

Current Situation and Development Prospects of Discharge Pretreatment during Recycling of Lithium-ion Batteries: A Review

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As the first step in recovering the decommissioned lithium-ion battery cells, discharge pre-treatment of decommissioned lithium-ion batteries plays an important role in ensuring the safety of the subsequent recovery process and improving the comprehensive benefits of lithium-ion battery recycling. However, current research on the recovery process of decommissioned lithium-ion batteries focuses on how to efficiently recover elements through fire and wet methods, as well as improve the recovery of active substances by direct reduction. Therefore, this review focuses on the latest research progress of

lithium-ion battery discharge pretreatment, shows the advantages and disadvantages of various existing lithium-ion battery discharge pretreatment technologies, and analyzes the development potential of discharge pretreatment technologies in further energy recovery, increasing cathode lithium content, and reducing the pollution of active substances. This paper aims to further review and look forward to the development of discharge pretreatment technology and provide a new perspective for improving the comprehensive benefits of the lithium-ion battery recycling process.

1. Introduction

Huge security risks always accompany large-scale waste recycling. Taking the recycling of lead-acid batteries and metal recycling as an example, the number of fires continues to increase.^[1] In Harper, G. et al.'s study, three large fires associated with the recycling industry were recorded: Shoreway, SAN Carlos, USA, in September 2016; Guernsey, USA, in August 2018; and Tacoma, Washington, USA, in September 2018.^[2] Considering that lithium-ion batteries carry much more energy than other traditional wastes,^[3] with the advent of large-scale industrialization of lithium-ion battery recycling, the discharge pretreatment process as a residual energy removal is particularly important to ensure the safety of the industry. The summary of the recovery process of the Li-ion batteries is shown in Figure 1. As can be seen from the schematic diagram of the process, discharge pretreatment is the first and necessary process in the resource recovery process of the battery cell. This step plays the most important role in releasing the residual energy in the decommissioned batteries, it will directly have a decisive impact on the safety of the subsequent process. As a common pre-treatment step for all subsequent recycling, the state of the passivated cell will also directly affect the efficiency and quality of the subsequent recycling process. Therefore, discharge pretreatment is an important part of lithium-ion battery recovery.

According to the International Energy Report, driven by the rapid development of electric vehicles, China already has about 5 million electric vehicle production capacity in 2020, and the global electric vehicle production capacity has reached 10 million.^[5] By 2030, the number of electric vehicles is expected

to grow to 225 million.^[5] According to the Automobile Market Research Branch of China Automobile Dealers Association (Passenger Car Market Information Association, abbreviated as Passenger Car Association) data, In 2022, China's electric vehicle (EV) sales reached 6.68 million units.^[6] The service life of new energy vehicles is estimated at 8 years, the average weight of each car battery pack is calculated at 300 kg, and the weight of retired batteries from EVs in China is expected to exceed 2 million tons in 2030. Larcher D. et al. show that with the commercialization of lithium-ion batteries in electric vehicles becoming more and more mature, the world has a great interest in using lithium-ion batteries as energy storage devices to further develop renewable energy and clean energy.^[7] In the future, the total use of lithium-ion batteries and the number of decommissioning will be a huge growth, and lithium-ion battery recycling will become a huge market size industry.

Lithium-ion batteries consist of a case, binder, electrolyte, anode materials, separator, current collector, cathode materials, and conductive additive. The details of the main structure diagram of the Li-ion cell are shown in Figure 2.^[8] The complex composition of lithium-ion batteries makes their elemental composition equally complex. Lithium-ion batteries not only contain lithium, copper, aluminum, nickel, manganese, cobalt, iron, and other high-value metal elements but also contain organic solvents, fluoride, and other components that can cause harm to the environment.^[4,9,10] The main material composition of lithium-ion batteries is shown in Table 1.

Considering the complex composition and rich element content of decommissioned lithium-ion batteries, the recycling of lithium-ion batteries can bring huge environmental and economic benefits. It can be seen that the recovery of lithium-ion batteries is of great significance, and the discharge pretreatment process also plays a crucial role in the process of lithium-ion battery recovery. The vast majority of lithium-ion battery recycling reviews mainly describe the Li-ion batteries recycling process, and these reviews mainly focus on the economy in the recycling process, the resource recycling processing process, and the development of basic theories and the latest research results.^[2,4,7,9,11–13]

Take the studies of Harper et al., Lv et al., Roy et al., and AniketChitr et al., as examples. Harper, G. et al. described the research progress of the recycling and reuse of lithium-ion batteries for electric vehicles and conducted an overall analysis of the entire recycling system of lithium-ion batteries for electric vehicles.^[2] Lv et al. made a critical analysis of the existing

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hydrometallurgical process, which covered with emphasized the secondary pollution problem in the hydrometallurgical process, as well as the risk of transition metal ion waste and waste acid pollution of groundwater and soil environment.^[14] Roy et al. discussed the green treatment of waste materials in the secondary processing stage, focusing on the bio-leaching of lithium-ion battery waste and the regeneration of electrode materials.^[15] Chitr et al. summarize the challenges faced in material recycling for decommissioned lithium-ion batteries, analyze the future direction of recycling-friendly binders, and highlight the future development of material recycling.^[16] It can be seen that most of the current reviews on lithium-ion battery recycling focus on the secondary utilization of high-value materials and metal recovery. The discharge pretreatment has been briefly introduced in various pieces of literature, and the important role of discharge pretreatment in ensuring the safety of the subsequent recovery process has also been emphasized. However, discharge pretreatment's basic theory, economy, and safety still lack systematic research and in-depth discussion.^[17]

Therefore, it is necessary to systematically study the research status of discharge pretreatment of lithium-ion batteries. Herein, we provide a timely review, which firstly analyzes the challenges faced by the prior art in terms of

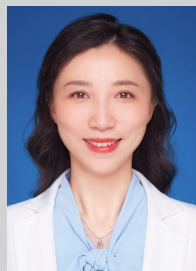
comprehensive income, discharge effect, and environmental impact. Further, the development potential of decommissioned lithium-ion battery discharge pretreatment in achieving further energy recovery, achieving higher cathode lithium content, and controlling lower active substance pollution was analyzed. Finally, the future research breakthrough direction of discharge pretreatment is prospected.

2. Discharge Pretreatment of Decommissioned Lithium-ion Batteries

In the process of lithium-ion battery recycling, the release of the remaining power is mainly achieved in two ways. The first pathway is to break down or destroy the cell under controlled conditions, with chemical passivation of the active substance occurring simultaneously. The second way is to discharge through an external circuit to release the remaining energy in the used lithium-ion battery. Controlled passivation can be achieved by the chemical passivation agent passivation method and the thermal passivation method. The external circuit discharge method can be achieved by saline discharge, metal



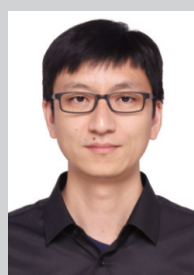
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Prof. Hui Xie received his Ph.D. degree from Hunan University in 2003 and is currently working at the School of Mechanical and Vehicle Engineering, Hunan University. Prof. Hui Xie engaged in Intelligent manufacturing and machine learning for new energy vehicle design and power battery recycling. As the chief scientist, he presided over the National Key R&D Program of China's "Key Technology and Control System of intelligent dismantling production line of retired products" (No. 2020YFB1713000).

