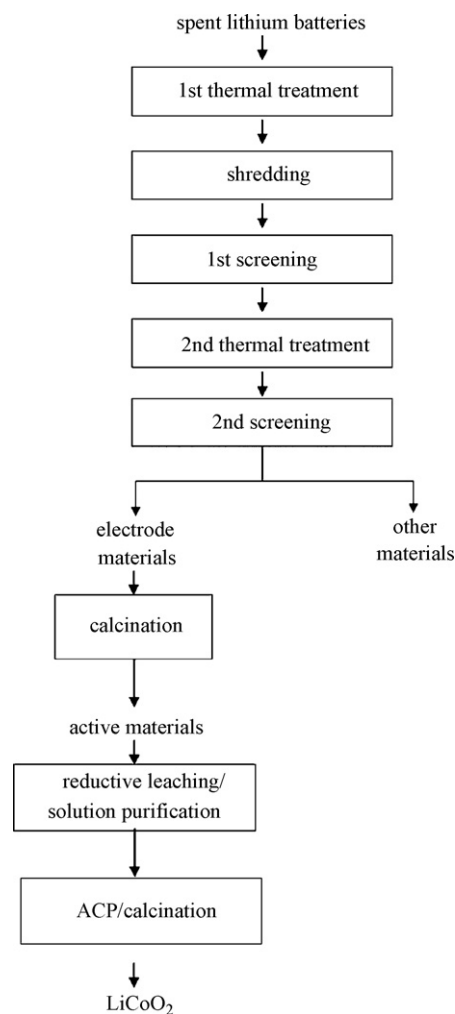

Fig. 7. A flow-sheet of proposed process for recycling spent lithium-ion secondary rechargeable batteries.

chemical precipitation with NH_4OH, which was chosen as precipitating agent in order to avoid the addition of other metal into the system, to separate aluminium, and (e) liquid–liquid extraction using Cyanex 272 [bis(2,4,4-trimethylpentyl) phosphinic acid] as the extractant agent, to separate cobalt from lithium resulting in a concentrated metal solution quite adequate for electrowinning. The principle flow-sheet of the hydrometallurgical process for the recovery of cobalt, lithium, aluminum and lead is shown in Fig. 8. The experimental results showed that around 55% of aluminium, 80% of cobalt and 95% of lithium were leached from the cathode when leaching solutions with H_2SO_4 and H_2O_2 were carried out. In the precipitation step, NH_4OH was added to the leach liquor to raise the pH and aluminium was partially separated from cobalt and lithium at pH 5. After filtration, the aqueous solution was submitted to a purification step by liquid–liquid extraction with Cyanex 272 and around 85% of cobalt was separated. It must be emphasized that these separation steps were investigated using single contacts in batch mode operation, so the process efficiency obtained in this study (around 50% of cobalt was recovered from the battery dust) might increase once optimized.
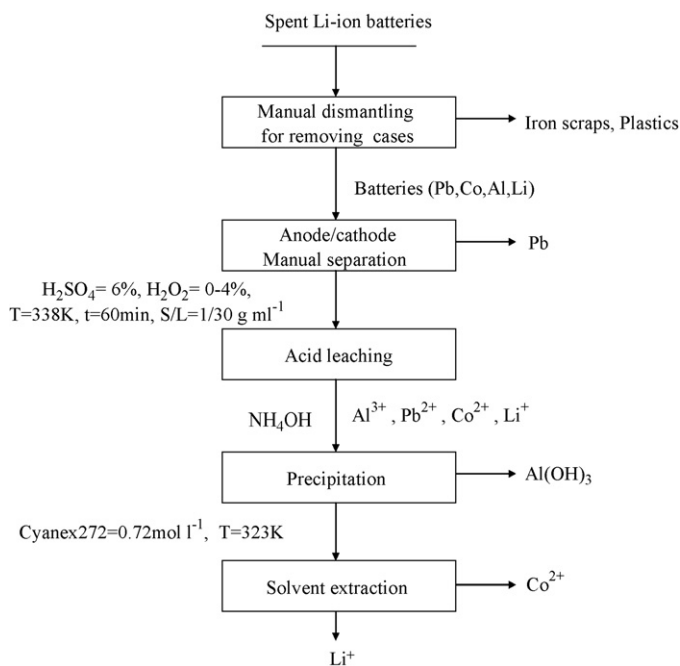
Fig. 8. Principle flow-sheet of the hydrometallurgical process for the recovery of cobalt, lithium, aluminum and lead.

