A Review of Processes and Technologies for the Recycling of Spent Lithium-ion Batteries

Songli Wang1,2,3, Yang Tian1,2,*, Xiaofeng Zhang1,2, Bin Yang1,2, Fei Wang2,3, Baoqiang Xu1,2, Dong Liang1,2 and Lipeng Wang2,3

1State Key Laboratory of Complex Nonferrous Metal Resources Clear Utilization, Kunming University of Science and Technology, Kunming 650093, PR China
2National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, PR China
3Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

*Corresponding author e-mail: emontian@hotmail.com

Abstract. Lithium-ion batteries (LIBs) have been widely applied in the fields of portable electronic devices and energy conversion and storage, with which a lot of spent LIBs have been produced. LIBs contain many valuable metal elements. At the same time, heavy metal elements in spent LIBs and organic compounds in electrolytes will cause serious environmental pollution. Therefore, the research on reclamation and harmless treatment of lithium-ion batteries have important strategic significance. This paper introduces the research progress of recovery and treatment technology of LIBs in recent years. Main technologies include wet recovery process, pyrometallurgical recovery process and wet electrochemical recovery process. Secondary pollution and safety concerns during these processes were also discussed.

1. Introduction

Compared with nickel-cadmium and nickel-hydrogen batteries, Lithium-ion batteries (LIBs) have many advantages, such as high specific energy density, long service life, high rated voltage, no memory effect and low self-discharge rate [1-2]. It is found that the electric vehicle sold through 2020 will produce 120–549 GWh, thanks to the development of new energy vehicles [3]. LIBs will therefore be used in large quantities. It is estimated that the global market of LIBs will go beyond 45 billion US dollars by 2020 [4]. The significance of recycling spent LIBs are mainly embodied in two aspects. Spent LIBs contain a variety of toxic substances, such as heavy metals, organic and inorganic compounds, which are prone to chemical reactions in the environment and harm for the environment [4-5]. Some of these compounds are carcinogenic and harmful to human beings. On the other hand, the grade of cobalt and lithium elements in Lithium cobalt oxide (LiCoO2) batteries is higher than that in lithium and cobalt ores. Cobalt is a scarce strategic metal in China and needs to be imported from abroad every year. Therefore, how to recycle these valuable metals efficiently has become hot topic. Up to now, some hydrometallurgical and pyrometallurgical processes have been reported or patented [6-9]. Hydrometallurgical processes include acid leaching, bioleaching, solvent extraction, and chemical precipitation. Acid leaching relied on dissolving materials from the battery after mechanical treatment.
in acid. Leaching of lithium and cobalt from LiCoO$_2$ was carried out with the help of one of four acids: HCl, H$_2$C$_2$O$_4$, H$_2$SO$_4$ or HNO$_3$ [10-14]. Solvent extraction was often used at the next stage after acid leaching. It was based on the addition of an extractant to dissolve metals so to separate the selected metal [15-16]. Chemical precipitation was made use of a precipitating agent that reacted with a metal in a solution producing an insoluble salt [17]. The electrochemical process was allowed achievement of pure metals from solution by electrowinning. Pyrometallurgical processes that included mechanical separation, thermal treatment, mechanochemical process and dissolution process [18]. During mechanical separation (often the first stage of recycling), the battery was milled and materials were separated from each other considering their properties such as density, conductivity and behavior in a magnetic field. In a thermal treatment, crushed materials (sometimes with additional substances) were put into a furnace at a given temperature and for a given time [19-22]. The mechanochemical process could recover lithium and cobalt from the positive electrode. The dissolution process was enabled separation of active materials from electrodes without crushing them [23-25]. These methods had different effects on hydrometallurgical and pyrometallurgical processes.

