36th International Electric Vehicle Symposium and Exhibition (EVS36)
Sacramento, California, USA, June 11-14, 2023

Lithium-ion battery recycling technologies towards sustainable electric vehicle industry

Xiao Lin[1], Gangfeng Liu[1], Xue Wang[1], Mengting Wu[2], Nana Chang[2]

[1] *Suzhou Botree Cycling Sci & Tech Co., Ltd., 99 Jinjihu Avenue, Suzhou 215128, China. xlin@botree.tech*

[2] *Gusu Laboratory of Materials, 388 Ruoshui Road, Suzhou 215123, China.*

Executive Summary

The global new energy vehicle industry has been developed rapidly and the global sales volume of new energy vehicles is increasing year by year. As a result, the production and installation of power lithium-ion batteries simultaneously increase. Battery recycling is crucial from the perspective of environment, safety, and resources. This paper will give an overview of the battery recycling market, our research on battery recycling and regeneration including a self-developed ultra-short separation system via a hydro-metallurgical process, a direct recycling method for various spent electrodes, and carbon footprint management system for the whole battery life cycle.

Keywords: Lithium-ion batteries, battery recycling technology, critical battery materials, life cycle assessment .

1 Introduction

According to the International Energy Agency (IEA), there was 16.5 million electric vehicles (EVs) in the world by the end of 2021; the total number of EVs worldwide is expected to reach about 200 million by 2030. Sales in 2021 were the highest in China at 3.3 million, followed by Europe with 2.3 million sold in 2021. In the United States, electric car sales doubled their market share to 4.5% in 2021, reaching 630 000 sold. Across emerging markets, electric car sales more than doubled, but sales volumes remain low. In the first half of 2022 sales have further increased, we estimate that the global EV sales share will be around 13%. As the most crucial technology, power lithium-ion batteries have achieved explosive growth in the production and sales with the gradual electrification of transportation.[1-2] The installed capacity of power lithium-ion batteries in 2021 was about 300 GWh with a year-on-year increase of 115%. As the first batch of new energy vehicles have been used for 8 years, the small peak of lithium-ion power battery retirement with cumulative capacity of more than 300,000 tons (35GWh) in 2021 has arrived.[3-4] Therefore, the recycling of spent power lithium-ion batteries will play a significant role in the new energy industry chain.

Nonetheless, an international standardised recycling system for spent batteries has not been formed yet, and there is much room for improvement in terms of business models, industrial standards and technologies.[5-6] Furthermore, recycling of spent power batteries has become a weak link in the green development of the power battery supply chain and even the new energy vehicle industry chain.[7] Therefore, as lithium-ion battery (LIB) material recycling is an integral part of the closed-loop chain, it is urgent to accelerate the development of spent lithium battery recycling.

There are two recycling methods for spent lithium-ion batteries: cascade utilization and dismantling recycling.[8] Cascade utilization is mainly for batteries whose capacity was reduced but not scrapped, which obviously affects the regular operation of EVs. After conducting technical inspection and screening, reassembly, those batteries can be used for sectors that require lower battery capacity such as low-speed EVs and energy storage power stations. Disassembly recycling can be divided into pretreatment and back-end regeneration. According to the different back-end regeneration technologies, it can be divided into pyrometallurgy, hydrometallurgy, and direct recycling technology.[9]

The pre-treatment process is used to separate different components of spent 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.[10]

The pyrometallurgical process is the high-temperature smelting of cathode and anode powders in a reductive atmosphere, which needs a certain reducing agent, the reduction and decomposition of the battery cathode material, to obtain high value-added metal elements. The pyrometallurgical process finally gets alloy products to achieve the separation and recovery of high value-added metal in the spent lithium battery. The pyrometallurgy technology is simple, but the smelting process is high energy consumption, high carbon emission, and can not recover lithium metal.[11-12]

Hydrometallurgy is becoming the most widely used process method for recycling spent batteries.[13-15] Usually, the cathode and anode powders are acid leached (if the powder contains aluminum particles, the aluminum is removed by alkaline leaching first), and high value-added metals, such as lithium, nickel, and cobalt, are transferred to the solution. After the leachate is purified, these metal elements are separated by chemical precipitation, extraction, and other methods. Then the high value-added products are obtained. 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. This costly recycling technology does not apply to cathode materials with little value.

