OVERVIEW OF EAST ASIA RECYCLING MARKET AND REVOLUTIONARY REGENERATION SOLUTION FOR SPENT BATTERIES

Xiao Lin
CEO
Botree Cycling
Suzhou, Jiangsu, China

Nana Chang
Junior Researcher
Botree Cycling
Suzhou, Jiangsu, China

Abstract
The development of green transport and electrification will cause exponentially increasing demands for Lithium-ion batteries (LIBs) in the next decades, which could cause a shortage of battery critical raw materials and have larger environmental impact. Thus, at the end of battery life, LIBs should be repurposed, remanufactured or recycled, feeding valuable materials back into the economy to form the closed loop chain of the whole life cycle of batteries. In recent years, the number of spent LIBs has reached its first peak and many companies have already begun to recycle the first batch of spent LIBs based on traditional processes. However, it is essential to develop a more efficient, cost-effective and eco-friendly solution with the growing financial and environmental requirements. This paper will show the current battery recycling market in East Asia and bring to light novel research and industrial application of revolutionary regeneration technologies for battery recycling from dismantling to separation and purification. An ideal regeneration technology with a short process, low energy consumption, and high recycling rates, will produce huge potential benefits both economically and to the environment. Hence, the recovery of spent LIBs will significantly contribute to the development of green and sustainable energy resources.

Introduction
As an advanced energy storage technology, Lithium-ion batteries (LIBs) have been widely integrated into renewable resources and electric vehicles (EVs), supporting the current agreements to reduce greenhouse gas emissions. According to the International Energy Agency (IEA) data, in 2020 the global electric car stock hit the 10 million mark, a 43% increase over 2019. China, with 4.5 million electric cars, has become the world's largest new energy vehicle market. It is foreseeable that the number of LIBs will continue to increase in the next decades due to the growing market demand. As predicted by some researchers, the market scale of LIBs will reach 77.42 billion dollars in 2024[1]. Such a big explosion of LIBs, however, has brought problems as well as benefits. The ever-growing demand on the critical metal materials of LIBs will cause not only the risk of supply interruption, but also the environmental issues associated with the mining and mineral processing activities, such as land and water pollution, ecosystem damage or greenhouse gas emissions. Therefore, LIB material recycling, as an indispensable link in the closed loop chain, has attracted global attention for its huge economic, environmental, and social values[2].

Battery Recycling Market in East Asia

Nowadays, the lithium-based power battery industry of East Asia has been mainly dominated by China, Japan, and South Korea, and each has its leading companies. Japan's Panasonic, supported by Sumitomo Consortium, has been developing LIBs since 1994. It started cooperation with Tesla in 2008 and built the ''Gigafactory'' in 2014. LG Chem (LGC) of South Korea began working on LIBs in 1996 and became the sole supplier of the Chevrolet Volt EV in 2020. CATL, a Chinese company, has not only become a leader in China's LIB industry, but also became the largest supplier of LIBs in the world since 2017. The IEA reports showed that the total installed capacity of global power batteries reached 137 GWh in 2020, with a year-on-year growth of 17%. Among them, CATL, for the fourth consecutive year, maintained the highest installed capacity with annual installed volume of 34 GWh, while LG Chem ranked second with 31 GWh. Panasonic ranked third, with 25 GWh installed for the year. Two South Korean power battery companies, SDI and SKI, ranked fifth and sixth, with growth rates of 81% and 284% respectively.