2. Structures of LIBs

LIBs are mainly made of cathode, anode separators, and electrolyte. When the battery was recycled, lithium-ion exchanged between cathode and anode electrodes as shown in Fig. 1 [26-28]. Typical cathode materials are metal oxides with layered structure, such as LiCoO$_2$, or materials with tunnel structure, such as LiMnO$_4$, and they all use aluminium as collector. The typical anode material is graphite, which is also a layered material with copper as collector. In 1991, Sony produced the world's first LIBs to the market, and it used LiCoO$_2$ as the cathode material. LiCoO$_2$ has good electrochemical and safety properties. LiCoO$_2$ is insensitive to manufacturing process and humidity and easy to manufacture. In recent years, other cathode materials had been produced, such as LiFePO$_4$ (LFP), LiMn$_2$O$_4$ (spinel structure), and Li(NiCoAl)O$_2$ (NCA) [29-30]. They are suitable for application in different products, and these materials are gradually becoming industrialized, especially with the advantages of high specific capacity, low price, safety and good cycle performance. Nickel cobalt lithium manganate cathode materials have been produced on a large scale in Europe, Korea, and Japan and in China.

There were mainly two types of electrolytes for lithium-ion batteries: liquid dielectrics and colloidal electrolytes. Liquid electrolyte was a solution of lithium salt in one or more organic solvents. The solvent of liquid electrolyte was Polycarbonate. Colloidal electrolyte was an ionic conductive material. It is a kind of material formed by dissolving salt and solvent in high molecular weight polymer or mixing with it. Colloidal electrolyte used for lithium-ion battery was typically formed by PVDF-HFP, LiPF$_6$ and LiBF$_4$ salt and carbonate solvent [31]. The lithium-ion battery used thin (16-40 micron) microporous membrane to insulate the cathode and anode of the battery. So far, all LIBs products were used liquid dielectric and microporous polyolefin materials as electrolytes and separators materials respectively [32]. The requirements for the separator for LIBs included six aspects.

1. High tensile strength in machine direction was used to ensure the strength requirement of automatic winding;
2. The width was not elongated or contracted;
3. Extruding without rupture of electrode material;
4. Effective aperture, less than 1μm;
5. Easy to be infiltrated by dielectric;
6. Compatible with electrolyte and electrode materials and maintaining stable properties;

The polyolefin materials were made from polyethylene, polypropylene or polyethylene and polypropylene composites.
3. Technologies for the Recycling of LIBs

Spent LIBs can produce 5%–20% cobalt, 5%–10% nickel, 5%–7% lithium, 15% organic chemical products and 7% plastics [33-34]. The recovery processes of LIBs were mainly divided into pyrometallurgical recovery process, hydrothermal recovery process, and wet electrochemical recovery process. According to different processes, the recycling processes of spent LIBs were needed to be pretreated and shown in Fig. 2. The complete pretreatment project included mechanical separation process, heat treatment process and wet recovery process. In the end, the cathode material, anode material, aluminium, copper, and iron shell of LIBs were separated. The detailed flow chart was as follows [35]. At present, wet recovery process, pyrometallurgical recovery process and wet electrochemical mixed recovery process had more industrial application prospects.

3.1. Hydrothermal Method

The wet recovery of lithium battery was used to extract the valuable metal by adding appropriate acid and alkali solvent and extractant after disassembling the battery, and then salting out the metal in the leaching solution to extract the valuable metal. The valuable metals included lithium, cobalt, copper, aluminum and so on. The main steps of the wet process recovery process were as follows in Fig. 3 [36]:

![Figure 1. Working principle of LIBs.](image1)

![Figure 2. Pretreatment process of spent LIBs.](image2)
Figure 3. Recycling of valuable metals from spent LIBs.

1. The spent LIBs were discharged, crushed, and then leached with alkaline solution. The iron shell debris of the battery was filtered out, and pH was adjusted to filter the dissolved aluminum in the form of aluminum hydroxide.

2. The solution of the previous step was adjusted pH by sulfuric acid, the copper foil and other residues were filtered, and cobalt was deposited by oxalic acid to form cobalt oxalate. And then it was oxidized roasting to form cobalt oxide.