Direct recycling is to obtain the cathode material from the electrode, and after proper treatment, repair the cathode material structure and reapply it to the LIB cathode material. It can avoid high energy consumption and high cost steps, so it shows great potential and advantages in recovering low value-added cathode materials.[16-17]

This paper is dedicated to providing a complete solution for the recovery of critical battery materials from EVs. Through the pre-treatment process, the innovative co-extraction separation process, the short direct recycling process, it is possible to realise a short-range, closed-loop, and sustainable recycling process of battery materials.

2 Innovative Battery Recycling Technologies

2.1 Pre-treatment

After discharging, the spent LIBs are lifted to the crushing section by the elevator. After single-stage coarse crushing, the raw materials are fed into the pyrolysis furnace through the upper hopper by the belt conveyor, and the pyrolysis reaction is carried out at 350 ~ 600 ℃ to decompose and remove the binder and residual organic components. Pyrolysis flue gas is collected by the gas collecting hood and enters the secondary combustion chamber. Combustion supporting air is passed through the nozzle to make $C_xH_yO_z$ alkanes gas fully combusted and converted to H_2O and CO_2. In addition, the organic substance in the battery can also be dissolved and removed by green organic solvent. The dissolved organic mixture is separated by distillation, and the recovered organic solvent then returns to the cleaning process. The cleaned components enter the following process. The features of the organic solvent cleaning process: i) The organic solvent itself is green organic; ii) The organic solvent can be recycled and used repeatedly in the cleaning section, with almost no solvent consumption. The operating cost is low.

After removing the organic components, the crude materials are treated by the magnetic separator to remove the iron sheet/shell. Then the electrode powders and copper or aluminum foils are separated by secondary crushing and vibration sieving. After dust removal, secondary combustion, and cooling, the waste gas generated in the pretreatment process (crushing, pyrolysis, and sieving) goes to the waste gas treatment system. The electrode powder is leached through the leaching process and then enters the next extraction process to obtain battery-grade metal salts.

2.2 Nickel-Cobalt-Manganese Co-Extraction

After removing the impurity, the leaching solution mainly consists of the salts of nickel (Ni), cobalt (Co), manganese (Mn), calcium (Ca), magnesium (Mg), zinc (Zn), and lithium (Li).[18] The traditional process uses (2-Ethylhexyl phosphoric acid mono-2-ethyl) hexyl lipid (P507) extractant for multiple extraction, allowing the metals to be extracted step by step, and then mixing them to produce ternary precursors.[19] Significantly, a novel extractant named BC196, independently developed by Botree Cycling, can co-extract Ni, Co, and Mn from solution in one step, and the stripping can be directly used to produce ternary precursor materials.

In order to demonstrate the performance of BC196 extractant, we first compared the extraction sequence of P507 extractant and BC196 extractant at different pH values. As shown in Fig.1, when using P507 as extractant, critical metals can only be separated by step by step extraction via adjusting pH, and additional impurity removal steps must be carried out between each extraction process, resulting in a longer process. By contrast, BC196 has high selectivity for Ni, Co, and Mn ions in the aqueous solution containing Ca and Mg impurity ions, which makes it possible to simultaneously extract Ni, Co and Mn, while leaving Ca and Mg in aqueous solution. As a result, it can greatly shorten the process flow and reduce the treatment cost.