Generally, the average life-span of LIBs in new energy vehicles is projected to be 5–8 years. One analyst estimates that 355,000 tons of retired LIBs were available for recycling in 2019 and it will reach about 800,000 tons in 2025[3] in China. Of these spent LIBs, more than 60% were lithium nickel-cobalt-manganese oxide (NCM); about 38% were lithium iron phosphate (LFP); and the others were less than 2%. China has made great efforts and achieved much progress both in science and technology investment of waste LIB recovery in recent years. Major LIB recycling companies operating in China include GEM, BRUNP, HUAYOU COBALT, TES-AMM, Umicore, etc. Many of the LIB collectors, such as BYD and Lishen, have partnered with BRUNP to bridge the gap between battery collection and recycling. In 2019, about 5.3 GWh of LIB were scrapped in China and it is expected to increase to 111.7 GWh in 2025[4]. In addition, Sumitomo Metal Mining Co. Ltd. (SMM) in Japan also has made some achievements in LIB recycling, especially for recovering the Cu and Ni contained in the waste LIBs. Predictably, the waste LIB recycling industry has broad prospects in the future, and China will become one of the largest markets for LIB recycling.

Battery Recycling Technologies

The recycling and utilization of retired LIBs is one of the important links in the industrial chain of new energy vehicles, and it is also the link with the highest environmental risk and the most urgent demand for technological progress. Usually, the key raw material of a LIB is cathode material, which represents the highest proportion of the cost of LIB materials and also directly determines the safety and performance of the battery. Therefore, the recovery of cathode metals is the primary objective for waste LIB recycling. In comparison with many precious metals like Co, Li, and Ni in NMC cathodes, LFP cathodes do not contain any precious metals, and it seems that there is little value for recycling LFP batteries. However, many Chinese enterprises chose LFP batteries in the early production stage because of their inherent merits, including lower cost, higher safety, and longer cycle life. Moreover, the market share of LFP batteries in stationary energy storage systems is growing rapidly recent years. Hence, it is also essential to recover LFP batteries due to their large quantities in the spent battery market.

LIBs are usually composed of stainless-steel shells, collectors, cathodes, anodes, electrolyte, and separators. The goal of recycling processes is to separate the components of spent batteries into different fractions that can be reintroduced into the production of useful materials. The general procedure for battery recycling includes pre-treatment and regeneration processes. The rest of this paper will focus on the current status of recycling technologies and the most promising processes for commercial application.

The pre-treatment process is used to separate different components of waste LIBs according to the different physical properties of the materials, mainly including discharge/deactivation, heat treatment, mechanical crushing, mechanical separation (particle size, gravity, magnetism, etc.), solvent dissolution, and so on. The pre-discharge process before dismantling a spent battery is very necessary in order to avoid accidents such as fire or explosion. Three common methods are brine immersion, conductor or semiconductor discharge, and low temperature freezing. The salt water discharge method is of low cost, gives a complete discharge, and is suitable for industrial scale production. Thus, most Chinese scompanies adopt the method of brine immersion as the discharge technology. After the crushing process, the volatile electrolyte is collected by the bag dust collecting device and then condensed for next burning treatment after removing the harmful components such as fluoride and phosphorus species. After the mechanical separation process, the black powder can be separated from the steel casings, Al/Cu pieces (10-30 mm) and separators, where the overall recovery efficiency (RE) of electrode materials is at least 95%.

The spent active materials obtained from the pre-treatment process can be regenerated and reused as battery materials through the following three methods[5]: i) pyrometallurgical, ii) hydrometallurgical, and iii) direct recycling methods (Figure 1).

