Application and recycling of lithium-ion batteries

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Abstract. As an emerging technology with a vast worldwide market application and potential over decades, electric vehicles (EVs) have played a significant role in human society to prevent the deterioration of the environment. Meanwhile, the research on lithium-ion batteries (LIBs) in EVs improving their performances, including energy density and cycle life, has recently attracted much attention, aiding the further development of the functions of EVs. This research can be divided into three parts. Firstly, the fundamental of LIBs is presented, including its theory and reasons for having low energy density. Then, the alternative Li-S battery technology employed for EVs is introduced, and its advantages and limitations for future research are illustrated. Lastly, the three main approaches for recycling used LIBs, pyrometallurgical recovery (Pyro.), hydrometallurgical metals reclamation (Hydro.) and direct recycling (Dir.) are elaborated, each of their strengths and weaknesses are shown, and their performances are compared by considering several aspects for selection.

Keywords: Lithium-Ion Battery, Battery Recycling, Electric Vehicles.

1. Introduction

With the development of human technology in recent years and the exhaustion of non-renewable energies, electric vehicles (EVs) are particularly popular all over the world in solving these challenges. This is mainly because they are powered by electricity, converted from renewable resources (wind, solar, hydrogen) or non-renewable resources (coals, crude oils) instead of using fossil fuels directly. For the storage of electric energy in EVs, various emerging technologies for batteries, ultracapacitors and fuel cells have been employed, one of the most widely used devices is lithium-ion batteries (LIBs) [1]. They have relatively higher specific energy (200–250 Wh/kg) [2], and their chemical compositions can also vary accordingly to satisfy different requirements and designs [3], such as lithium cobalt oxide (LCO), lithium iron phosphate (LFP) and lithium nickel–manganese–cobalt oxide (NMC) which are employed for EVs [3]. However, LIBs still have some room for development in several fields, including increasing the energy densities and anode capacities, developing the safety level and cycle life, decreasing the charging time, and other performances [4].

The recycling treatment and the cycle life of LIBs are one of the main issues facing LIB technology. It was predicted that the considerable growth of the sales of EVs in the global market is likely to cause an exponential rise in the accumulated end-of-life disposed LIBs in the next decade [5]. Hence, it is of great necessity to find suitable recycling methods that lead to minimum environmental emissions in cost, pollution, and energy usage by regaining the recovered materials from the used LIBs and reusing them

DOI: 10.54254/2755-2721/58/20240695

sustainably after the completion of EVs service life [5]. Furthermore, for the energy density aspect, LIBs have much lower energy densities compared to fuel cells employed in conventional cars or solid-state cells, which means a massive number of LIBs are needed to be packed together and assembled in EVs to provide the same amount of energy for EVs, contributing to a huge increase in mass and rolling resistance. Lithium/sulphur (Li-S) battery is a newly developed technology in recent years. It is investigated to perform better than LIBs because of its higher energy density, broader temperature range while operating, and lower manufacturing cost due to the large availability of sulphur, making it a better choice applying for EVs [1]. Nevertheless, this technology still has some limitations, like self-discharge and capacity fades caused by high discharge current [1]. Hence, its cycle life is relatively shorter, thereby causing this electrochemical system not to be manufactured on a large industrial scale, and further studies needs to be carried out [1]. This also adds to the importance of recycling LIBs.

There are three main recycling approaches for used LIBs: pyrometallurgical recovery (Pyro.), hydrometallurgical metals reclamation (Hydro.) and direct recycling (Dir.) [5]. Each of them has distinct procedures with unique advantages, such as low energy efficiency, high recovery rate, better reliability, and cheaper production costs [5]. Nevertheless, various disadvantages of these methods make the selection among them need to be very careful. Therefore, their performances are thoroughly compared according to aspects such as energy utilization, processing cost, reliability, waste production, and maintainability [5], selecting the most suitable approach.

2. Fundamentals of LIBs

LIBs are the rechargeable energy storage device widely applied in various fields, ranging from small electronic devices like smartphones and earphones to relatively large applications like electric vehicles. The LIBs mainly consist of four parts: anode, cathode, electrolyte, and separator. The anode is generally made of graphite, which acts as the host for lithium ions during cycling. When the batteries are discharged, the lithium ions are formed and extracted from the anode by passing through the electrolyte, generating electric current and releasing electrical energy simultaneously. The cathode is typically made of lithium oxides, which enables the capture or release of lithium ions from or to the anode. The release of energy during discharging and the storage of energy during charging is achieved by various electrochemical reactions. The anode and cathode are separated by a separator, permitting the flow of lithium ions and inhibits the direct contact of two electrodes, thereby preventing the occurrence of short circuits. The electrolyte is usually solid or liquid, allowing the movement of ions between electrodes.

