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# Short literature review of $Li^+$ batteries recycling

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**Abstract.** Currently, lithium-ion batteries are widely used in advanced electronic devices and electric vehicles due to their low weight, high energy density and long service life. Therefore, the number of waste lithium batteries is also increasing, and it is very important to recover the valuable resources in them. This paper reviews some conventional means of recycling lithium-ion batteries and mentions future directions. The application and recycling of all-solid-state lithium batteries will help to solve the problem of waste lithium batteries.

## 1. Introduction

For a long time, the consumption of traditional fossil energy has given rise to many social problems, such as air pollution, climate change and environmental damage[1]. At the same time, many countries around the world are facing the challenges posed by the energy crisis due to uncontrollable factors such as wars and natural disasters. In response to the common crisis, the world's major countries have reached a consensus on controlling carbon emissions. The green energy automotive industry is becoming the focus of attention around the world under the goal of "carbon neutrality" . With the development of renewable energy technologies, lithium, as a material with promising applications, will play an important role in reducing carbon emissions[2]. The low mass and high energy density of lithium-ion batteries (LIBs) have made them a favourite in the new mobile electronics industry since Japan's Sony developed the first commercially available high-performance LIB back in 1991[4]. The cathode of a common LIB consists of a lithium-containing metal oxide, such as LCO ($LiCoO_2$), while the anode is dominated by copper or graphite[3]. As related technologies continue to be refined, high-capacity rechargeable power batteries are being used in electric vehicles.

As a core component of new energy vehicles, the production and disposal of lithium-ion power batteries are increasing along with the growing new energy vehicle industry. Global demand for lithium will be around 12,000 tonnes in 2020 and is expected to increase to 25,000 tonnes by 2025. Waste batteries are expected to reach 101 Gwh by 2023, about 1.16 million tonnes[5-8]. The amount of valuable recyclables is positively correlated with the amount of discarded lithium batteries. The global lithium-ion battery market was valued at US$56 billion in 2021; the recycling and dismantling of used lithium-ion batteries is expected to reach a value of US$17,796 million by 2025[9]. But the number of those discarded LIBs that are recycled is very small. Relevant data show that the recycling rate of discarded lithium-ion batteries is insufficient (lower than 1%)[10]. So that recycling these valuable metallic elements, such as cobalt, lithium, manganese and nickel, can reduce the cost of producing new batteries and create economic benefits. On the other hand, the chemicals in LIBs at the end of their useful life must be disposed of in a reasonable manner. Although the recovery efficiency of traditional and reliable lithium battery recycling processes, whatever physical or chemical processes, has been satisfactory, the disposal of highly corrosive waste liquids that accompany the extraction of valuable items can be troublesome. Especially in chemical treatment processes, highly acidic or alkaline liquids can be generated[42]. Moreover, the flammable electrolyte solution poses a potential hazard when conventional $Li^+$ batteries are being recycled[18]. Besides, pre-processing of LIBs is usually performed manually, which is recognized in many current studies. This illustrates how these methods may still need to be changed when they are used in industry[43]. Therefore, it is important to find excellent ways to recycle discarded lithium batteries, or to design new varieties of LIBs, such as all-solid-state batteries (ASSBs)[11].The purpose of this paper is to synthesize the relevant research results in recent years, call for the recycling of lithium-ion batteries to be taken care of, and look forward to the development of all-solid-state batteries.

## 2. Working principle of lithium battery

Since the commercialization of LIB in the 1990s, there has been a continuous search for safer, more stable materials with higher conductivity to meet the growing technological demands of lithium-ion batteries.

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Rechargeable batteries all consist of a cathode, anode, conductive electrolyte and separator.

### 2.1 Composition of lithium-ion batteries

The composition and mass percentage of lithium batteries in common use today are shown in Table 1

**Table 1:** The chemical composition of LIBs[3,12-14]

| Cell components | Chemical composition | | %wt. |
|---|---|---|---|
| External casing | Fe-Ni alloy | | 20-26 |
| | Al | | 10 |
| **Cathode** | | | 25-30 |
| Aluminium | Al | Current collector foil | 5-8 |
| Binder | Usually PVDF | | 1-2 |
| Metal oxide | Lithium | | 1.5-7 |
| | Co | $LiCoO_2$ | 5-20 |
| | Nickel | $LiNiO_2$ | 5-10 |
| | | $LiNi_{0.5}Co_{0.15}Al_{0.05}O_2$ | 5 |
| | Manganese | $LiMnO_2$ | |
| | $LiNi_4Co_3Mn_2O_2$ | | |
| Separator | Microporous PP or PE | | 4-10 |
| **Electrolyte** | | | 10-15 |
| Lithium materials | $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiPF_6$ | | |
| Organic solvents | DMC-EC,PC-DME, BL-THF | | |
| **Anode** | | | 15-25 |
| Copper | Copper | Current collector foil | 8-10 |
| Binder | Mostly PVDF | | 1-2 |
| Graphite | | | 15-17 |

Sony used LCO as electrode when they invented the lithium battery, while today's giants of the electric car industry, Tesla, use NCA and NMC[15]. The organic liquid electrolyte commonly used in lithium-ion batteries consists of lithium salt ($LiPF_6$, $LiAsF_6$), organic solvents like DMC (dimethyl carbonate), EC (ethylene carbonate) and additives[16]. In contrast, the electrolyte for solid-state batteries (SSE) is either a conductive solid-state polymer (like polyethylene oxide, PEO), or an oxide/sulfide based chemical (like $LiNbO_3$, $Li_3PS_4$ ) [17-19]

### 2.2 The electrode reaction equation

Take $LiMO_2$ type as an example, where $M$ represents Co, Ni, Mn or the mix.