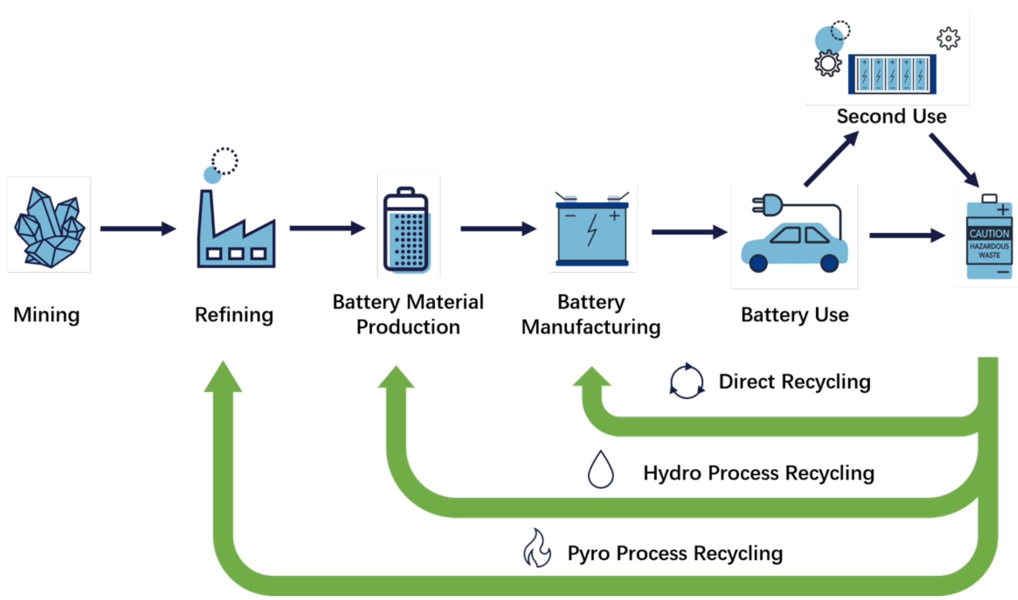

Figure 1. Regeneration technologies in LIB lifecycle.

Pyrometallurgy is a method of extracting valuable metals from waste LIBs at high temperature. The typical pyrotechnic process is to recover Ni and Co in alloy form by high-temperature reductive smelting. However, this process is accompanied by the loss of Li and Al metals in the slags. In order to solve the difficulty of Li recovery during the incineration process, carbothermal reduction technology has attracted much attention. For example, Xu et al.[6] developed a novel and environmentally friendly roasting process for recovering both Co and $LiCO_3$, which is well applicable to NCM ternary materials and has great prospects in industrial application. Although the pyrometallurgical technology has many advantages such as simple operation, large productive capacity, and is highly adaptable to various cathode materials, it still faces challenges in energy consumption and environmental pollution.

Compared with pyrometallurgical process, hydrometallurgy technology features high metal recovery rate, low energy consumption, and high-value-added products. The common hydrometallurgy methods mainly include leaching, extraction, precipitation and so on. Leaching agents usually consist of inorganic acids and organic acids[7]. Among inorganic acids, HCl exhibits a better leaching effect than H_2SO_4 and HNO_3 due to its intrinsic reducibility. In fact, the inorganic acids are usually used in conjunction with reductants such as H_2O_2 and Na_2SO_3 because valuable metals in low valence are much easier to be leached and more stable in solution (e.g., Co^{2+} is more soluble than Co^{3+}), and thus they can further improve the leaching kinetics and leaching rates. It should be noted that although inorganic acids can leach the metal components efficiently, they would inevitably bring about secondary pollutants (SO_3, Cl_2, and NO_x) and complicated separation and purification steps. In order to address the environmental problems in the leaching process of inorganic acids, many organic acids such as oxalic acid, citric acid, acetic and malic acid have been used as alternative leaching agents. Previous studies show that several organic acids like citric acid and ascorbic acid display a higher leaching rate of Co than that of inorganic acids owing to their intrinsically stronger reducing abilities. Nevertheless, the processing capacities of organic acids is smaller than that of inorganic strong acids. From the perspective of industrial production, inorganic acids are more practical as leaching agents.

In addition to chemical leaching, bioleaching, which uses organic or inorganic acids produced during microbial metabolic processes, exhibits many advantages, such as low operational cost, small equipment investment, and environmental friendliness[8]. Typically, the thiobacillus ferroxidans have been used in the leaching process of LCO material. The leaching rate of Li can reach 80% with the dissolution of H_2SO_4 transformed from sulfur in the metabolic process of bacteria and the leaching rate of Co can reach 90% under the acid dissolution combined with the reduction of Fe^{2+}. This biohydrometallurgical method, however, relies too much on bacterial metabolism with a long treatment cycle and difficult training process, which almost makes it impossible to be industrially developed at the current stage.