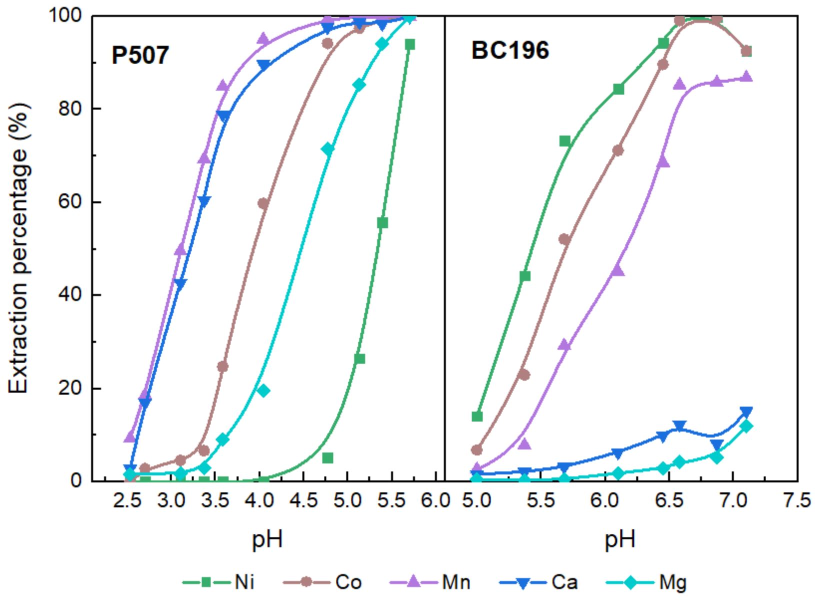

Figure 1. Selectivity comparison of P507 and BC196 extractants at different pH values.

We then used the leaching solution of spent lithium-ion battery to conduct 100-cycle extraction experiments on BC196 extractant to verify its cycling stability. Tab. 1 lists the element composition of the leaching solution, and it can be seen that the content of impurity elements except nickel, cobalt, manganese and lithium is low. The result of the 100-cycle experiment is displayed in Fig. 2. After 100 times of 'extraction and reverse extraction', the concentration of Ni, Co, Mn, Zn, and aluminum (Al) ions almost remains the same; the extraction rate of these ions has a good cycle performance, which indicates that BC196 has an excellent cycling stability. It should be noted that the large fluctuations in the curves of Ca and Mg are ascribed to their low content, inevitably leading to a certain detection error.

Table 1. Leaching solution element composition

Elements	Concentration (g/L)						
	Ni	Co	Mn	Ca	Mg	Al	Zn
Leaching solution	46.20	20.56	23.93	0.43	0.20	0.013	0.165

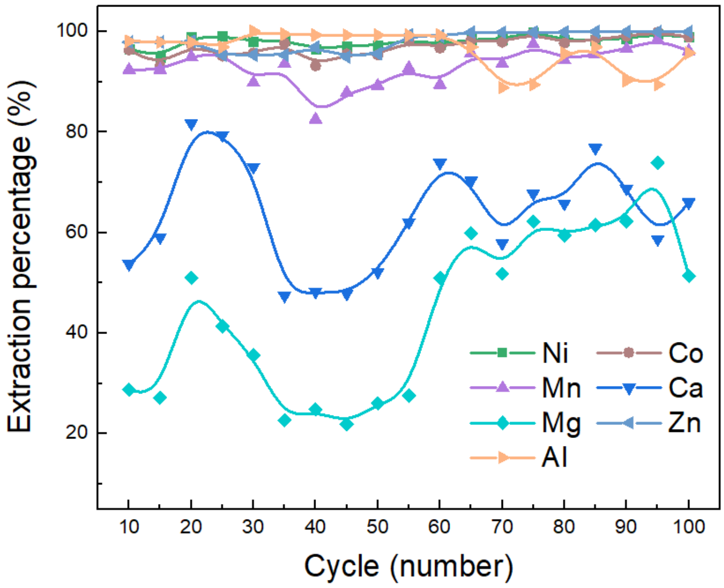

Figure 2. The cycling stability of BC196 extractant.

After that, we used BC196 extractant for the separation experiment of Ni and Mg for three months and Ni, Co, and Mn co-extraction experiment for 2.5 months respectively. The main to complex ratio and separation coefficient are used to measure the extraction effect. Tab. 2 respectively show the results of Ni-Mg separation experiment and Ni-Co-Mn co-extraction experiment. The above results indicate that the separation effect of Ni, Co, and Mn from Ca and Mg impurities is very good under BC196 extraction system, especially in the separation of Ni and Mg with a very high separation coefficient.