5.4. Combination of mechanical dismantling and separation, electrochemical and thermal treatment

Ra and Hana [13] developed a process for recovering and renovating depleted $LiCoO_2$ cathode material in spent LIBs in a single synthetic step using Etoile–Rebatt technology. The recycling procedure, as schematized in the flow chart of Fig. 9, consists of five steps: dismantling, discharging, separation, detachment, and recycling treatment. Spent LIBs, which have already been depleted of their performances, were dismantled to eliminate package, protection circuit module, positive temperature coefficient element, safety vent, etc. Unit cells were soaked in brine and completely discharged for security. Then, anode, separator, electrolyte, and cathode in the unit cell were separated. As shown in Fig. 10, 16.678 kg of black pastes separated from cathode were electrochemically and thermally treated in a laboratory-made recycling instrument. The separated pastes were immersed in the ER-MRT-13 solution containing 4 M LiOH and KOH, and located on the bottom of the reaction vessel and at a distance of 70 cm from the platinum electrodes located in another vessel for product collecting. The recycling reaction was carried out at a fixed temperature between 40 and 100 °C. During the recycling reaction, the platinum working electrode was galvanostatically charged at a fixed current density between 0.001 and 1.00 mA cm^{-2}. In detail, recycling reaction simultaneously consists of the dissolution of the depleted $LiCoO_2$, the deposition of the dissolved $LiCoO_2$ on the platinum working electrode, the formation of the recovered and renovated $LiCoO_2$ film, as well as the precipitation of the recovered and renovated $LiCoO_2$ powder from the surface of the $LiCoO_2$ film. The recycled $LiCoO_2$ was filtered and washed with doubly distilled water, and then dried at 80 °C for 10 h. 12.564 kg of $LiCoO_2$ was recovered from 16.678 kg of black pastes separated from cathode.

The structural and compositional purities of the recovered and renovated $LiCoO_2$ were confirmed by elemental analyses, X-ray diffraction pattern analyses, and Raman spectroscopy. Since recycling using the Etoile–Rebatt technology is performed in an open system, its upper limit in capability depends on just voluminal scale of recycling instrument. While the renovated $LiCoO_2$ phase is simply obtained from spent LIBs in an economical recycling way, the recovered and renovated $LiCoO_2$ exhibits a prospective electrochemical activity and battery performance: an initial discharge capacity of 134.8 mAh g^{-1} and the discharge capacity retention of 95.9% after 50 cycles.