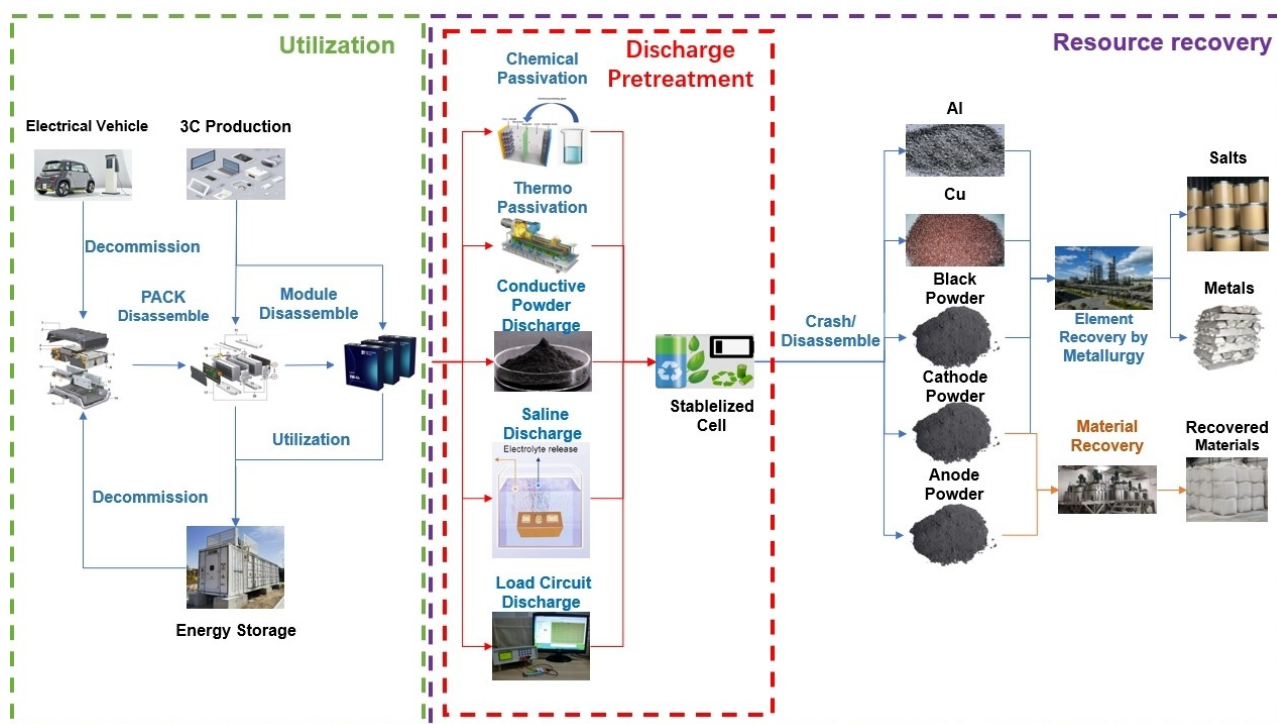


Figure 1. The brief diagram of the lithium battery recycling process.

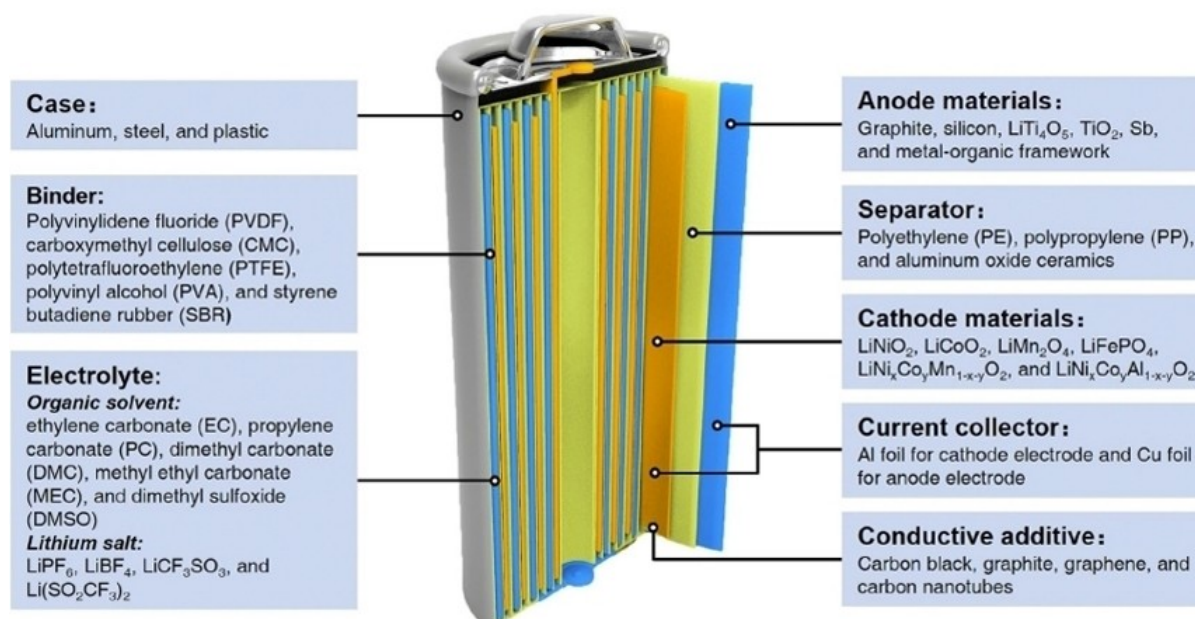


Figure 2. The main structure diagrams of lithium-ion batteries. Adapted from Ref. [8]. Copyright (2023) with permission from Elsevier.

powder discharge, and load circuit discharge. In the current studies,^[18–20] the researchers mainly focused on the advantages and disadvantages of different discharge pretreatment technologies in terms of discharge efficiency, potential environmental pollution, battery model adaptability, and auxiliary material consumption. Different discharge mode overviews are shown in Table 2.

2.1. Controlled passivation

The discharge pretreatment can be achieved through passivation of the electrochemical system. This passivation process is based on the reaction between the cathode and anode or the anode and a specific chemical environment. One possible way is to break the cell directly using a protective atmosphere, such

Table 1. Material composition of lithium-ion battery.^[4] NAC is short for LiNiCoAlO₂ material, LPF is short for LiFePO₄, LMO/LOM is short for LiMnO₂, LTO is short for Li₄Ti₅O₁₂, C refers to the elemental mass of carbon, Carbon refers to the carbon material conductive agent used in the electrode.