3. The copper and cobalt in the solution was extracted by copper and cobalt extractant respectively.

4. The solution of the previous step was deposited with sodium carbonate and then oxidized and roasted to form lithium cobalt oxide.

The advantage of wet recovery process was that it could selectively recover metal by adjusting temperature, pH and solvent type, and could achieve high recovery rate. But there were many shortcomings in this process: The lithium-ion battery was treated with wet process needing to have a more fixed chemical composition, which limited the flexibility of recycling different types of lithium-ion batteries. Pure wet process, the recovered metals could only exist in the form of compounds, and it was obviously impossible to get a metal single. It restricted the application of the valuable metal in some fields of industry. Wet process needed to consume a lot of acid and alkali solvents, and these waste acid and alkali solvents were also a challenge to the environment. The wet process could only show its economy when the process was large scale application.

3.2. Pyrometallurgy Method

Umicore used a pyrometallurgical technology with a single furnace for battery recycling in Fig. 4[37-39]. The first step was preparation of a batch for the furnace. Spent LIBs were mixed with small amounts
of coke, slag, silicon oxide or limestone. The furnace was divided into three zones; in the first, the batch was preheated in order to evaporate the electrolyte: the temperature slowly increased but should be less than 300°C (excessive heating temperature may lead to explosion). The second zone was for plastics pyrolysis: the temperature in this section was 700°C, which caused melting of plastics; the hot gasses emitted in this process were used in the preheating stage. In the last zone, smelting and reduction took place. During this process, a slag (containing aluminum, silicon, calcium and iron) and an alloy (containing copper, cobalt, nickel, lithium and small quantities of iron) were obtained. The temperature in this zone was in the range 1200°C-1450°C.

Figure 4. Umicore recycling technology.

3.3. Mixed Recovery Process by Wet Electrochemical Method.

The wet electrochemical method was a full cycle process consisting of three parts as shown in Fig. 5 [40]. The process mainly included the steps of battery separation, dissolving adhesive of electrode material and recovering valuable metals, recycling lithium and recovering the remaining substances.

① Split the battery: the battery was split under full discharge. The battery shell was opened. The battery coil core was then treated in the next step. After that, the spent battery had no shell, and was carried out the next separation.

② Dissolving adhesive of battery and recovering valuable metals: The sulphuric acid solution was used to dissolve the cobalt of the battery separation, and the oxalic acid was used to deposit a large amount of cobalt to form cobalt oxalate. The remaining copper and cobalt were leached with the suitable leaching conditions and agent.

③ Recovery of lithium and the remaining substances: Sodium carbonate was used to deposit lithium to form lithium carbonate precipitates. Lithium carbonate and cobalt oxalate were used as precursors to produce lithium cobalt oxide cathode materials.
The lithium carbonate obtained by step 3 was prepared by electrochemical method in Fig. 6, including the following procedure: [41]

1. In the electrolysis process, nickel electrode and platinum electrode was regarded as anode and cathode respective. During the process the current was maintained at 1.0 mA/cm², the temperature was maintained at 100 °C, and the electrochemical reaction was maintained at 20h.

2. Samples of lithium cobalt oxide were washed with distilled water and dried for 24 hour at 80°C.

The recovery process could recovery lithium, cobalt, aluminium and copper from spent LIBs. And the recycling process is environmentally friendly.
3.4. Main Problems and suggestions.
A lot of factors will effect whether the spent LIBs recycling will really be implemented. These factors may be related to the economy of the recycling process, as well as to health, safety and the environment. In addition, laws and regulations may promote the development of spent LIBs recycling. Therefore, the successful recovery of spent LIBs needs to meet the following conditions.

First, the cost of collecting spent LIBs should be reasonable. With the development of portable electronic devices and new energy vehicles, the spent LIBs have been widely used. However, the large-scale recovery processes of spent LIBs are difficult. Secondly, the storage and transportation of spent LIBs in the collection process are also a problem. Safety and environmental protection issue need to be addressed during transportation and storage. Therefore, without hindering recycling, it is a challenge to develop management rules to protect the public and the environment.