5.5. Combination of dismantling, chemical deposition and solvent extraction

Nan et al. [14] developed a recycling process of metal values based on hydrometallurgical method for spent LIBs for their laboratory experiment, with the exploitation of battery dismantling machine (CN Application No. 200410051922.1) and the investigation of solvent extraction on the separation of copper and cobalt. The overall recycling process comprises the dismantling of spent LIBs, the recovery of cobalt, copper and lithium using chemical deposition and solvent extraction methods, and the reuse of recovered compounds to synthesize $LiCoO_2$ cathode material. It is shown that about 90% cobalt was deposited as oxalate with less than 0.5% impurities, and Acorga M5640 and Cyanex 272 were efficient and selective for the extraction of copper and cobalt in sulfate solution. Over 98% of the copper and 97% of the cobalt was recovered. $LiCoO_2$ positive electrode material with good electrochemical performance was also synthesized by using the recovered compounds of cobalt and lithium as precursors. This process is thought to be feasible for the recycling of spent LIBs in scale-up, and consequently an overall flow chart for the recycling of metal values from spent LIBs based on a hydrometallurgical process is presented for scale experiment in Fig. 11. According to this process given in this flow chart, their scale experimental results have demonstrated that metal values of cobalt, copper and lithium could be effectively recovered and reused, and the recovered products had high purities. The treatment cost could be reduced effectively because the spent LIBs were dismantled with the specially designed machine and most of the cobalt was recovered by chemical deposition as oxalate. Acorga M5640 and Cyanex 272 extractants could be recycled after stripping with sulfuric acid. Waste solutions produced in the different steps could also be treated innocuously. It is noted that some other cathode material such as $LiCo_{1-x}Sn_xO_2$, $LiCo_{1-x}Mg_xO_2$ and $Li(MnNiCo)O_2$ will be used since the cathodes of commercial LIBs are not always pure $LiCoO_2$ with the development of the commercial LIBs and although these additive elements are impurities when resultants are used as chemical reagents, while these impurities can be acted as additive elements when the resultants are used as precursors to synthesize $LiCoO_2$ electrode materials. Therefore, it is thought that this process is feasible for the large-scale recycling of spent LIBs.
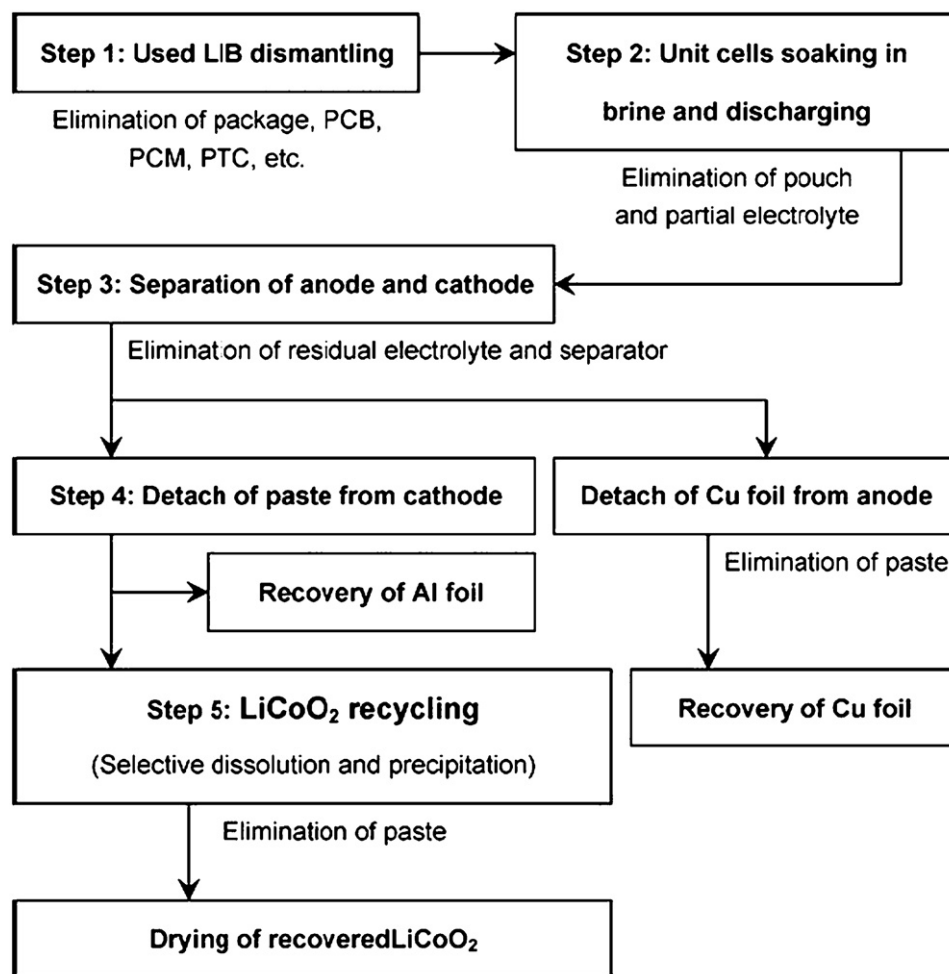
Fig. 9. Schematization of used lithium-ion rechargeable battery (LIB) recycling steps using the Etoile–Rebatt technology.

5.6. Combination of dismantling, acid leaching, solvent extraction and chemical precipitation

Zhang et al. [26] developed a hydrometallurgical process for the separation and recovery of cobalt and lithium from spent LIBs. This process consists basically of: (a) leaching of the anode materials of the LIBs with hydrochloric acid; (b) separation of cobalt from lithium with solvent extraction and (c) precipitation of lithium as carbonate. In this process, the battery package which is a plastic case was first demolished to remove the LIBs. Then the batteries were cut in half crosswise to separate the metallic cases from the internal battery rolls consisting of the cathode and anode plus an insulator. The anode materials consisting mostly of $LiCoO_3$ and a small amount of polymeric substance and carbon powder, pasted on aluminum foil were collected completely by scraping. After leaching, the leach solution and insoluble residue were separated by filtration. Solvent extraction was carried out batchwise by shaking mechanically both the organic and aqueous phases at ambient temperature ($\sim$25 °C) for about 30 min of contact time. The pH was adjusted to the desired level by the addition of concentrated sodium hydroxide solution. Precipitation was carried out by the

addition of a saturated sodium carbonate solution to the concentrated raffinate obtained from the extraction step. The best conditions were found to be (a) acid leaching: 4 M hydrochloric acid at a temperature of 80 °C and a S:L ratio of 1:10 for 1 h; (b) solvent extraction: 0.90 M PC-88A as solvent extractant with in kerosene at an O:A ratio of 0.85:1 and pH 6.7 in a single stage; (c) lithium scrubbing: at an initial pH of 1.0 and an O:A ratio of 10:1; (d) H_2SO_4 stripping: 2 M H_2SO_4, O:A ratio of 5:1; (e) lithium precipitation: at a temperature close to 100 °C. Under these conditions, over 99% of cobalt and lithium could be leached. The purity of the cobalt recovered could reach 99.99% or better. The content of cobalt in the lithium precipitates was less than 0.07%. The recovery of lithium approached 80%. An overall process flow-sheet is suggested based on the experimental investigations in Fig. 12.