Battery	NAC-graphite	LPF-graphite	LMO (spinel)-graphite	LOM (spinel)-LTO	LOM (spinel)-LTO
Electrode Mass fraction/%					
Element					
Li	1.9	1.1	1.4	2.8	2.8
Ni	12.1	0	0	0	0
Co	2.3	0	0	0	0
Al	0.3	0	0	0	0
O	8.3	9	12.4	22.3	22.3
Fe	0	7.8	0	0	0
Mn	0	0	10.7	12.4	12.4
C	16.5	15.3	16.3	0	0
Carbon	2.4	2.1	2.3	4.5	4.5
Binder	3.8	3.4	3.7	4.5	4.5
Thermal	1.2	1.3	1.2	1.2	1.2
Insulation					
Electronic part	0.3	0.3	0.4	0.2	0.2
Aluminum	8.9	9.4	9.2	8.8	8.8
Casing					
Electrolyte	11.7	14.2	11.8	13.4	13.4
Solvent					
Plastics	4.2	4.6	4.5	3.6	3.6
Steel	0.1	0.1	0.1	0.1	0.1
Copper	13.3	13.8	13.5	2.6	2.6
Aluminum	12.7	13.3	12.5	13.7	13.7

as nitrogen, carbon dioxide, or a mixture of carbon dioxide and argon. Patents published by Akkuse in Finland and Duesenfeld in Germany have been published for this method.^[21,22] According to the patents, exposure of the anode electrode to a mixture of carbon dioxide and nitrogen or argon will achieve a passivation layer containing a certain amount of lithium carbonate. Main Text Paragraph.^[21,22] Retrivg's patent shows an alternative passivation method that uses water directly as a passivation agent, an oxygen barrier, and a heat dissipator. During this process, crushing and disassembly are operated in

water that prevents both detonation and uncontrolled energy release.^[23] Yun Zhao et al. studied the process of disassembly of charged decommissioned lithium-ion batteries directly in pure water. The active lithium in the anode material reacts directly with water to passivate into lithium hydroxide, meanwhile, the water separates the air and absorbs the heat generated by the passivation process to prevent thermal runaway.^[24] The advantage of this chemical passivation method is that the process principle is simple and easy for large-scale industrialization, but the disadvantage is that the specific passivation effect is difficult to quantify and control in the rapid processing process. In addition, the gas or water used for passivation will also be mixed with organic matter, so the water or gas after passivation needs further treatment to be harmless. Wang X. et al. and Wang H. et al. Used liquid nitrogen frozen electric cells to embrittlement organic binder, reduce the severity of reaction and system temperature when positive and anode electrodes contact, and improve the effect of peeling efficiency between active substances and current collectors.^[25,26] However, due to the large use of liquid nitrogen, the passivation process in this way is expensive. The pyrometallurgical recovery process represented by Umicore obtained the passivation in the process of pyrometallurgy.^[27,28] Under high temperatures and a reducing atmosphere, the active substance inside the battery spontaneously occurs redox reaction, and the energy contained in it is released during the fire smelting process and provides part of the energy for the whole process.^[27,28] This method has the advantage of rapid industrialization, but the composition of the crude alloy obtained by fire metallurgy is complicated, and the metal separation work is also difficult.^[29] It means that this discharge pretreatment method (pyrometallurgical recovery process) needs to be further optimized to reduce energy consumption and further developed to separate the material during the pretreatment process.

2.2. External circuit discharge

The active substance inside the decommissioned lithium-ion battery maintains the working mode of the original rocking chair battery, and the electron migration occurs in the external circuit, which can also complete the discharge of the decommissioned lithium-ion battery. According to the research, the widely studied methods of external circuit discharge include

Table 2. Different discharge mode overview.

Method	Pre-treatment medium	Residual electric energy conversion results	Waste production	reference
Controlled chemical passivation	Heat treatment or Chemical atmosphere	Heat and Chemical energy	Waste gas or waste-water	[21–29]
Saline discharge	Saline	Chemical energy	Waste gas and waste-water	[18–20, 30–32]
Conductive powder discharge.	Conductive powder	Heat	Waste heat	[19, 36]
Load circuit discharge	External load circuit	Electric energy	none	[19, 37, 38]

the saline discharge method, load circuit discharge method, and conductive powder discharge method.

Saline discharge. For large quantities and varieties of lithium-ion batteries, the method of using conductive aqueous electrolyte as an external circuit to discharge has been widely studied because of its good variety adaptability, and easy of scale expansion. As one of the most common chemical by-products, NaCl is the first pure salt that has been used to study the feasibility of saline discharge. Lu et al. analyzed the effect of its concentration on discharge efficiency and summarized the relationship between the concentration of NaCl solution and the discharge rate.^[30] Studies by Li et al and Ojanen et al show that the discharge of lithium-ion batteries using NaCl solution can release more than 70% of the electrical energy in the original batteries.^[31,32] Zheng et al. conducted a comparative analysis of the discharge performance between NaCl solutions and other solutions, including H₂SO₄ and NaOH solutions, leading to the discovery of chlorine gas production.^[33] Considering the weaker corrosion observed under NaCl solution pretreatment, it can be concluded that salt solutions exhibit superiority over alkaline and acidic solutions in terms of their electrochemical behavior. Xiao et al. established a set of O₂-controlled mechanisms by studying the discharge process of saline in sodium chloride (NaCl), potassium chloride (KCl), sodium nitrate (NaNO₃), magnesium sulfate (MgSO₄), and sodium hydroxide (NaOH) solutions, and explained the reason why the electrode corrosion of saline discharge system in MnSO₄ solution was smaller. Recent studies by Yao LP et al. have shown that FeSO₄ solution is a more environmentally friendly option for saline discharge, especially for lithium iron phosphate batteries, and can effectively reduce cationic contamination of decommissioned Li-ion batteries and reduce battery voltage to 0.5 V after 5 hours of discharge.^[18] Zheng's research shows that the aqueous solutions of halide salts cause severe corrosion at the edge of the battery,^[19] while the corrosion of the battery by the salt water of the MgSO₄ has decreased,^[34] but it cannot completely avoid the corrosion of the battery. Electrochemical corrosion means mutual contamination between salt water and decommissioned lithium-ion batteries. This pollution is mainly reflected in the saltwater immersion in the battery after corrosion, and the organic solvents, halogens, nickel, cobalt, and other metal elements inside the battery dissolve into the saltwater system.^[35] This kind of pollution can lead to secondary pollution of the environment by the saline used for discharge, as well as the complexity of the subsequent recovery process and the increase in treatment costs. On the other hand, Wu et al. show that, in the process of saline discharge, the saline discharge system with different salt compositions will produce oxygen, hydrogen, chlorine, and other gases.^[20] These gases will be produced due to external electrochemical reactions at the anode and cathode extremes, respectively, and have the potential to hurt the environment. In addition, this kind of spontaneous discharge process is also difficult to precisely controlled.