Table 2. Experimental results of Ni-Mg separation and Ni-Co-Mn co-extraction

Concentration (g/L)	Ni, Mg Separation			Ni, Co, Mn Co-extraction		
	Ni	Mg	Co	Ni+Co+Mn	Ca	Mg
Leaching solution	1.26	4.49	0.096	47.5	0.6	0.2
Raffinate	<0.01	4.11	0.0063	0.0016	0.001	0.0152
Strip liquor	>100	<0.01	2.17	104.72	0.0046	0.0001

Based on these results, we conducted a pilot test on the co-extraction system of Ni, Co, and Mn established a pilot test line with a capacity of 133 L/h to further verify the co-extraction of Ni, Co, and Mn by BC196. The recovery rate of the key metals Ni and Co is more than 99% and Mn is more than 93%. BC196 extractant can achieve one-step extraction of Ni, Co, and Mn, thus shortening the extraction process and declining the extraction cost.

The significant differences are summarized as the following:

① The typical process uses $H_2SO_4 + H_2O_2$ to dissolve all the cell components fully, while Botree employs the selective leaching method, which can achieve lithium pre-extraction;

② The typical process extracts Mn, Co, and Ni metals as sulphate salts at separated stages, while Botree employs a co-extraction method to extract Ni, Co, and Mn metals as metal sulphate salts at once;

③ The typical process adds $MnSO_4$, $CoSO_4$, and $NiSO_4$ salts together to produce NCM precursor, while in Botree's process, NCM precursor can be directly produced from the Ni, Co, and Mn mixed solution.

The core of Botree's short processes is the newly developed extractant system. Traditional extractant has poor selectivity over Mn, Co, and Ni with the impurity ions like Ca and Mg. Thus additional impurity removal steps must be applied between each metal extraction process, resulting in a rather long flow. Instead, Botree's new extractant system has high selectivity over Ni, Co, and Mn with Ca and Mg impurity ions, which can achieve efficient Ni, Co, and Mn extraction, while leaving Ca and Mg in the aqueous solution.

Based on the pilot results, Botree's new process can reduce the overall energy and chemicals consumption by at least 10% and 15%, respectively. Since the consumed energy and chemicals mainly contribute to GHG during the recycling process, this new process will result in at least a 10% lower carbon footprint than the current ones, thus further increasing the carbon credit benefits.

2.3 Direct Recycling Method

In addition to the above-mentioned hydrometallurgical process to recover valuable metal elements from spent lithium-ion batteries, Botree Recycling is also committed to the manufacturing process of short direct recycling of spent electrodes. As shown in Fig. 3, the non-destructive de-powdering solutions and key equipment is applicable to the dominant retired batteries including LFP, lithium nickel cobalt manganese oxide (NCM), and lithium manganese oxide (LMO). The direct recycling process involves electrode de-powdering, material regeneration, and performance testing. This method can avoid the excess use of traditional complex chemical reagents during hydrometallurgical process and exhibit the advantages of high recovery rate, short process, low cost, etc.

The most valuable components of LIBs mainly include black mass (cathode material and graphite), electrolyte, copper foil and aluminum foil. The direct recycling technology requires a low content of impurities in the cathode material powder, as the separation process of the cathode material from the other components is crucial. Most separation processes are based on different material properties such as density, solubility, hydrophobicity, magnetisation, etc.[20] After soaking the spent electrode, the electrode part and the current collector are effectively separated to obtain the electrode material and copper foil or aluminum foil.The separated cathode material will be handled in the regeneration process. After the performance testing of regenerated cathode material, it will be evaluated to assess whether it meets industry standards.This method can effectively shorten the material recovery process, avoid the steps of high energy consumption and high cost, and effectively recover the electrode material.