5.7. Combination of leaching, solvent extraction and electrowinning

Lupi and Pasquali [28] developed a hydrometallurgical process to recycle lithium-ion and lithium-polymer batteries with lithium/cobalt/nickel oxide ($LiCo_xNi_{1-x}O_2$, $0 < x < 1$) as one of
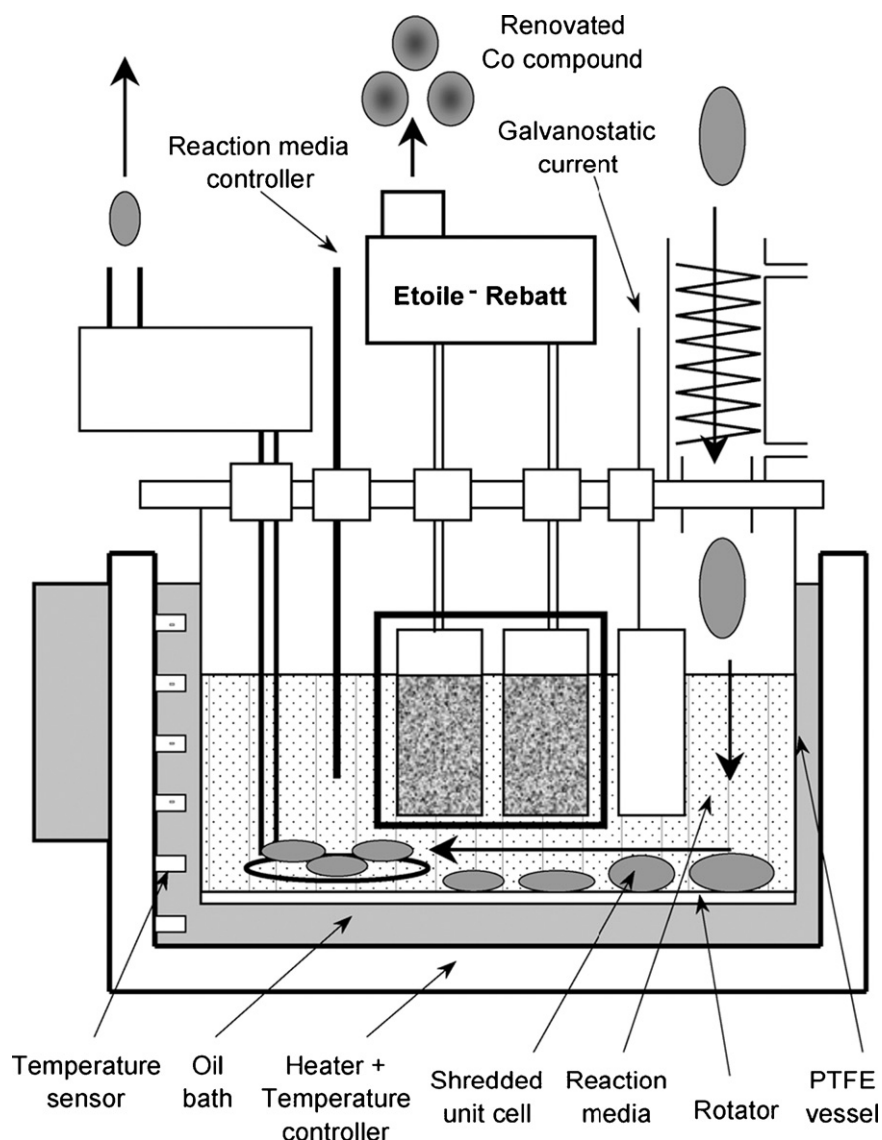
Fig. 10. Schematization of the recycling instrument using the Etoile–Rebatt technology.
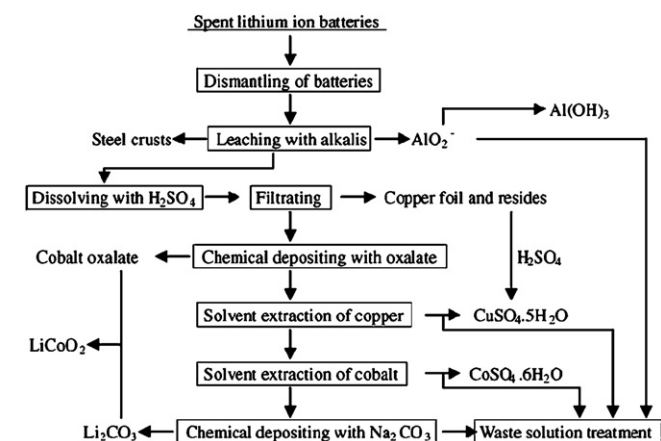

Fig. 11. The flow chart of the recovery of metal values from spent lithium-ion batteries for scale experiment.