Conductive powder discharge. The predischARGE treatment can also performed by using the conduction powder as an external circuit to complete the transfer of electrons, in which

energy is consumed in the form of thermal work. Zheng studied the method of using iron powder and graphite powder to bury the cells for discharge, and the research showed that this way of burying the cells in the conductive powder can effectively reduce the battery voltage to less than 1 V.^[19] Although the discharge rate of buried iron powder is ideal, there is a risk of thermal runaway when the temperature rises sharply during the discharge process.^[19] Wang et al. studied the method of using copper powder and graphite powder to bury the battery cell for discharge, and the research results showed that the copper powder burial could reduce the open circuit voltage of the battery to 0.5 V within 0.5 hours, but the temperature of the discharge process also rose sharply, and there was a great risk of thermal runaway.^[36] Although the overall temperature of graphite powder buried discharge is controlled, the discharge rate is relatively slow.^[19,36]

Load circuit discharge. The load circuit discharge method is a direct ohmic discharge method of the battery through the load circuit. In addition to the consumption of energy in the battery through the simplest resistive load circuit, the residual electric energy in the battery can also be recovered by using the switching power supply as the load. Zheng's study used a test device consisting of a constant current switching power supply to conduct discharge studies on decommissioned lithium-ion batteries. The results show that the residual power inside the decommissioned power battery decreases with the reduction of the power rate when discharging at different rates under the same cut-off voltage.^[19] Duesenfeld. Crop. and TES-AMM Crop. have studied the discharge mode of the load circuit to recover the power, and have released the power of the decommissioned lithium-ion battery through the DC/DC external load circuit and stored it in the commercial energy storage system.^[37,38] However, due to the large workload of clamping and transplanting in the discharge process, this discharge mode with the function of energy recovery is only suitable for large quantities of batteries with specific specifications. In addition, the load circuit discharge method still needs optimization in its equipment investment cost and operating cost, as well as further evaluation of the best discharge level.

3. Development Prospects of Discharge Pretreatment of Decommissioned Lithium-ion Batteries

In addition to the key factors that directly affect the overall efficiency of discharge pretreatment technology, such as discharge efficiency, potential environmental pollution, battery model adaptability, auxiliary material consumption, etc., the results of discharge pretreatment and the impact of cell passivation on the subsequent recovery process should not be ignored. With the development of the entire lithium-ion battery recycling technology, in the case of taking into account a certain efficiency, comprehensive consideration of further energy recovery in the process of discharge pretreatment, to achieve a higher cathode lithium content, and control a lower

level of active substance pollution will be conducive to improving the recovery efficiency of the entire lithium-ion battery recycling process.

3.1. Further energy recovery

Gur's research shows that the energy density of current commercial lithium-ion battery systems is between 150 and 210 Wh/kg.^[38] If the average attenuation is 70% when decommissioned, the charging state is 40% when decommissioned, and the initial energy density is 150 wh/kg, the recoverable energy of 1 million tons of decommissioned lithium-ion batteries is about 42 MWh. According to research by Happer et al., a typical British household uses up to 4,600 kWh of electricity per year.^[2] That means the electricity in one million tons of decommissioned lithium-ion batteries could power more than 9,000 homes for an entire year. Happer's study also put the cost of electricity in the UK at 14.3 pence per kilowatt in 2020.^[2] If we use the price of electricity in the UK electricity market as a benchmark, every million tons of battery energy that can be fully recovered is expected to bring a profit of about £6 million.

It can be seen that when the recycling of decommissioned lithium-ion batteries becomes a sizeable industry, the recovery of the electrical energy in the decommissioned lithium-ion batteries can produce considerable economies of scale. When powder discharge or simple external load discharge is used, the residual electrical energy in the battery is converted into heat energy. If we want to recover this energy, we need to design further heat recovery systems. When using controlled passivation, energy is often released through direct reactions between active substances or direct REDOX side reactions, which makes energy recovery quite difficult.

However, when discharged in a way such as saline discharge, the residual electrical energy in the battery is mainly converted into gas by electrochemical reactions. To make full use of this part of the energy, it is necessary to make an accurate design of the discharge system to avoid the production of by-products such as chlorine gas. Shaw-Stewart et al. studied various saline discharge systems. The main reaction of saline discharge in an alkaline system and acid system is studied by theoretical calculation and experiment. The competitive reaction of electrolyte salts is also studied.^[39] Shaw-stewart et al. demonstrated the possibility of controlling the reaction products of saline discharge by adjusting the composition of saline. This means that there is a potential to recover electrical energy by collecting the reaction products of saline discharge. For example, the saline system could be adapted so that as much electricity as possible is used to produce hydrogen and oxygen, and both gases could be recovered further.

Referring to the process of lithium-ion battery production, the use of DC/DC modules or switching DC power supplies to directly transfer the energy inside the lithium-ion battery to the bus or energy storage system is a more energy-efficient choice. At present, Duesenfeld and TES-AMM company have studied

the direct energy recovery discharge mode, but at present, this discharge mode lacks a clear economic model to guide further development of the technology. More importantly, the optimal discharge cutoff condition and the optimal discharge process in this discharge mode also lack in-depth research.

3.2. Higher Cathode Lithium-ion Content

The risk of thermal runaway in the subsequent recovery of lithium-ion batteries mainly comes from the REDOX reaction between the inlaid lithium ions in the anode material and the cathode material. Lixiang Wu et al. studied the relationship between open circuit voltage, cathode lithium ion content, and recovery ignition and explosion risk, and found that the lower the open circuit voltage, the higher the cathode lithium ion content, the lower the ignition and explosion risk.^[20] Therefore, reducing the lithium-ion content in the anode material as much as possible and increasing the lithium-ion content in the cathode material is conducive to the safety of the overall subsequent recovery process.

In terms of cathode material element recovery, the most widely recognized development direction at present focuses on the recovery of major metal elements based on hydrometallurgy.^[40] Lisa Bruckner et al. reviewed in detail the current process of element recovery of cathode materials based on the theoretical system of hydrometallurgy. The whole wet process mainly includes four steps: leaching, impurity removal, extraction, and lithium precipitation.^[17] In the study of Francois Larouche et al., and Boyu Liu et al., for example, in the recovery process based on hydrometallurgy, the current lithium-ion recovery rate is mostly based on the lithium-ion content in the cathode material.^[41,42] This means that the lithium remaining in the graphite anode requires additional recycling or direct disposal. Therefore, increasing the lithium content in the cathode material after discharge is conducive to improving the overall lithium-ion recovery rate, while reducing the leaching of the anode for the recovery of lithium ions in the anode graphite lattice during the industrialization process, making an important contribution to the improvement of the comprehensive benefit of the entire recovery system.

In terms of anode material reuse, most current recycling methods need to remove the remaining lithium ions in the anode material. Madhusoodhanan Lathika Divya et al. used deionized water and DMF to wash the lithium-containing SEI structure outside the graphite.^[43] Yue Yang et al. used 1 mol/L hydrochloric acid and H₂O₂ solution to treat decommissioned graphite materials at 80 °C to remove impurities such as lithium in the graphite.^[44] Yue Yang et al and Ma, X et al used a mixed solution of sulfuric acid and H₂O₂ to remove impurities such as lithium.^[45,46] K. Liu et al. chose pure concentrated sulfuric acid as an impurity removal agent to purify the recovered graphite.^[47] Hong Duc Pham et al. used the recovered graphite for the anode of the potassium ion battery and also carried out chemical purification treatment to remove residual lithium and other metal elements, and the purification process mainly used a 32% sodium chloride solution.^[48] Madhusoodhanan Lathika

Divya et al.^[49] reviewed the research progress in the preparation of graphene from waste graphite recovered from decommissioned lithium-ion batteries. In these processes, the lithium in graphite is often dissolved in intercalation solvents consisting of H_2SO_4 , KMnO_4 , NaNO_3 , and KClO_3 during the preparation of graphene oxide using the HUMMER process.^[49] Lai et al. attempted to use choline chloride and glycerin (molar ratio 1:2) to formulate a deep eutectic solvent to leach impurities from the spent graphite anode.^[50] Since the lithium-ion battery is a rocking chair battery, increasing the lithium content in the cathode material will also significantly decrease the lithium-ion content in the anode material. Further reducing the residual lithium ions in the anode material is conducive to reducing the difficulty of removing lithium ions in the anode material reuse process, and is conducive to the concentrated recovery of lithium elements.