Appropriate treatment methods must be determined for the recycling of the spent LIBs. Different types of spent LIBs contain different materials, and even some batteries contain harmful and dangerous components. Up to now, recycling methods of spent LIBs were mainly divided into wet method, pyrometallurgical method and electrochemical method. Different methods have different advantages and disadvantages. Therefore, it is particularly important to develop more efficient and environmentally friendly recovery methods. What’s more the relevant laws and policies should be established.

Finally, we must consider whether we can produce valuable products by recycling spent LIBs. Whatever the product is, its quality must be too difficult to compete with that produced with raw materials. Products that recovered in the pyrometallurgical process are compared with the metals directly obtained from the ore and refined to the same purity. Products fabricated by hydrometallurgy and electrochemical smelting should also be purified. If valuable products cannot be produced, the recovery processes need to be funded by a regulatory mechanism like a support of government.

4. Conclusion
A LIBs recycling is a relatively new but rapidly expanding process. Cobalt and lithium are the most valuable material in the spent LIBs. Almost all companies mainly focus on the cobalt and lithium recovery. But some companies also recover copper, aluminium, iron and manganese [42, 43].

Specialists estimate an increase of the lithium price in the next years, and the refinement of this metal should be more profitable in the future. The development of recycling processes focus on improving their efficiency and reducing costs of recovered metals. There are many processes proposed including the use of bacteria to dissolve materials [44-48]. Spent LIBs recycling is a relatively new process. If it is hopeful and effective in the near future, it will help to save natural resources and limit dependence on minerals supply.

Acknowledgments
This research financially supported by the Yunnan Ten Thousand Talents Plan Industrial Technology Champion Project Foundation of China (YNWR-CYJS-2018-015), and by the Yunnan Ten Thousand Talents PlanYun ling Scholar Project Foundation of China (2017HB009).

References
[1] Wei S, Zhong Z, Liu J, et al, Hierarchical MoO2/N-doped carbon heteronanowires with high rate and improved long-term performance for lithium-ion batteries. Journal of Power Sources 306 (2016): 78-84.
[2] Winslow, Kevin M., S. J. Laux, and T. G. Townsend, A review on the growing concern and potential management strategies of waste lithium-ion batteries. Resources Conservation & Recycling 129 (2018): 263-277.
[3] Ambrose, Hanjiro, et al, Driving rural energy access: a second-life application for electric-vehicle batteries. Environmental Research Letters 9.9 (2014).
[4] Cao, Guozhong, Solvent-salt synergy offers a safe pathway towards next generation high voltage Li-ion batteries. Science China. Materials 10 (2018): 1-3.
[5] Chen, Y., et al, Thermal treatment and ammoniacal leaching for the recovery of valuable metals from spent lithium-ion batteries. Waste Management 75 (2018): 469-476.

[6] Li L, Lu J, Ren Y, Ascorbic-acid-assisted recovery of cobalt and lithium from spent Li-ion batteries. Journal of Power Sources 218.12 (2012): 21-27.

[7] Heydarian A, Mousavi S M, Vakilchaf F, Application of a mixed culture of adapted acidophilic bacteria in two-step bioleaching of spent lithium-ion laptop batteries. Journal of Power Sources 378 (2018): 19-30.

[8] Xiao S, Ren G, Xie M, Recovery of Valuable Metals from Spent Lithium-Ion Batteries by Smelting Reduction Process Based on MnO–SiO2–Al2O3 Slag System. Journal of Sustainable Metallurgy 27.2 (2017): 1-8.

[9] Vikström H, Davidsson S, Höök M, Lithium availability and future production outlooks. Applied Energy 110.110 (2013): 252-266.

[10] Li L, Dunn J B, Xiao X Z, Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment. Journal of Power Sources 233.233 (2013): 180-189.