the cathode materials. Their work aims at recovering Ni metal of high purity by electrowinning. The operations involved in this process are: cathodic paste leaching, cobalt–nickel separation by solvent extraction with modified Cyanex 272 in kerosene, Ni metal recovery by electrowinning at constant current density, and Ni powder recovery by electrolysis at constant potential, carried out on a partially depleted electrolyte. Then nickel has been recovered by means of both galvanostatic and potentiostatic electrowinning. Nickel electrowinning performed at $250\,A\,m^{-2}$ current density, $50\,°C$ temperature, pH 3–3.2, with an electrolyte having about $50\,g\,L^{-1}$ Ni and $20\,g\,L^{-1}$ H_3BO_3 composition, produces a good aspect Ni deposit with a current efficiency and a specific energy consumption of about 87% and $2.96\,kWh\,kg^{-1}$, respectively. The electrolysis at constant potential of a solution containing $1.7–1.8\,g\,L^{-1}$ of Ni produces a very pure powder in 80 min, leaving less than 100 ppm of nickel in solution.
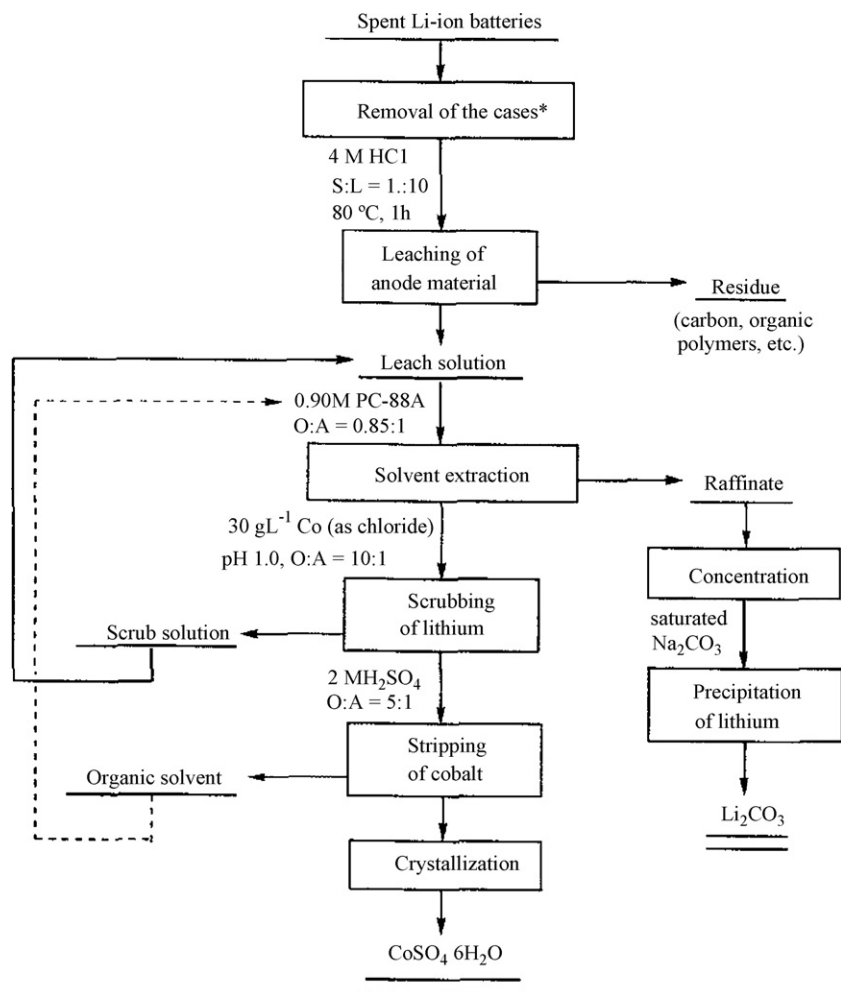
Fig. 12. Flow-sheet of the hydrometallurgical process for the recovery of cobalt and lithium from spent lithium-ion secondary batteries (The dotted line indicates that the organic phase is returned to the extraction step for reuse.). (*) The cases involve an external plastic and an internal metallic case.

5.8. Combination of mechanical shredding, electrolyte extraction, electrode dissolution and cobalt electrochemical reduction