In terms of material repair, if the main cause of material performance attenuation is due to the absence of lithium ions in the cathode material, the material can be repaired by supplementing lithium ions.^[51] Ji et al. used organic lithium sources mixed with retired LiFePO_4 materials for sintering to supplement the lithium ions lost during the cycle of LiFePO_4 materials, and the material capacity reached 157 mAh/g after repairing.^[52] Wang et al. obtained LiCoO_2 material with an ideal performance by applying hydrothermal lithium supplement to LiCoO_2 after circulation, and then mixing it with $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LATP) and finally using high-temperature solid phase reaction material for lithium supplement repair.^[53] Zho et al. used an H-type electrolytic cell to conduct electrochemical lithium inlay repair of retired LiFePO_4 materials, in which the positive electrolyte was separated by anion exchange membrane, zinc plate was the anode, waste LiFePO_4 suspension was the cathode, and the electrolyte was lithium saline solution.^[54] Liu et al. used lithium salicylate (LSA)-assisted eutectic salts direct regeneration (OAER) process to achieve the replenishing of lithium in an extremely low state of health Ni-rich cathode (Low SOH NCM).^[55] If more lithium ions can be migrated to the cathode material during the discharge pretreatment process, the lithium ion content of the cathode material can be increased. This result will effectively improve the performance level of repair products and reduce the consumption of lithium containing raw materials in the repair process.

In order to further improve the quality of the recovered material after discharge and increase the lithium content of the cathode material after discharge pretreatment as much as possible, more accurate control of the discharge pretreatment process is needed. The realization of this control depends on a full understanding of the electrochemical process in the discharge treatment and the final aging process of lithium-ion batteries. The aging of the electrochemical performance of lithium-ion batteries is a comprehensive reflection of the aging of the internal anode material, cathode material, SEI, and electrolyte. SEI is a special structure. The research results of Goodenough et al. show that SEI film is a passivation film spontaneously generated between the anode material and electrolyte interface, as well as between the cathode and electrolyte interface during the operation of a lithium battery.^[56]

Vetter, Borodin, Delp, and others confirmed through research that SEI membrane also plays a role in proton transduction and is an important component of the stable operation of lithium-ion battery systems.^[57–59] According to the types of aging loss, Han, Birkel, and Pastor-Fernandez et al. divided the aging loss of lithium-ion batteries into the loss of active lithium ions (LLI), loss of active substances (LAM), and decay of conductive properties (CL).^[60–63] In terms of the aging of the anode SEI, the study of Han et al. and Lin et al. revealed that the thermodynamic instability and the change of graphite volume expansion would lead to the repeated growth and thickening of the SEI film, resulting in the loss of active lithium ions and the loss of active substances.^[62,64] In terms of the attenuation of active substances in the anode, Vermeer's research summarized the loss of active substances caused by the collapse of the graphite material structure, the loss of active lithium ions caused by the precipitation of lithium metal, and the attenuation of electrical conductivity caused by the weak contact between the particles of active substances.^[65] In terms of the decay of cathode active substances, Vermeer's research shows that the cathode materials undergo phase transitions and volume changes during the cycle, resulting in the LAM and the decay of CL.^[65] Birki et al. summarized a more detailed correlation diagram of the attenuation mechanism, as shown in Figure 3.^[61] Based on these aging mechanism studies, it can be found that there are a large number of irreversible lithium ions caused by LLI and CL in the anode material and at the anode SEI film interface of the battery with life cut-off voltage.

To achieve the goal of higher cathode lithium content, it is necessary to reverse the irreversible lithium-ion removal caused by LLI and CL in the anode material and the anode SEI film. The most direct way is to discharge decommissioned lithium-ion batteries below the open circuit voltage to reduce the potential difference between the cathode and anode as much as possible. The study of He et al. confirmed that after deep discharge, the graphite anode material was used to determine the layer spacing by XRD. The results show that the interlayer spacing $d(002)$ returns to the original graphite lattice state, which confirms that the intercalated lithium can be completely removed under the condition of deep discharge.^[66] Zheng et al. prepared lithium ferrous phosphate/graphite batteries, and carried out 1 C/1 C charge-discharge cycles under the cutoff voltages of 1.5 V, 1.0 V, 0.5 V, and 0.0 V, respectively. The SEI film resistance R_{SEI} increased step by step with the cutoff voltage decreasing and the increase amplitude was significant. The change of R_{SEI} means the continuous decomposition and re-formation of the membrane.^[67]

Liu et al. adopted the commercial 18650 lithium iron phosphate graphite battery as the test object to operate the EIS test when the discharge cutoff voltage was 3.6 V, 3.12 V, 2.9 V, 2.0 V, 1.0 V, 0.0 V, -1.0 V and -1.4 V. After fitting the EIS test results, it is shown that the SEI film fitting resistance R_{SEI} related to the SEI film changes dramatically when the cut-off voltage is 2.0 V, which means that the SEI film decomposes under deep discharge in the electrochemical system.^[69] Juarez-Robles et al. studied the capacity fading mechanism during the long-term cycle of over-discharge LiCoO_2 and found that SEI film

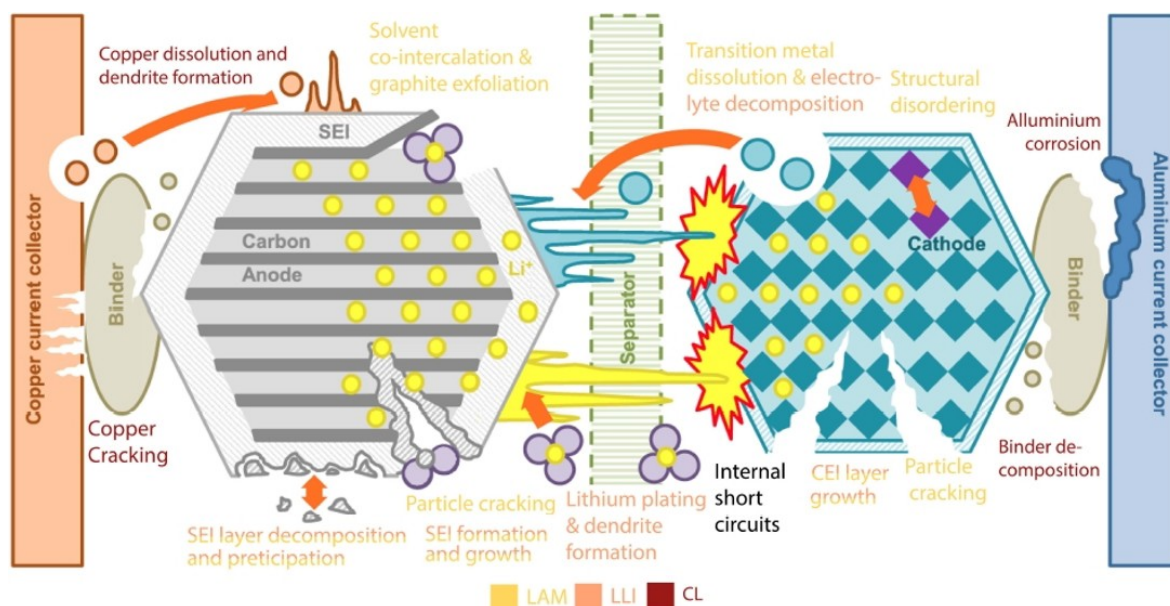


Figure 3. Graphic summary of detailed aging mechanisms. Adapted from Ref. [61]. Copyright (2023) with permission from Elsevier.