In terms of the reasons for the low energy density of LIBs, which refers to the amount of energy stored in a given weight or volume. Compared to fuel cells and solid-state cells, the choice of electrodes and electrolyte materials limits the energy density of LIBs, like the intrinsic restrictions of how much lithium can be stored inside each cell [6]. Furthermore, to improve the cycle life and durability, reducing energy density acts as a necessary trade-off to satisfy other needs. Additionally, the limited voltage range of LIBs also causes low energy density. The limited voltage range is essential because if it is too high, there are possibilities of safety hazards, which are extremely dangerous in EVs [6]. The electrode thickness is another reason. To allow LIBs to perform better, their internal resistance needs to be as small as possible, leading to the design of thinner electrodes and reducing the battery's energy density. Therefore, it is very significant to develop new alternative battery technologies to improve the low energy density drawback of traditional LIBs.

3. Lithium/sulfer (Li-S) battery

A Li-S battery employs sulphur at the cathode and lithium metal at the anode [1]. During the cycling process, plenty of reactions take place inside the battery. In the discharging state, the lithium metal is oxidized to lithium ions, and the sulphur is gradually reduced to different polysulfides and then to the low-order polysulfides and lithium sulphide [1]. In the charging state, reverse reactions happen with the reduction of lithium ions and the oxidation of lithium sulphide and low-order polysulfides [1]. Figure 1 shows a diagram of a Li-S batterie's structure and the reactions that occur between the sulphur and lithium metal [7]. It can be seen that the number of sulfides in the Li-S battery each time is influenced by state of charge (SOC), and the battery behaves differently from the charging state to the discharging state according to the species inside [1]. Due to the variety and complexity of these electrochemical reactions, most Li-S batteries are made through electrochemical and mathematical (analytical) modes [1]. For instance, one of the best mathematical Li-S battery models involves eight species: Li^+, $S_{8(l)}$, S_8^{-2}, S_6^{-2}, S_4^{-2}, S_2^{-2}, S^{-2} and A^- [8]. Various reactions such as electrochemical reactions, dissolution and precipitation reactions, and multi-component transport in electrolytes occur between these species inside the cell [8], like the oxidation reaction of Li to Li^+ at the anode, the reduction reaction of $S_{8(l)}$ to S_8^{-2} at the cathode, dissolution of sulphur, and precipitation of lithium sulphides [8]. This mathematical model enables the prediction of the discharge of Li-S battery excellently in response to different concentrations of species inside [8].

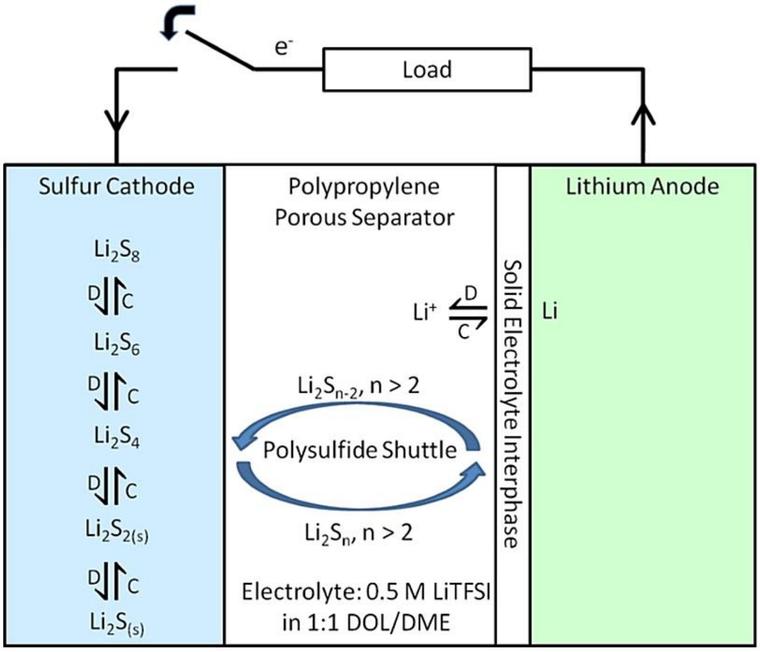

Figure 1. A schematic structure of a Li-S battery [7].