[11] Fan B, Chen, X, Zhou, T, A sustainable process for the recovery of valuable metals from spent lithium-ion batteries. Waste Manag Res 34.5 (2016): 474-481.

[12] Ordoñez J, Gago E J, Girard A, Processes and technologies for the recycling and recovery of spent lithium-ion batteries. Renewable & Sustainable Energy Reviews 60 (2016): 195-205.

[13] Bertuol D A, Machado C M, Silva M L, Recovery of cobalt from spent lithium-ion batteries using supercritical carbon dioxide extraction. Waste Manag 51 (2016): 245-251.

[14] Sonoc A, Jeswiet J, Soo V K, Opportunities to Improve Recycling of Automotive Lithium Ion Batteries. ProcediaCirp 29 (2015): 752-757.

[15] Wang, Yue Hua, et al, Preparation of Regenerated Cathode Material Lithium Nickel Cobalt Oxide LiNi0.7Co0.3O2 Form Spent Lithium-Ion Battery. Materials Science Forum 944 (2019): 1179-1186.

[16] Yang Y, Xu S, He Y, Lithium recycling and cathode material regeneration from acid leach liquor of spent lithium-ion battery via facile co-extraction and co-precipitation processes. Waste Management 64.1 (2017): 589-598.

[17] Guo Y, Li Y, Lou X, Improved extraction of cobalt and lithium by reductive acid from spent lithium-ion batteries via mechanical activation process. Journal of Materials Science 53.19 (2018): 13790-13800.

[18] Li J, Wang G, Xu Z, Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent LiCoO2/graphite lithium batteries. Journal of Hazardous Materials 302 (2016): 97-104.

[19] Chagnes A, Pospiech B, A brief review on hydrometallurgical technologies for recycling spent lithium-ion batteries. Journal of Chemical Technology&Biotechnology 88.7 (2013): 1191-1199.

[20] Xiao J, Li J, Xu Z, Recycling metals from lithium ion battery by mechanical separation and vacuum metallurgy. Journal of Hazardous Materials 338 (2017): 124-131.

[21] Sun L, QiuK, Vacuum pyrolysis and hydrometallurgical process for the recovery of valuable metals from spent lithium-ion batteries. Journal of Hazardous Materials 194. (2011): 378-384.

[22] Song D, Wang X, Zhou E, et al. Recovery and heat treatment of the Li (Ni1/3Co1/3Mn1/3) O2cathode scrap material for lithium-ion battery. Journal of Power Sources 232(2013): 348-352.

[23] Freitas M B J G, Garcia E M, Electrochemical recycling of cobalt from cathodes of spent lithium-ion batteries. Journal of Power Sources 171.2 (2007): 953-959.

[24] Setiawan H, Petrus H T B M, Perdana I, Reaction kinetics modeling for lithium and cobalt recovery from spent lithium-ion batteries using acetic acid. International Journal of Minerals, Metallurgy and Materials 26.1 (2019): 98-107.