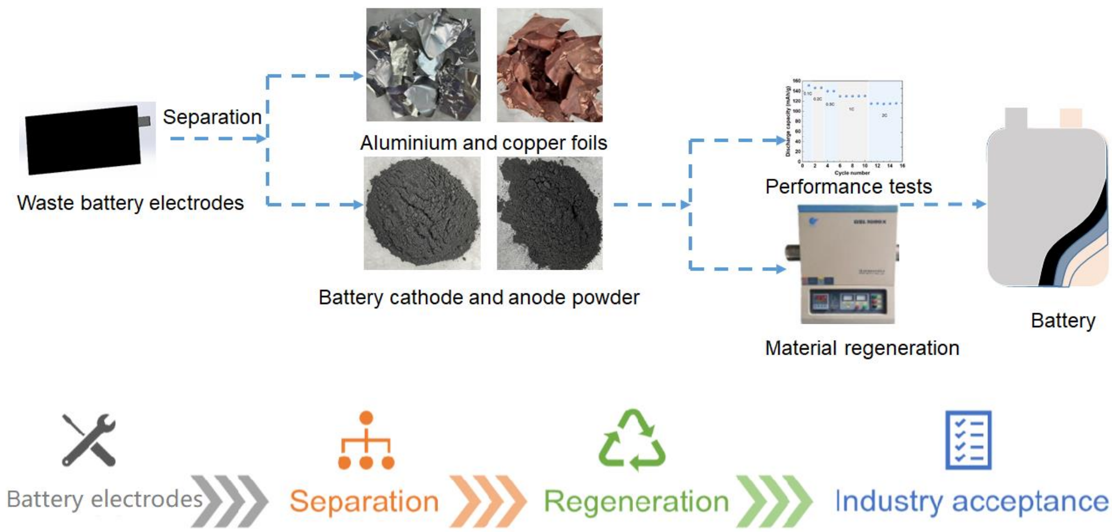

Figure 3. The direct recycling process of spent electrodes.

3 Life Cycle Assessment of Recycling Process

LIBs have become the dominating battery technology for EVs, mainly because of their high energy density and high charge-discharge efficiencies[21]. The typical life cycle of an EV power battery consists of mining, refining, cathode production, battery manufacturing, battery use, and end-of-life phase, which is schematically illustrated in Fig. 4.