decomposition occurred below 2.7 V, and the V-DOD curve of the battery cell was shown in Figure 4.^[68] The research results of deep discharge of existing lithium-ion batteries confirm the possibility of complete removal of anode embedded lithium ion and anode SEI delithium during deep discharge. However, the ideal discharge cut-off voltage and discharge process control conditions are not clear, and the deep discharge process of post-cycle batteries needs to be further studied.

3.3. Lower active substance contamination

In the current discharge methods, there is a risk of contamination of active substances. The contamination of active

substances means that these pollutants need to be targeted in the subsequent recycling process. This risk is particularly obvious in the process of saline discharge and the process of external load circuit discharge. In the process of hydrometallurgical extraction of metal elements, the removal of additional impurities and the separation of metal elements require a specific design of the system, which makes the system more complex.^[70] It is more difficult to remove impurities in repair regeneration, and impurities can easily remain in the recycled product, which can negatively affect the performance of the manufactured battery. In the latest study, Fink et al. demonstrated the influence of impurities such as copper and aluminum on material properties and also conducted a detailed study on the removal process of these impurities.^[71] The study by Zhao et al. reviewed in detail the negative effects of impurity elements on material repair and the difficulty of impurity removal in the process of material repair.^[72] This means that controlling the pollution of active substances in the discharge pretreatment process is of great significance for improving the performance of subsequent products.

In the deep discharge process, which is different from the conventional operating voltage window, the electrode side reaction may deposit new components on the active substance and lead to the contamination of the active substance. The most typical internal contamination of active substances comes from the precipitation of anode copper collector fluid and its deposition on the cathode. Maleki et al., in an early work, discharged a lithium-ion battery in a system composed of lithium cobaltate as the cathode and graphite as the anode, with LiPF₆/EC/DMC/DEC as the electrolyte. The over-discharge tolerance of lithium-ion batteries is poor, and the presence of copper elements on the cathode will be detected while capacity attenuation occurs. This means that rapid failure of the electrochemical system, electrochemical etching of the copper foil

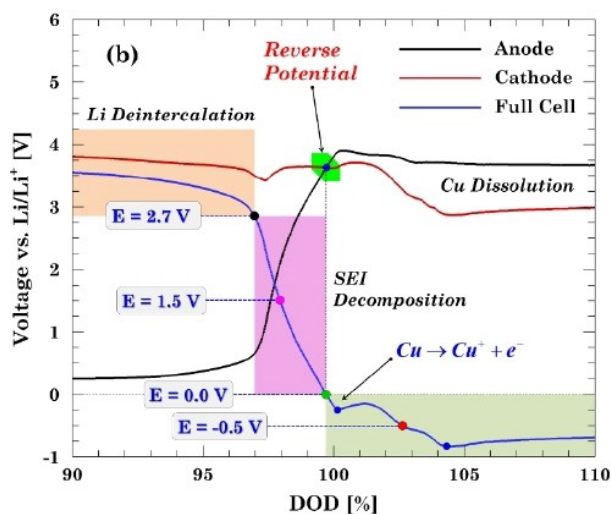


Figure 4. V-DOD curve when the discharge cutoff voltage is below -1 V. Adapted from Ref. [68]. Copyright (2020) The Author(s).

current collector used in the anode electrode, and copper contamination of the cathode occur under over-discharge under abuse conditions.^[73] He et al. used a working electrode composed of platinum electrode and copper electrode, taking lithium metal as the reference electrode and LiPF₆/EC-EMC as the electrolyte, to calibrate the REDOX potential of copper in the carbonate electrolyte used in commercial lithium batteries, under the condition that platinum electrodes were extremely inert. According to the test results of cyclic voltammetry, the oxidation potential of Cu to Cu⁺ is 3.92 V vs. Li/Li⁺, the oxidation potential of Cu⁺ to Cu²⁺ is 4.17 V vs. Li/Li⁺, the lithium reduction potential of Cu⁺ to Cu is 3.19 V vs. Li/Li⁺, and the lithium oxidation potential of Cu²⁺ to Cu⁺ is 3.28 V vs. Li/Li⁺.^[66] The CV curve is shown in Figure 5. Hendricks et al. carried out a deep discharge of nickel-cobalt-aluminum (NCA) oxide/graphite system batteries and the cut-off voltage values were 0.5 V, 0.25 V, and 0 V, respectively. The electrodes were then tested with XPS and XAFS. The results show that copper is detected in all batteries with discharge cutoff voltage below 0.5 V, and the deposited copper mainly exists in Cu₂O and Cu(OH)₂ phases.^[74] Langner et al. studied the risk of copper precipitation in the non-cut-off voltage-limited discharge process of lithium battery recycling. Through the characterization and calibration of battery temperature, open circuit voltage, capacity, and electrode copper content, it is concluded that copper precipitation may occur in the process of multiple cell series discharge due to the non-uniform internal resistance voltage drop between cells.^[75]

In addition, the puncture short circuit and gas production caused by over-discharge may lead to complete damage to the internal structure of the battery cell and serious internal material mixing and pollution. Guo et al. through the over-

discharge abuse test of terpolymer lithium-ion batteries and the calculation of the internal short-circuit equivalent circuit model, found that in the case of uncontrolled over-discharge, the dissolution of copper current collector used in anode electrode and its evolution on the cathode electrode will cause the internal short circuit of the battery, making the electronic insulation between the two poles ineffective.^[76] The internal short circuit of the battery process is shown in Figure 6(a). Juarez-Robles et al. studied the electrochemical mechanism during the long-term cycle of over-discharged LiCoO₂. After the formation of lithium ions with LiCoO₂ as cathode and graphite as anode, the battery is charged and discharged at discharge cutoff voltages of 2.7 V, 1.5 V, 0.0 V, and -0.5 V, respectively. In the process of a low cut-off voltage cycle, obvious gas production occurs. Internal damage caused by an apparent internal short circuit was observed after disassembly.^[68] This study agrees with Guo et al.'s calculations. The results of over-discharge are shown in Figure 6(b and c). At present, although the mechanism of copper precipitation has been studied in a certain depth, how to control the side reaction represented by copper precipitation and reduce the pollution of active substances in decommissioned lithium-ion batteries still needs further research on the reaction mechanism. Only after the full understanding of the main reaction and side reaction mechanism during deep discharge of decommissioned Li-ion batteries under different systems, we can better control the discharge process to avoid internal interactive pollution of active substances.