After the above leaching process, the recovery of separated metal elements in the solution can be respectively or together extracted by combined processes including solvent extraction, chemical precipitation, and electrochemical deposition (Figure 2). The solvent extraction method usually adopts specific organic solvents, forming complexes with metal ions (Ni^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}), to separate and recover metal ions in the solution. Such an extraction process can usually be completed in a short time (less than 30 min) at room temperature. Commonly used extractants include Cyanex272, D2EHPA, PC-88A, and TOA, etc. However, Li is difficult to extract from the leaching solution and it is generally recovered in the form of $LiCO_3$ precipitation. Chemical precipitation is simple to operate and the equipment requirements are relatively low, but it requires more strict process parameters and the purity of the recovered metal ions is low. The selection of precipitators and precipitation conditions (pH, temperature) play a key role in removing impurity ions and improving the recovery efficiency of targeted metal ions. The leached metal ions can be also collected via deposition on the cathode of an electrolytic cell at a certain potential. But it is hard to precipitate only one metal ion from the complex solution because the deposition potentials of various metal ions like Co and Ni are too close to separate.

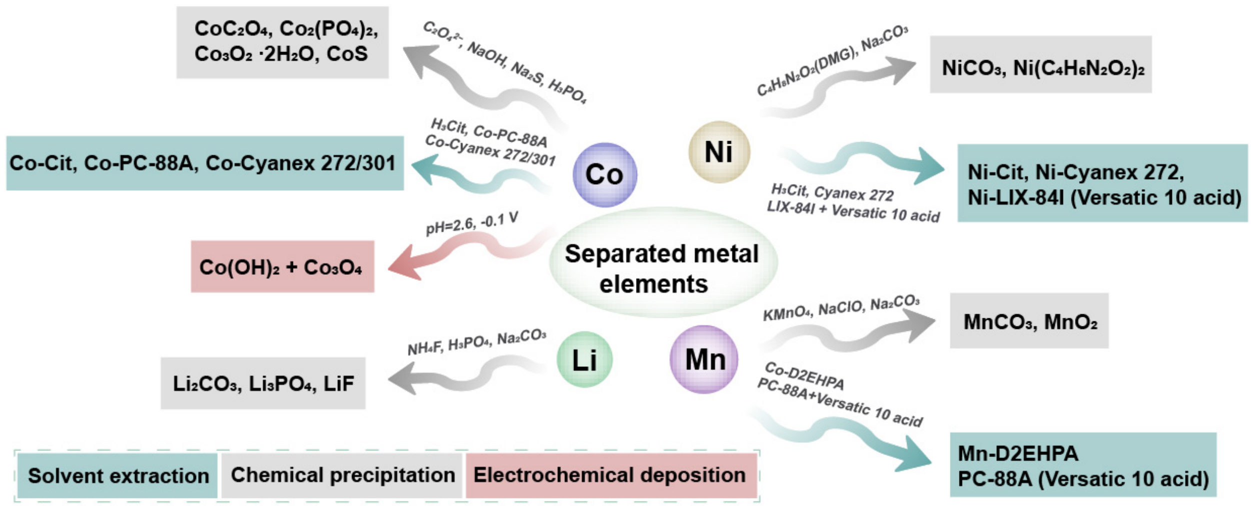

Figure 2. Recycling separated metals from the leaching solution[7].