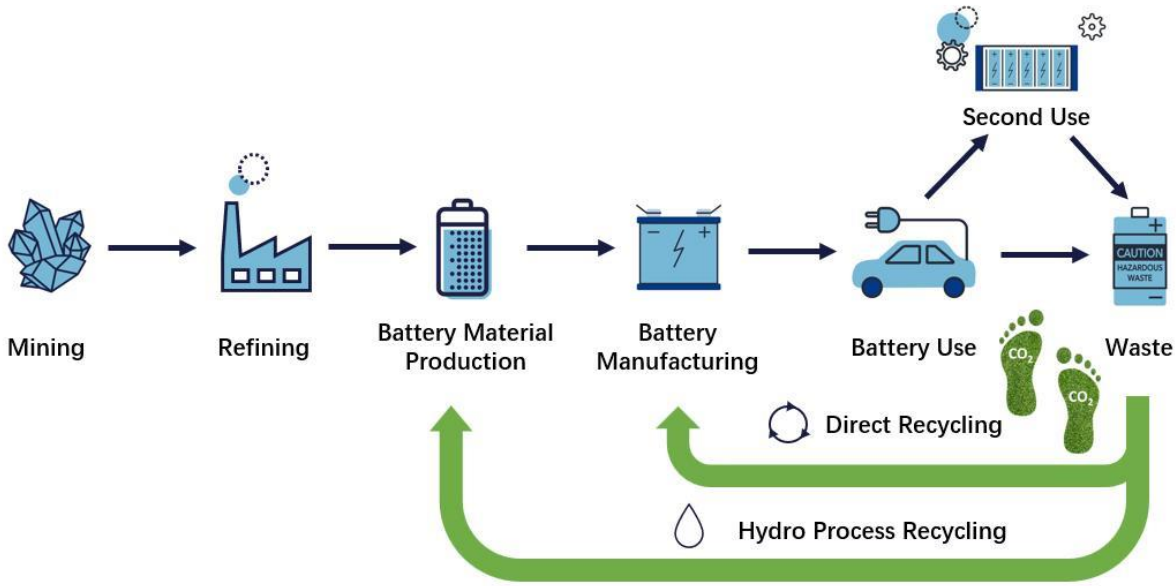

Figure 4. Life cycle of a typical EV battery

The current power battery manufacturing process is quite energy-intensive, especially as the upstream raw material production generates massive greenhouse gases (Fig. 5).[22] The typical 'cradle-to-gate' carbon footprint of a power battery varies from 50 to 130 kg CO_2-eq/kWh, depending on different geographic grid mixes.[23] Power batteries will enter the TWh era around 2025, to produce a huge number of batteries with an average carbon footprint of 100 kg CO_2-eq/kWh and this will generate approximately 100,000,000 tons of greenhouse gas, which is a significant amount.[24]

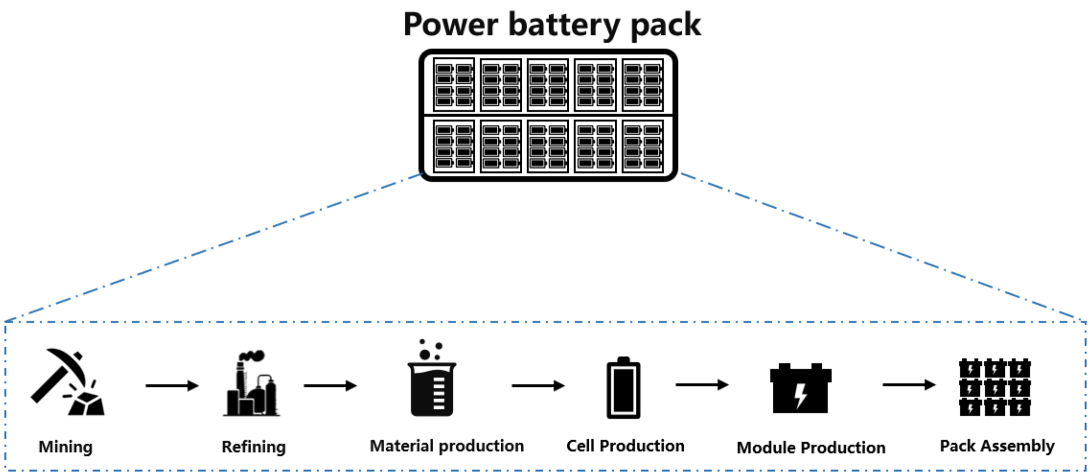

Figure 5. Schematic of the battery manufacturing process.[22]

Efficient recycling of the spent batteries and reproducing new battery materials can effectively reduce its life cycle carbon footprint by at least 30%. However, the recycling itself will also generate new carbon footprint, and 90% of them originate from the raw materials (acid and alkali) and energy (electricity and heat) input during the hydrometallurgical recycling process of batteries.[25]

Botree Cycling's self-developed ultra-short co-extraction separation system can effectively reduce the caustic soda/sulfuric acid and electricity consumption by 15% and 10% respectively, which can lead to a 12% reduction of overall carbon footprint in the hydrometallurgical recycling process of batteries (Fig. 6).