*The cathodic half reaction:*

$$LiMO_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_{1-x}MO_2 + xLi^+ + xe^-$$

*The anodic half reaction:*

$$6C + xLi^+ + xe^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_xC_6$$

*Overall reaction:*

$$LiMO_2 + 6C \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_xC_6 + Li_{1-x}MO_2$$

During the discharge process of a battery, lithium ions produced at the negative electrode move through the electrolyte across the separator toward the cathode. Vice versa, during charging, electrons provided by an external power source combine with lithium ions to form lithium metal, causing it to grow on the anode graphite[20]. The presence of electrolytes will aid in the movement of $Li^+$ during the chemical reactions described above.

## 3. Wasted LIB recycling process

Current common methods of lithium-ion battery recycling include physical and chemical processes. In conventional LIBs the liquid electrolyte can be cleaned off by using solvents like N-methyl-2-pyrrolidon after the batteries has been dismantled[21]. But the situation is different for ASSBs. Because of the striking differences in both chemistry and structure of ASSBs compared to conventional LIBs, there are some special points of recycling that need to be considered.

### 3.1 Physical Processes

Physical processes include disassembly, dissolution and pyrolysis. Of them all, the dissolution process has been the most popular of late, while also maximising the recovery of valuable materials[3]. As selected organic solvents capable of dissolving adhesives (PVDF, PTFE), N, N-dimethylformamide (DMF), N, N-dimethylacetamide (DMAC), N-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO) were used to separate the lithium salt from the binder. The solid mixture obtained by separation will be used to carry out the next steps. For instance, Jin et al. used flotation to recycle valuable metals in end-of-life LIBs, firstly, the crushed materials were screened out by air separation, the screened mixture was put into a high-temperature calciner for roasting, and finally, the obtained products were classified for recycling. The recovery rate of lithium and cobalt reached 92%[22].

### 3.2 Chemical Processes

Chemical processes are primarily hydrometallurgical methods which include processes such as acid or alkali leaching, biological processes and so on. Multiple steps will result in greater costs[3].

#### *3.2.1 Acid leaching*

Inorganic acid leaching usually involves the use of strong inorganic acids such as HCl[23-25], $H_2SO_4$[26-28], $HNO_3$[29], and $H_3PO_4$[30,31]. In addition, reducing agents such as $H_2O_2$ and $Na_2SO_3$ are used to further enhance leaching efficiency. HCl showed the best leaching results. Wang et al. leached cathode materials in HCl system and showed that the leaching rate of Ni, Co, Mn and Li was 99%[32]. In order to avoid toxic gases ($NO_X$, $Cl_2$) produced by the inorganic acid leaching process, the organic acid leaching process is of interest. Organic acids (such as acetic acid, ascorbic acid or malic acid) are biodegradable. Not only do they not pollute the environment, they are also easily recycled[33]. Based on citric acid leaching, an atom-economical process for recycling waste NCM batteries was developed. Under optimal conditions, with the help of the reducing agent D-glucose, 99% of Li, 91% of Ni, 92% of Co and 94% of Mn can be recovered by leaching[34]. Although organic acids have shown many advantages in leaching cathode materials from used lithium-ion batteries, their high expense costs have led to their not being widely used in industry.

#### *3.2.2 Alkaline leaching*

The acid leaching process is less selective and is accompanied by high concentrations of $H^+$, which can easily damage the equipment. Ammonia leaching is based on the complexation of $M^{2+}$ with ammonium ions in alkaline systems to form stable metal-ammonia complexes. Some scholars have used ammonium sulphate ($(NH_4)_2SO_4$) as a leaching agent and sodium sulphite ($Na_2SO_3$) as a reducing agent to selectively leach valuable metals[35]. Ku et al. used a mixed system of ammonia, ammonium carbonate, and ammonium bisulfate for alkaline leaching of cathode materials from used batteries, which can achieve the effect of selective separation of different metal ions[36].

#### *3.2.3 Biological processes*

Biological leaching process has more obvious environmental protection, safety and other advantages, and the economic cost is small. At present, due to the difficulty of microbial cultivation and the long period of strain cultivation, it is still in the stage of laboratory research community, failing to realise the application in industry. But there was good news from the laboratories. For example, acidithiobacillus ferrooxidans uses elemental sulphur and $Fe^{2+}$ to produce metabolites, sulphuric acid and $Fe^{2+}$ in the solution to recover Li and Co from $LiCoO_2$ of LiBs[37].

### 3.3 Recycle of ASSBs

In addition to conventional lithium-ion battery recycling methods, all-solid-state batteries can be disposed of using direct recycling methods[38].The main step in direct recovery is the lithium regeneration process. In this process, the lithium-depleted cathode material is reacted with a lithium source to restore its original stoichiometry, and then heat-treated to restore the surface structure and morphology[39-41]. Direct recycling therefore has the advantage of low energy costs and environmental friendliness.

## 4. Discussion

A review of research findings in recent years reveals that hydrometallurgy, as the most commonly used recycling method, has the advantages of less pollution and high recovery. At the same time, its high recycling cost and potential danger are still the reasons that hinder the development of lithium battery recycling industry. Biological leaching is an environmentally friendly and efficient process, but the long culture cycle of the colonies causes it to remain in the lab stage at present. All-solid-state batteries, as a potential wildly used battery, can help to solve the above problems.

## 5. Conclusion

Recycling of lithium-ion batteries is very important today. Processing methods should be developed that have the lowest environmental impact and the highest recycling efficiency leading to savings in primary raw materials, improved economic efficiency, reduce energy consumption and the cost of safe management of waste and hazardous substances. At the same time, the application and recycling of newer lithium-ion batteries has a bright future. The unique structure and recovery method of ASSBs will be future research directions.

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