Taking spent LFP materials as an example, the current recycling process via a typical hydrometallurgy method is illustrated in Figure 3. The LFP powder is firstly mixed with leaching agents (H_2SO_4 as the leachant and H_2O_2 as the oxidant) to prepare a slurry. The leaching rates of Li and Fe are largely influenced by the process parameters including solid/liquid ratio, reagent dosage, leaching temperature and time, pH, etc. In particular, at pH=2~3, Fe and phosphate will precipitate in the form of $FePO_4$,[9] existing in the residue. Meanwhile, the insoluble anode graphite powder will also go into the ferrophosphorus residue. Thus, Li can be selectively leached into solution. As for most battery recycling companies in China, the value of ferrophosphorus residue has been ignored during the recycling process, so far. The next step is the impurity removal process. According to the different components of impurity elements in the leaching solution, several agents such as NaS and NaOH are added to react with Cu, Al, and Fe elements in the solution to generate precipitation, and filtrate is prepared for the lithium precipitation process. A certain amount of Na_2CO_3 solution is used as the bottom liquid and the Li-containing filtrate is gradually added into it. Then the Li_2CO_3 precipitation could be obtained from the mother liquor at a proper temperature and stirring rate. Finally, the battery grade Li_2CO_3 product can be prepared by repeatedly washing the as-obtained Li_2CO_3 precipitation. The RE of Li can exceed 98% through such a recycling process.

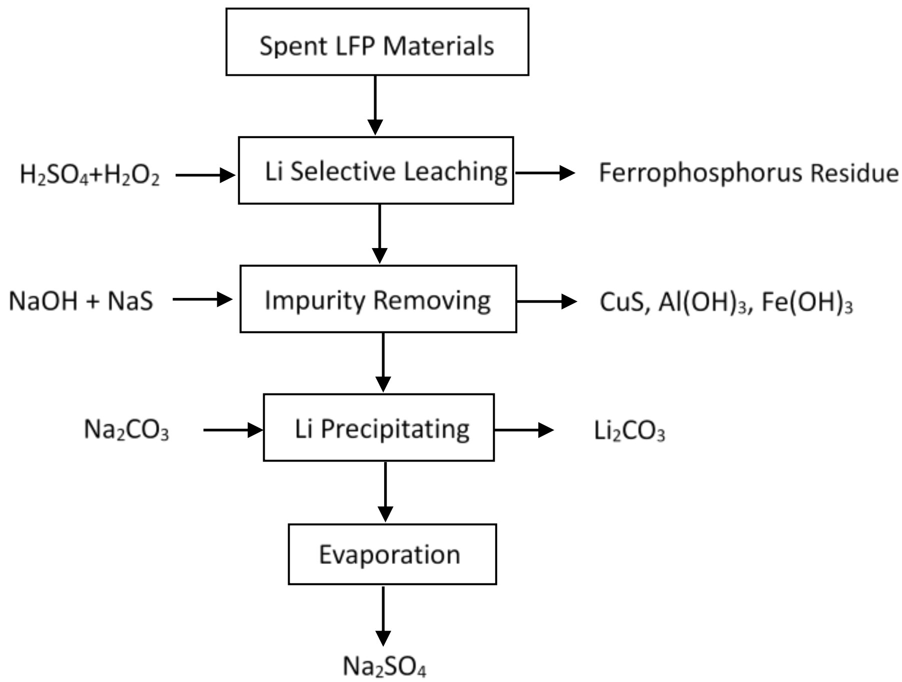

Figure 3. Current recycling process of spent LFP materials via a typical hydrometallurgy method

Although hydrometallurgy technologies can effectively extract precious metal elements from the waste LIBs, there are still some challenges in such a long recovery process, including high reagent consumption and a large amount of waste residue, waste liquid and waste gas. Direct recycling, defined as the regeneration of material components directly, free of destroying the chemical structure and causing secondary pollution, shows great potential in the recovery of low-value-added cathode materials such as LFP and LMO because several energy-intensive and costly processing steps can be avoided. Wang et al.[10] reported that the LFP active materials can be directly regenerated through solid state reaction after being separated from Al foil according to their density. The reused LFP materials display excellent electrochemical performances for LIBs. Such a direct recycling method can not only recover more materials with potential additional revenues, but also decrease the energy consumption and environment impacts. Nevertheless, direct recycling of battery materials is still limited to lab-scale application because this method is strict in the content of impurities.