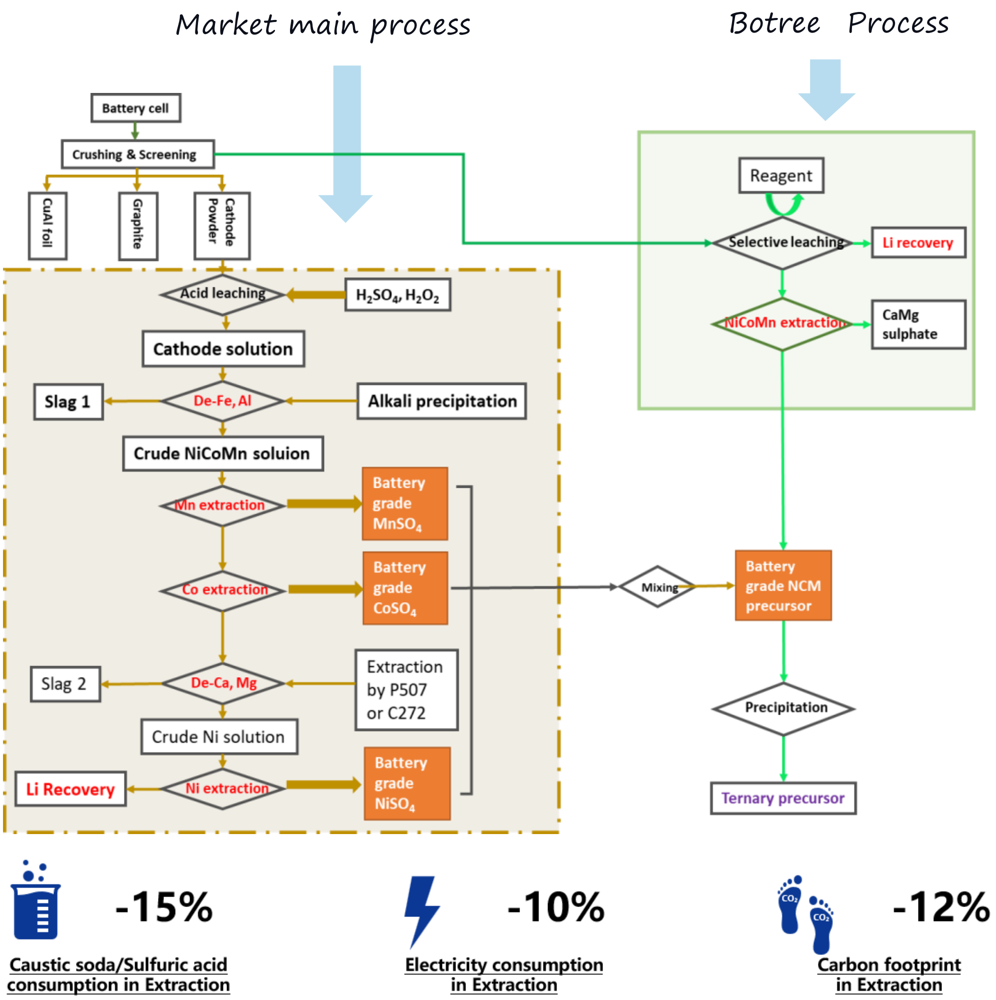

Figure 6. The advantages of Botree Cycling's recycling process.

Meanwhile, Botree Cycling is working hard on the research, improvement, and industrialisation of other ultra-short battery recycling processes, which aim to reduce the carbon footprint by 90%.

Acknowledgments

This work was financially supported by the Task 48 Battery Swapping of the Hybrid and Electric Vehicle Technology Collaboration Programme (HEV TCP) in the International Energy Agency (IEA) and Suzhou Science and Technology planning project (ZXL2022372).

References

[1] Tian Chunzheng et al. *Industrial structure and development prospect of power lithium battery[J]*.Chinese Journal of Power Sources, 2018, 42(12): 1930-1932.

[2] Yang Y et al. *On the sustainability of lithium ion battery industry–A review and perspective[J]*. Energy Storage Materials, 2021, 36: 186-212.

[3] Zhang X et al. *Toward sustainable and systematic recycling of spent rechargeable batteries[J]*. Chemical Society Reviews, 2018, 47(19): 7239-7302.

[4] GGII, "*Analysis on the Market Prospect of Lithium battery recycling in China in 2020.* " https://www.gg-lb.com/art-41003-yj.html.

[5] Li Lingyun. *Current status and development trend of Li-ion batteries for new energy vehicles in China[J]*. Chinese Journal of Power Sources, 2020, 44(04): 628-630.

[6] Sun S, et al. *Management status of waste lithium-ion batteries in China and a complete closed-circuit recycling process[J]*. Science of The Total Environment, 2021, 776: 145913.

[7] Christensen P A, et al. *Risk management over the life cycle of lithium-ion batteries in electric vehicles[J]*. Renewable and Sustainable Energy Reviews, 2021, 148: 111240.