In addition to internal cross-contamination, the discharge process has the risk of contaminating the cell with external elements. In the process of saltwater discharge, the salt water will be immersed in the battery cell because of the corrosion of

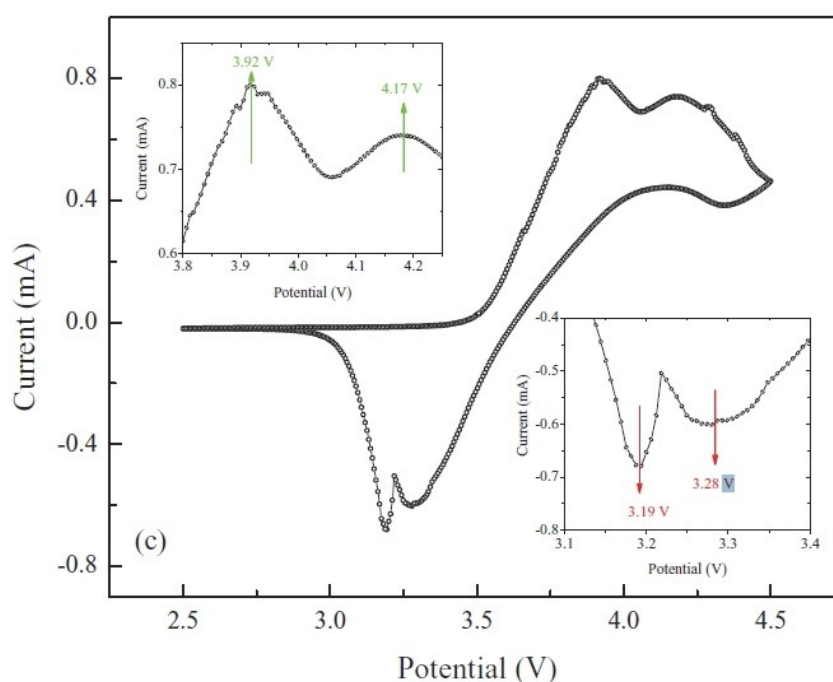


Figure 5. Scanning curve of Pt-Cu electrode cyclic voltammetry. Adapted from Ref. [66]. Copyright (2013) The Author(s).

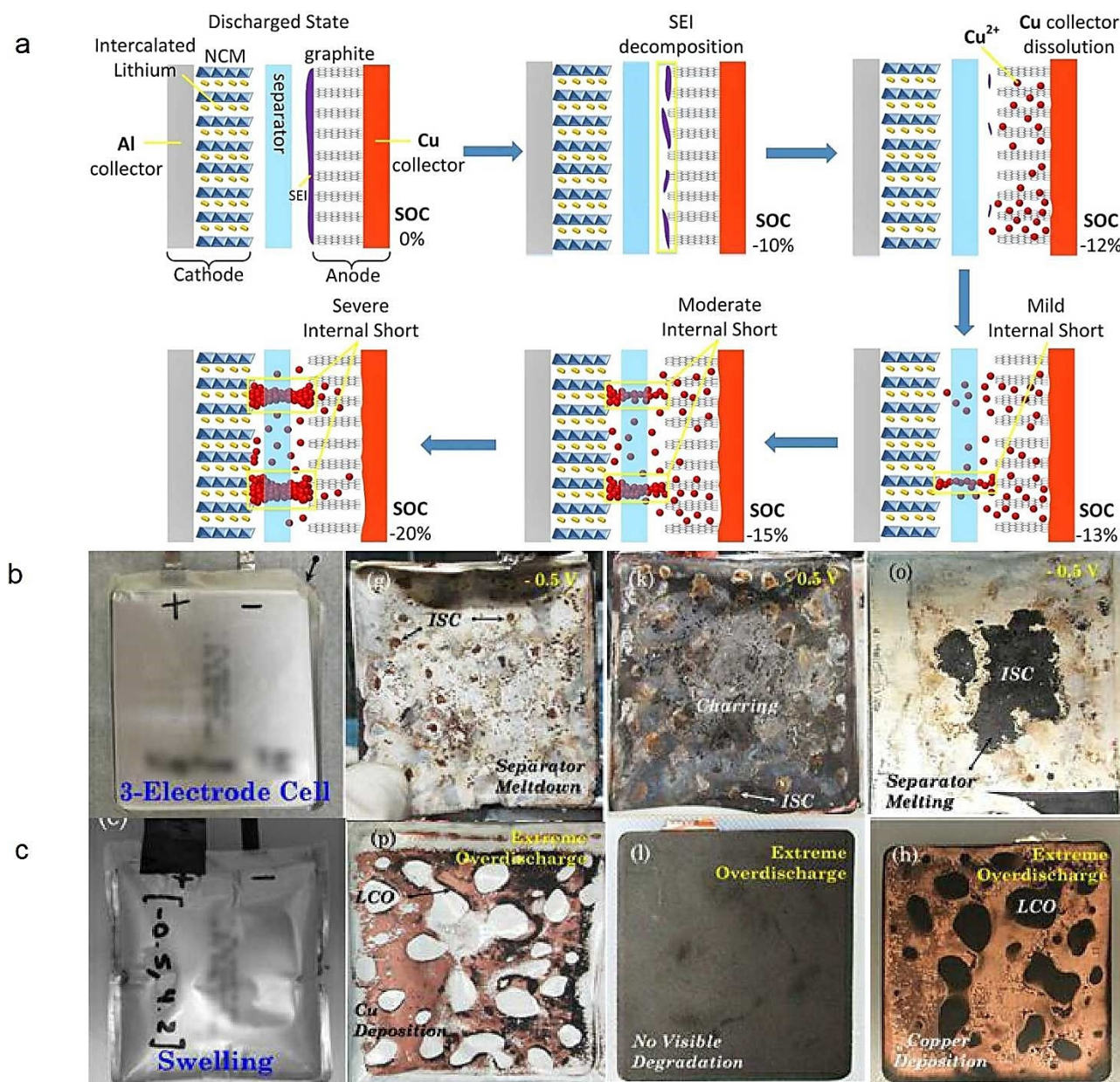


Figure 6. a) Schematic diagram of the electrochemical process of internal short circuit caused by over-discharge. Adapted from Ref. [76]. Copyright (2016) The Author(S). b) Discharge cut-off voltage of -0.5 V battery and disassembled pole plate, aluminum-plastic film, separator. c) Discharge cut-off voltage of -1 V battery and disassembled pole plate, aluminum-plastic film, separator. Adapted from Ref. [68]. Copyright (2020) The Author(s).