[25] Castillo S, Ansart F, Laberty-Robert C, et al, Advances in the recovering of spent lithium battery
compounds. Journal of Power Sources 112.1 (2002): 247-254.
[26] P. W. Gruber, P. a. Medina, G. a. Keoleian, S. E. Kesler, M. P. Everson, and T. J. Wallington, Global Lithium Availability. Journal of Industrial Ecology 15.5 (2011): 760-775.
[27] Gao, Guilian, Luo, Xingmin, Lou, Xiaoyi, Efficient sulfuric acid-Vitamin C leaching system: Towards enhanced extraction of cobalt from spent lithium-ion batteries. Journal of Material Cycles and Waste Management 10 (2019): 1-8.
[28] Li L, Bian, Yifan, Zhang, Xiaoxiao, Economical recycling process for spent lithium-ion batteries and macro-and micro-scale mechanistic study. Journal of Power Sources 377 (2018): 70-79.
[29] Zhang W, Xu C, He W, et al, A review on management of spent lithium ion batteries and strategy for resource recycling of all components from them. Waste Manag Res 36.2 (2018): 99-112.
[30] Nan J, Han D, Zuo X, Recovery of metal values from spent lithium-ion batteries with chemical deposition and solvent extraction." Journal of Power Sources 152. None (2005): 278-284.
[31] Matsumura T, Nobuyuki Imanishi, Atsushi Hirano, et al, Electrochemical performances for preferred oriented PLD thin-film electrodes of LiNi0.8Co0.2O2, LiFePO4 and LiMn2O4.Solid State Ionics Diffusion & Reactions 179.35 (2008): 2011-2015.
[32] Lee CK, Rhee K-I, Preparation of LiCoO2 from spent lithium-ion batteries. Journal of Power Sources 109.1 (2002): 17-21.
[33] Li H, Wu D, Wu J, et al, Flexible, High-Wettability and Fire-Resistant Separators Based on Hydroxyapatite Nanowires for Advanced Lithium-Ion Batteries. Advanced Materials 29.44 (2017). 147-189
[34] Kang J, GaminiSenanayake, JeongsooSohn, et al, Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272. Hydrometallurgy 100.3 (2010): 168-171.
[35] MeshramP, Pandey B D, Mankhand T R, Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. Hydrometallurgy 150 (2014): 192-208.
[36] Zeng X, Li, Jinhui, Singh, Narendra, Recycling of Spent Lithium-Ion Battery: A Critical Review. Critical Reviews in Environmental Science & Technology 44.10 (2014): 1129-1165.
[37] Liu, Pengcheng, et al, Study on the reduction roasting of spent LiNi0.8Co0.2Mn0.02 lithium-ion battery cathode materials. Journal of Thermal Analysis and Calorimetry 136.3 (2019): 1323-1332.
[38] Boyden, Anna, V. K. Soo, and M. Doolan, the Environmental Impacts of Recycling Portable Lithium-Ion Batteries. ProcediaCirp 48 (2016): 188-193.
[39] Kang, Jingu, et al, Preparation of cobalt oxide from concentrated cathode material of spent lithium ion batteries by hydrometallurgical method. Advanced Powder Technology 21.2 (2010): 175-179.
[40] Liang S, Qiu K, Organic oxalate as leachant and precipitant for the recovery of valuable metals from spent lithium-ion batteries. Waste Management 32.8 (2012): 1575-1582.
[41] Zhang P, Yokoyama T, Itabashi O, et al, Hydrometallurgical process for recovery of metal values from spent lithium-ion secondary batteries. Hydrometallurgy 50.1 (1998): 61-75.
[42] Chen L, Tang X, Zhang Y, et al, Process for the recovery of cobalt oxalate from spent lithium-ion batteries. Hydrometallurgy 108.1 (2011): 80-86.
[43] Dutta, Debhina, et al. "Close loop separation process for the recovery of Co, Cu, Mn, Fe and Li from spent lithium-ion batteries. Separation & Purification Technology 200 (2018).
[44] Zhao J M, Shen X Y, Deng F L, et al, Synergistic extraction and separation of valuable metals from waste cathodic material of lithium ion batteries using Cyanex272 and PC-88A. Separation & Purification Technology 78.3 (2011): 345-351.
[45] Balasubramanian, N, Waste minimization and recovery of valuable metals from spent lithium-ion batteries – a review. Environmental Technology Reviews 2.1 (2013): 101-115.
[46] Parhi P K, Padhan E, Palai A K, et al, Separation of Co (II) and Ni (II) from the mixed sulphate/chloride solution using NaPC-88A. Desalination 267.2 (2011): 201-208.
[47] Zheng, Xiaohong, et al, A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries. Engineering 4.3 (2018): 361-370.

[48] Mishra D, Kim D J, Ralph D E, et al, Bioleaching of metals from spent lithium ion secondary batteries using Acidithiobacillusferroxidans. Waste Management 28.2 (2008): 333-338.