[8] Yang Y, et al. *On the sustainability of lithium ion battery industry–A review and perspective[J]*. Energy Storage Materials, 2021, 36: 186-212.

[9] Zhang X, et al. *Toward sustainable and systematic recycling of spent rechargeable batteries[J]*. Chemical Society Reviews, 2018, 47(19): 7239-7302.

[10] Zhang G, et al. *Recent advances in pretreating technology for recycling valuable metals from spent lithium-ion batteries[J]*. Journal of Hazardous Materials, 2021, 406: 124332.

[11] https://csm.umicore.com/en/battery-recycling/our-recycling-process/, accessed on 2022-11-06

[12] Zhou M, et al. *Pyrometallurgical technology in the recycling of a spent lithium ion battery: evolution and the challenge[J]*. ACS ES&T Engineering, 2021, 1(10): 1369-1382.

[13] Zheng X, et al. *A mini-review on metal recycling from spent lithium ion batteries[J]*. Engineering, 2018, 4(3): 361-370.

[14] Chen M, et al. *Recycling end-of-life electric vehicle lithium-ion batteries[J]*. Joule, 2019, 3(11): 2622-2646.

[15] Lin J, et al. *Environmentally benign process for selective recovery of valuable metals from spent lithium-ion batteries by using conventional sulfation roasting[J]*. Green Chemistry, 2019, 21(21): 5904-5913.

[16] Gaines L, et al. *Direct Recycling R&D at the ReCell Center.* Recycling 2021, 6 (2), 31.

[17] Xu P, et al. *A Materials Perspective on Direct Recycling of Lithium-Ion Batteries: Principles, Challenges and Opportunities[J]*. Advanced Functional Materials, 2023: 2213168.

[18] Zhang G, et al. *Recent advances in pretreating technology for recycling valuable metals from spent lithium-ion batteries[J]*. Journal of Hazardous Materials, 2021, 406: 124332.

[19] Wang W Y, et al. *Recovery of high-purity metallic cobalt from lithium nickel manganese cobalt oxide (NMC)-type Li-ion battery[J]*. Journal of Material Cycles and Waste Management, 2019, 21(2): 300-307.

[20] Jiang, G, et al. *Direct Regeneration of* $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ *Cathode from Spent Lithium-Ion Batteries by the Molten Salts Method.* ACS Sustainable Chemistry & Engineering 2020, 8 (49), 18138-18147.

[21] Jens F. Peters et al. *Providing a common base for life cycle assessments of Li-ion batteries[J]*, 2018, 171: 704-713.

[22] Yangtao Liu, et al. *Current and future lithium-ion battery manufacturing,* iScience, 2021: 24, 102332,

[23] Qiang Dai, et al. *Life cycle analysis of lithium-ion batteries for automotive application*, Batteries, 2019, 5(2), 48

[24] Martin Beermann, *Carbon footprint of EV battery production NCM, NCA, LFP chemistries*, IEA HEV TCP Task 40 CRM4EV WEBINAR, October 19, 2021.

[25] Parlikar A et al. *The carbon footprint of island grids with lithium-ion battery systems: An analysis based on levelized emissions of energy supply[J],* Renewable and Sustainable Energy Reviews, 2021, 149: 111353.

Presenter Biography

Dr. Xiao Lin, CEO of Botree Cycling

Member of the National Technical Committee SAC/TC294 on Discarded or Disused Chemicals Disposal of Standardization Administration of China. Operation Agent of IEA HEV TCP Task 48 Battery Swapping, participant of IEA HEV Task 40 CRM4EV, Leaders in Innovation Fellowships Royal Academy of Engineering Funded by Newton Fund.

Working in novel separation and purification technologies for critical battery metals, revolutionary solution for battery recycling and materials regeneration. Finished 50+ research and commercial projects, granted prizes like national technology invention and national key practical technologies of environmental protection. Published 40 papers, been authorized 30+ patents, participated in the formulation of national standards, and been one of main writers of “Power battery blue book” (China) and “White book of power battery recycling” (China).