Lain [34] developed a new process for recycling lithium-ion cells and batteries. In order to gain maximum value, the process aims to recover every component from the cell at ambient temperatures. There are four main stages: mechanical shredding, electrolyte extraction, electrode dissolution and cobalt reduction. First, the cells are posted into an inert, dry atmosphere for mechanical shredding in order to avoid exposing the cell contents to water vapor, which would hydrolyze the electrolyte and in order to reduces the impact of internal short circuits, which can be violent in contact with oxygen. Second, the liquid electrolyte is dispersed in the pores of the electrode and separator. However, by immersing in a suitable solvent for a few hours, the electrolyte can be extracted. After separation from the residual solids, the solvent can be recovered by evaporation at reduced pressure, leaving pure electrolyte. The requirements are that the boiling at reduced pressure is below the lithium salt decomposition temperature ($\sim$80 °C), and that the material is available in an anhydrous state. Third, the cell pieces are immersed in the solvent, which

is stirred, heated to around 50 °C. The binder dissolves, separating the electrode particles from the residual copper, aluminum, steel and plastic. The latter can be further separated based on their physical properties, e.g. density, magnetism. The electrode particles are filtered from the binder solution, which is then concentrated to recover the bulk of the solvent for reuse. Fourth, the residual electrode particles are lithium cobalt oxide, and one or more types of carbon, which need to be separated further before they can be reused. Electrochemical reduction is chosen to recover these metals in order to avoid adding any chemicals to the system. As the cobalt (III) is reduced to cobalt (II), lithium is released from the solid structure. Oxygen is generated at the counter electrode, giving a (simplified) overall equation of:

$$2LiCoO_2(s) + H_2O \Leftrightarrow 2CoO(s) + 2LiOH(aq) + \tfrac{1}{2}O_2(g)$$

$$(10)$$
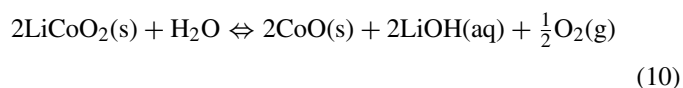
Aqueous lithium hydroxide is used as electrolyte, and the current collector is graphite. This process was considered to have significant market opportunities to be a successful recycling technology.

Table 3
Summary of recycling processes or treatment methods for the components of lithium-ion batteries

Components	Elements	Recycling processes	References
Shells	Fe	Mechanical processes; thermal treatment	[9,4,11,14]
	Plastics	Mechanical processes	[9,11]
Aluminum foil	Al	Mechanical processes; acid leaching; chemical precipitation	[9,11]
Anode	Cu	Mechanical processes	[9]
	C (graphite)	Mechanical processes; thermal treatment	[9,4,35]
Adhesive agent	PVDF binder	Thermal treatment	[4,5]
Electrolyte (organic liquid—$LiPF_6$, $LiBF_6$, $LiClO_4$)		Thermal treatment; solvent extraction	[4,27,34]
Cathode ($LiCoO_2$, $LiNiO_2$, $LiMnO_4$)	Co	Mechanochemical process; dissolution process; thermal treatment; acid leaching; bioleaching; solvent extraction; chemical precipitation; electrochemical process	[1,4,5,11,14,23,26,31,34,35, 39,40,43,50–53,55]
	Li	Mechanochemical process; thermal treatment; dissolution process; acid leaching; bioleaching; Solvent extraction	[1,4,5,11,14,23,26,31,34,35, 39,40,43,50–53]
	Ni	Mechanochemical process; chemical precipitation; electrochemical process	[4,28,40]
	Mn	Chemical precipitation	[4]

5.9. Combination of dissolution, heat treatment, acid leaching and chemical precipitation

Tong et al. [35] studied a process for recycling of $LiCoO_2$ cathode materials from spent LIBs, in which propylene carbonate was used as the solvent to recycle electrolyte and NMP was used as the solvent to separate the active materials from current collectors at 70 °C. Carbon powder was removed by heat-treatment. Cobalt compounds were dissolved by HCl solution and recycled as $Co(OH)_2$. The recycled $Co(OH)_2$ was used as the starting material to synthesize $LiCoO_2$. The net recovery of cobalt was more than 99%. The analytical results of recycled $LiCoO_2$ showed that this recycling process was practical.

6. Final remarks

At present time, most of research work of recovery and recycling of LIBs are concentrated on the recovery or recycling of the precious metals such as cobalt, nickel and lithium of the electrode materials since cobalt is a rare and precious metal, and nickel and lithium are expensive. The studies on the recovery or disposal of other materials such as graphite, electrolyte in spent LIBs are only few and need to be carried out further. Table 3 summarizes the recycling processes or treatment methods for the components of lithium-ion batteries.

The metallurgical technologies are the main methods which are used to recycle or dispose of the spent LIBs. Therefore, the technologies of the recycling, recovery and utilization will be developed with the development of the metallurgical technologies. Especially, the metallurgical technologies on using microorganism have become considerably mature in the field of mineral processing. However, there are only rare reports on recycling of spent LIBs by using microorganism. The studies on this respect should be carried out more.

The fact that development of the manufacture technologies of LIBs will change their composition elements means that their electrode materials and electrolyte will definitely be changed continually and therefore the studies of technologies for recycling spent LIBs will consequently be changed. This will affect the direction of research work on the recycling technologies of spent LIBs.

The occurrence and rapid development of lithium polymer ion secondary batteries bring forward new problems to be solved. The treatment of their electrodes will be the main problems which need a lot of research work to be carried out on.