The challenges facing various recycling technologies are analyzed in the preceding paragraphs, along with potential suggestions or solutions. An ideal regeneration technology with a short process, low energy consumption, and high recycling rates plays a crucial role in the future of the LIB recycling field.

Recycling Benefits

There are many potential benefits both economically and environmentally for the recovery of spent LIBs. Through recycling, active materials can be reproduced and LIBs can be remanufactured, which is of great significance to establish the closed-loop industry chain of power batteries. Based on the recycling process, fewer raw materials need to be extracted from the limited ore resources and the battery production costs will possibly dramatically decrease. Also, significant negative environmental factors related to ore mining and processing can be avoided to some extent.

In particular, the RE of Co, Ni, and Mn should be not less than 98% and the RE of Li, Fe, and Al should be at least 90%. Based on the latest average metal prices in China (Li $108,000/t, Co $62,000/t, Ni $21,000/t, Mn $2,800/t, Al $3,000/t), the recycling income of the LIB ternary battery series is much higher than the average recycling cost (hydrometallurgy process is about $2,500/t[11]), among which NCM622 has the highest income of about $9,090/t and NCM523 has the lowest income of about $8,630/t. By contrast, the recycling income of an LFP battery is very low, only about $1,550/t, which is exactly on par with its recycling cost via a hydrometallurgy process. Despite this fact, according to industry forecasts, the average environmental benefits of LFP battery recycling is projected to reach $360 million in 2025. Most importantly, the power battery recycling protocol is consistent with the strategy of sustainable development, and would be of great help in the development of a society with low carbon emission life and green travel.

Summary

In summary, the huge market and potentially rich profits of waste battery recycling will largely promote the innovation and progress of regeneration technologies. As a major battery manufacturer, China will also accelerate the formulation of battery recycling regulations and standards. Based on the vast resources of spent LIBs in few years, it is very likely that a highly efficient and green battery recycling technology will be developed, greatly decreasing the carbon emission during the whole life cycle of battery.

Reference

1. Swain, B., "Cost effective recovery of lithium from lithium ion battery by reverse osmosis and precipitation: a perspective." *Journal of Chemical Technology & Biotechnology*, 2018, *93* (2), 311-319.
2. Zheng, X., "A Mini-Review on Metal Recycling from Spent Lithium Ion Batteries." *Engineering* 2018, *4* (3), 361-370.
3. GGII, "Analysis on the Market Prospect of Lithium battery recycling in China in 2020. " *https://www.gg-lb.com/art-41003-yj.html.*
4. Li L., "Power battery cascade utilization and recycling technology.", 2020.
5. Gaines, L., "Direct Recycling R&D at the ReCell Center." *Recycling* 2021, *6* (2), 31.
6. Xiao, J., "Novel Approach for in Situ Recovery of Lithium Carbonate from Spent Lithium Ion Batteries Using Vacuum Metallurgy." *Environ Sci Technol* 2017, *51* (20), 11960-11966.
7. Xiao, J., "Challenges to Future Development of Spent Lithium Ion Batteries Recovery from Environmental and Technological Perspectives." *Environ Sci Technol* 2020, *54* (1), 9-25.
8. Sun, S., "Management status of waste lithium-ion batteries in China and a complete closed-circuit recycling process." *Science of The Total Environment* 2021, *776*: 145913.
9. Li, H., "Recovery of Lithium, Iron, and Phosphorus from Spent $LiFePO_4$ Batteries Using Stoichiometric Sulfuric Acid Leaching System." *ACS Sustainable Chemistry & Engineering* 2017, *5*: 8017−8024.
10. Wang, L., "Regeneration cathode material mixture from spent lithium iron phosphate batteries." *Journal of Materials Science: Materials in Electronics* 2018, *29* (11): 9283-9290.
11. Tao, Z., "Research on the business model of power battery recycling industry in China." *Automotive Industry Research*, 2018, 10: 33-42.