the salt water. The salt in salt water will soak the active substance and cause foreign salt to contaminate the active substance. Chemical passivation, such as carbon dioxide passivation, results in a large deposit of lithium carbonate on the anode, which needs to be treated separately in the subsequent recovery process (these similar treatments are detailed in Section 3.2. Higher cathode lithium content). At present, the latest research to prevent external pollution problems focuses on the adjustment of saline systems and the protection of battery corrosion. In Severi Ojanen's research, iron powder and octan powder were used in the process of saline discharge, and active metal powder was used as a sacrificial agent to provide electrons in the process of saline discharge,

which played a role in protecting the battery pole and shell. The immersion pollution of salt water into the battery cell is controlled.^[32] In the study of Lixiang Wu et al., a graphite electrode was used to replace and cover the metal electrode, which effectively prevented the corrosion of the original metal electrode and also effectively controlled the immersion pollution of salt water on the battery core.^[20] However, the corrosion-resistant saline discharge method that can discharge stably for a large number of batteries is still to be developed

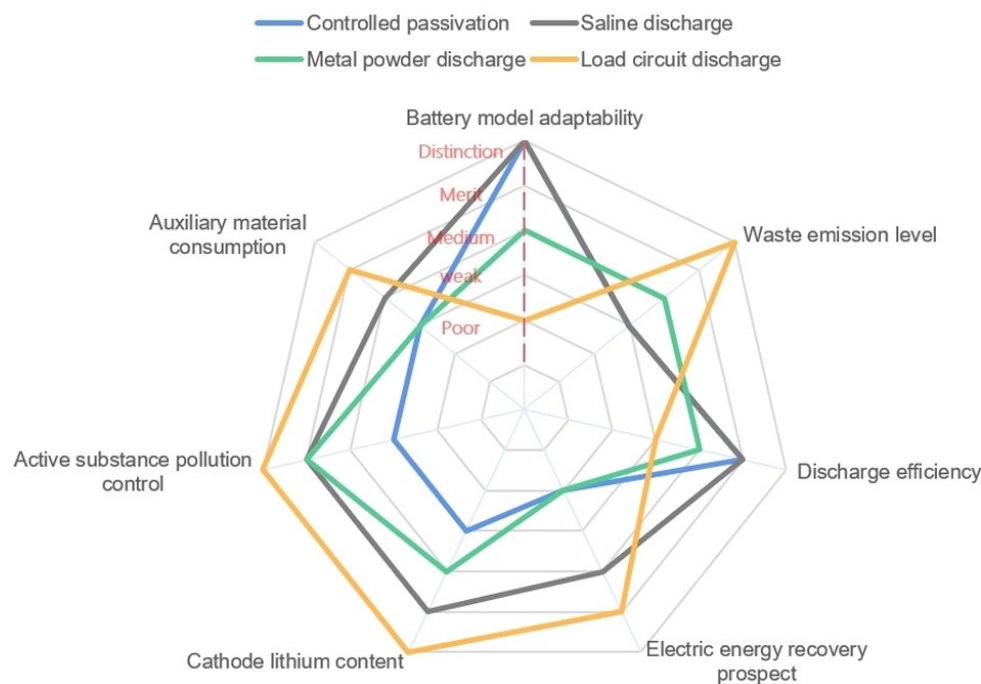


Figure 7. The comparison of different types of discharging methods in terms of battery model adaptability, waste emission level, discharge efficiency, energy.

4. Summary and Outlook

With the increase in the recovery amount of decommissioned lithium-ion batteries, it is becoming more and more important to pursue safer and more comprehensive benefit discharge pretreatment technology in the process of lithium-ion battery recycling. From the most basic level, one of the key research directions in the future is to continuously overcome the respective shortcomings of different discharge modes of decommissioned Li-ion batteries in terms of discharge efficiency, potential environmental pollution, adaptability of different types of batteries, and consumption of auxiliary materials. In addition, the more important research direction will be to further explore the huge potential of discharge pretreatment in improving the comprehensive benefit of the whole recovery process. This potential can be tapped in three ways. First, the recovery of the remaining energy in the lithium-ion battery is considered in the discharge pre-treatment process. Secondly, increase the content of lithium ions in the positive electrode of decommissioned lithium-ion batteries after discharge, which can effectively reduce the loss of lithium ions in the subsequent element recovery process, effectively reduce the lithium consumption in the material repair process, and thus significantly improve the material utilization rate of the entire recovery process. Thirdly, if the component pollution in the discharge pretreatment process can be effectively controlled, it will reduce the material consumption and power consumption in the subsequent recycling process.

When we take into account the aforementioned factors to assess the overall effectiveness of discharge preconditioning, we can ascertain the future research prospects for various discharge preconditioning methodologies. The methods of

controlled passivation, saline discharge, metal powder discharge, and load circuit discharge were compared in terms of battery model adaptability, waste emission level, discharge efficiency, electric energy recovery prospect, cathode lithium content, and active substance pollution control. By dividing the corresponding levels of different discharge methods in different performances into five grades: poor, weak, medium, merit, and distinction, a radar chart (Figure 7) can be created. Through the radar map, we can intuitively see that the saltwater discharge and the load circuit discharge occupy the largest radar map area, so their future development potential is greater. Load circuit discharge has great disadvantages in battery model adaptability and discharge efficiency. In the future, it is necessary to improve the compatibility of discharge equipment with different types of batteries to improve the adaptability of the battery model, as well as further in-depth study of discharge mechanism to develop a faster load circuit discharge method, under the condition of obtaining electric energy recovery efficiency. The saline discharge technology also needs to further reduce the consumption of auxiliary materials, reduce the secondary discharge caused by the discharge saline, and tap the control potential of product pollution by reducing the corrosion of the battery cell by the saline. For controlled passivation, there are outstanding advantages in battery model adaptability, but how to control product pollution, complete efficient energy recovery, reduce secondary emission levels and improve the cathode lithium-ion content still needs further research. Although the metal powder discharge can achieve the discharge effect, it has almost no advantage except the waste emission level, and the development prospect is the least optimistic from the analysis of the radar map.

It is not difficult to see from the above analysis that the pretreatment technology with the greatest industrial potential should be load circuit discharge and saline discharge. At present, saline discharge has the best industrialization prospects in the near future because of its battery model adaptability and simple method. However, in order to further realize the large-scale industrial application of saline discharge, there are three problems to be solved. First, the saltwater system is designed specifically to avoid the corrosion of the battery core; Second, adjust the discharge brine system to further control the discharge process. Thirdly, the industrial saline discharge device is designed so that the saline discharge process can be produced in continuous commercial process. Although the load circuit discharge method has great potential, its application in large-scale industrialization is greatly limited by the adaptability of battery models. In the process of industrialization, in addition to further research on external circuit discharge technology and large-scale external circuit discharge equipment, it is also necessary to retire similar models of lithium-ion batteries to a certain scale. This means that lithium-ion batteries (especially power batteries and energy storage batteries) need to form a relatively standardized PACK structure and cell packaging form when they are designed and produced.

All in all, future research on the discharge process of decommissioned lithium-ion batteries should not only focus on improving the efficiency of existing processes. It is more important to comprehensively consider the entire recovery process, and synchronously improve the efficiency of the entire decommissioned lithium-ion battery recovery process through the discharge pretreatment process.

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Conflict of Interests

The authors declare that they have no known competing

Keywords: lithium-ion battery · recycle · discharge · pretreatment · passivation

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