In the future time, the comprehensive and practical recycling technologies will be needed in which not only the useful resources such as precious metals should be recovered but also other materials harmful to environment should be disposed of appropriately.

References

[1] D.P. Mantuano, G. Dorella, R.C.A. Elias, M.B. Mansur, J. Power Sources 159 (2006) 1510–1518.
[2] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenïorio, J. Power Sources 130 (2004) 291–298.
[3] A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, M.B. Mansur, J. Power Sources 115 (2003) 367–373.
[4] S. Castillo, F. Ansart, C. Laberty-Robert, J. Portal, J. Power Sources 112 (2002) 247–254.
[5] C.K. Lee, K.I. Rhee, J. Power Sources 109 (2002) 17–21.
[6] Q. Wu, W. Lu, J. Prakash, J. Power Sources 88 (2) (2000) 237–242.

[7] C. Iwakura, Y. Fukumoto, H. Inoue, S. Ohashi, S. Kobayashi, H. Tada, M. Abe, J. Power Sources 68 (2) (1997) 301–303.

[8] J. Chen, C. Yao, S. Sheu, Y.C. Chiou, H.C. Shih, J. Power Sources 68 (2) (1997) 242–244.

[9] S.M. Shin, N.H. Kim, J.S. Sohn, D.H. Yang, Y.H. Kim, Hydrometallurgy 79 (2005) 172–181.

[10] Y. Qin, S. Qi, Nonferr. Metal (Part of Metallurgy) 1 (2006) 13–16.

[11] G. Dorella, M.B. Mansur, J. Power Sources 170 (2007) 210–215.

[12] Z. Zhang, J. Yang, Nonferr. Min. Metall. 21 (2005) 46–47 (in Chinese).

[13] D. Ra, K. Hana, J. Power Sources 163 (2006) 284–288.

[14] J. Nan, D. Han, X. Zuo, J. Power Sources 152 (2005) 278–284.

[15] A. Lundblad, B. Bergman, Solid State Ionics 96 (1997) 183–193.

[16] E. Plichta, M. Salomon, J. Power Sources 21 (1987) 25–31.

[17] C.M. Sabin, Battery paste recycling process, US Patent 5,690,718. (1997).

[18] C.K. Lee, K.I. Rhee, Hydrometallurgy 68 (2003) 5–10.

[19] J.C. Alfonso, N.G. Busnardo, R.G.Busnardo, in: Gaballah, I., Mishra, B., Solozobal, R., Tanaka, M. (Eds.), Proceedings of REWAS, 2004, vol. III. TMS, Warrendale, Pennsylvania, USA, 2004, pp. 2783–2785.

[20] B.R. Conard, Hydrometallurgy 30 (1992) 1–28.

[21] H. Zhong, J. Li, L. Chai, Rare Earth Metal Hard Alloy 144 (2001) 1–3.

[22] J. Kondás, J. Jandová a, M. Nemeckova, Hydrometallurgy 84 (2006) 247–249.

[23] D. Mishra, D.J. Kim, D.E. Ralph, J.G. Ahn, Y.H. Rhee, Waste Manage. 28 (2008) 333–338.

[24] R. Shackle, M.H. Calif, Method for recycling metal containing electrical component, US Patent 5,352,270. (1994).

[25] V. William et al., Method and apparatus for neutralizing reactive material such as batteries, US Patent 4,637,928. (1982).

[26] P. Zhang, T. Yokoyama, O. Itabashi, T.M. Suzuki, K. Inoue, Hydrometallurgy 47 (1998) 259–271.

[27] M. Bahgat, F.E. Farghaly, S.M. Abdel Basir, O.A. Fouad, J. Mater. Process. Tech. 183 (2007) 117–121.

[28] C. Lupi, M. Pasquali, Miner. Eng. 16 (2003) 537–542.

[29] S. Kawakami, K.K. Canon, Japan Eur. Pat. Appl. EP 613198 A1, 31 August 1994.

[30] M. Contestabile, S. Panero, B. Scrosati, J. Power Sources 83 (1999) 75–78.

[31] M. Contestabile, S. Panero, B. Scrosati, J. Power Sources 92 (2001) 65–69.

[32] F. Ansart, S. Castillo, C. Laberty-Robert, M. Pellizon-Birelli, in: Proceedings of the Congre's Gaston Plante ̆, CNAM, Paris, October 2000, pp. 1–5.

[33] Lithium Battery Recycling Facility, Toxco Inc., 3200 E. Frontera Street, Anaheim, CA 92806, USA.

[34] M.J. Lain, J. Power Sources 97 (98) (2001) 736–738.

[35] D. Tong, Q. Lai, X. Ji, Chinese J. Chem. Ind. Eng. (China) 56 (2005) 1967–1970 (in Chinese).

[36] J.A.S. Tenório, D.C. Oliveira, A.P. Chaves, Carbon–zinc batteries treatment by ore processing methods, in: Proceedings of the Global Symposium on Recycling Waste Treatment and Clean Technology (REWAS'99), vol. II, TMS, 1999, pp. 1153–1160.

[37] Q. Zhang, F. Saito, Hydrometallugy 47 (1998) 231–241.

[38] Y. Tanaka, Q. Zhang, F. Saito, Power Technol. 132 (2003) 74–80.

[39] S. Saeki, J. Lee, Q.W. Zhang, F. Saito, Int. J. Miner. Process. 74S (2004) S373–S378.

[40] Zhang F.Q., J. Lu, F. Saito, C. Nagata, Y. Ito, Adv. Power Technol. 11 (2000) 353–359.

[41] J. Frenay, S. Feron, Domestic battery recycling in western Europe, in: J.H.L. Van Linden, D.L. Stewart Jr., Y. Sahai (Eds.), Proceedings of the Second International Symposium on Recycling of Metals and Engineered Materials, The Minerals, Metals and Materials Society, 1990, pp. 639–647.

[42] D.S. Kim, J.S. Sohn, C.K. Lee, J.H. Lee, K.S. Hanc, Y.I. Lee, J. Power Sources 132 (2004) 145–149.

[43] H. Brandl, M.A. Faramarzi, Particuology (China) 4 (2006) 93–97.

[44] T. Rohwerder, T. Gehrke, K. Kinzler, W. Sand, Appl. Microbiol. Biotechnol. 63 (2003) 239–248.

[45] C. Cerruti, G. Curutchet, E. Donati, J. Biotechnol. 62 (1998) 209–219.

[46] W. Verstraete, J. Biotechnol. 94 (2002) 93–100.

[47] G. Rossi, Biohydrometallurgy, McGraw-Hill, Hamburg, New York, 1990.

[48] J.N. Moore, S.N. Luoma, Environ. Sci. Technol. 24 (1990) 1278–1285.

[49] S. Stefan, A.I. Nicole, Environ. Manage. 30 (2002) 68–76.

[50] D. Han, J. Nan, Chin. J. Power Sources 29 (2005) 128–131 (in Chinese).

[51] P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, K. Inoue, Hydrometallurgy 50 (1998) 61–75.

[52] J.R. Lin, C.Fan, I.L.Chang, J.Y.Shiu, Clean process of recovering metals from waste lithium-ion batteries. US Patent 65514311 (2003).

[53] T.Tanii, S. Tsuzuki, S.Honmura, T.Kamimura, K.Sasaki, M. Yabuki, K. Nishida, Method for crushing cell. US Patent 6524737 (2003).

[54] X. Ou, X. Sun, Q. Zhao, F. Fan, Chinese Inorg. Chem. Ind. 37 (2005) 11–14 (in Chinese).

[55] J. Myoung, Y. Jung, J. Lee, Y. Tak, J. Power Sources 112 (2002) 639–642.

[56] Y. Shen, Chinese Nonferr. Metals 54 (2002) 69–71 (in Chinese).

[57] X. Sun, J. Wei, X. Wang, M. Ye, J. Yan, X. Gao, Chin. J. Power Sources 28 (12) (2004) 794–797 (in Chinese).

[58] M. Yoshimura, K.S. Han, S. Tsurimoto, Solid State Ionics 106 (1998) 39–44.

[59] K.S. Han, S.W. Song, T. Watanabe, M. Yoshimura, Solid State Ionics 135 (2000) 273–276.

[60] K.S. Han, S. Tsurimoto, M. Yoshimura, Solid State Ionics 121 (1999) 229–233.

[61] S.W. Song, K.-S. Han, I. Sasagawa, T. Watanabe, M. Yoshimura, Solid State Ionics 135 (2000) 277–281.

[62] T. Watanabe, H. Uono, S.W. Song, K.S. Han, M. Yoshimura, J. Solid State Chem. 162 (2001) 364–369.

[63] K.S. Han, S.W. Song, S. Tsurimoto, H. Fujita, I. Sasagawa, K.H. Choi, H.K. Kang, M. Yoshimura, Solid State Ionics 151 (2002) 11–18.

[64] A. Lundblad, B. Bergman, Solid State Ionics 96 (1997) 173–181.

[65] P. Suresh, S. Rodrigues, A.K. Shukla, S.A. Shivashankar, N. Munichandraiah, J. Power Sources 112 (2002) 665–670.

[66] R.J. Gummow, M.M. Thackeray, Solid State Ionics 53–56 (1992) 681–687 (North-Holland).

[67] X.H. Hu, X.P. Ai, H.X. Yang, Sh.X. Li, J. Power Sources 74 (1998) 240–243.