Other techniques, like electrical circuit modelling, can also be applied to Li-S batteries, but only a few research have focused on this technique [1]. In some research, an impedance spectroscopy approach is employed to investigate the properties of Li-S batteries in charging and recharging states [1]. The results obtained from the spectra can be used to determine the parameters of a second-order electrical circuit model, and each of them is expressed as a function of the used capacity [1].

Li-S batteries have several strengths compared to traditional LIBs, like higher energy density and specific energy, lower manufacturing cost due to the large availability of sulphur, better reliability, more comprehensive operating temperature range, and higher safety level [1]. However, they still have some restrictions that hinder them from producing on an industrial scale and commercializing widely. The main limitation is the fade of battery capacities because of cycling and the high current of discharging, which results from the change in compositions on the surface of the lithium cathode and a solid product layer formed on the surface of the sulphur anode during cycling [1]. Since the polysulfide ions are relatively insoluble and the S_8 is relatively insoluble, they tend to remain in the positive electrode of batteries, leading to the shuttling of the Li_2S_2 and Li_2S ions and reducing batteries' cycle life [1]. Self-discharging is also a problem Li-S batteries face [1]. Therefore, more studies related to solving self-discharging and improving their cycle life need to be done in the future [1].

4. Major approaches for recycling LIBs

The recycling of LIBs typically consists of two main processes because of the complexity in assembling the battery packs and the diversity of electrode materials: physical and chemical processes [9]. Figure 2 shows the typical processes for recycling retired LIBs [9]. However, before starting the recycling steps, spent LIBs need to be discharged in the first place since residual energy still exists, which is dangerous and likely to cause fire and explosion during recycling [9]. For the physical processes, they made up of pretreatments, including thermal pretreatment, crushing, magnetic separation, screening, washing [9]. Several methods also allow the electrode materials to be directly obtained from used LIBs without chemical treatment [9]. The chemical processes can be divided into two main parts: Pyro. and Hydro., which include leaching, extraction and chemical precipitation [9].

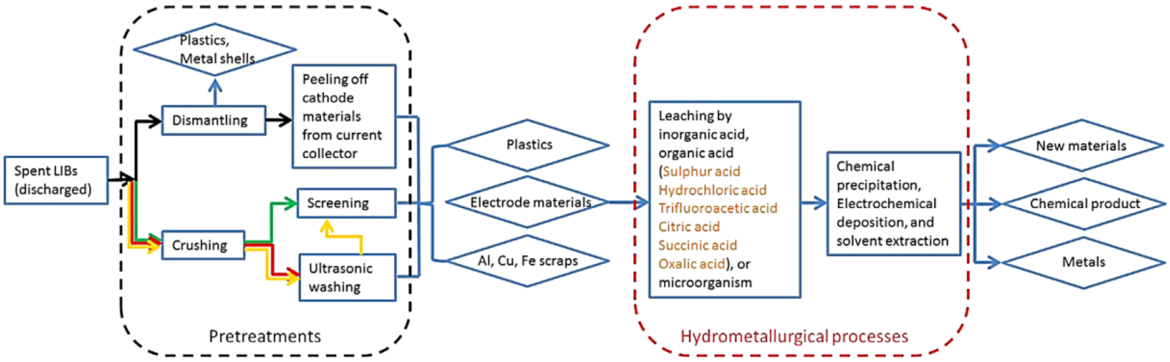

Figure 2. A flowchart of the general processes for recycling used LIBs [9].

4.1. *Pretreatment*

The pretreatment process is mainly done by separating various materials and metallic scraps of LIBs according to their physical properties, like density, magnetism, electric and thermal conductivity [10]. Components in LIBs of similar physical properties can be collected separately by carrying out the pretreatment process. This process has the advantage of helping increase the energy efficiency and recovery rate of recycling in later pyrometallurgical and hydrometallurgical processes [9].

Many studies on pretreatments have been done with a series of combined steps, proving these advantages. For example, a pretreatment process is performed by combing crushing, ultrasonic washing, and precipitation steps [9]. First, a 12 mm aperture screen acts as a prime choice to crush the LIBs [9]. Then, the resulting components are transferred into an ultrasonic washing container, agitating for 15 minutes at room temperature, followed by filtering through a 2 mm screen to separate $LiCoO_2$ in the cathode and crushed current collectors, such as Al foils [9]. The ultrasonic washing step is found to be an alternative approach to reduce the pollution and energy assumption compared to the conventional crushing or thermal pretreatment steps of recycling [9]. The amount of Co obtained from spent LIBs also increases due to the little loss during chemical precipitation, indicating these combined steps can be better employed on an industrial scale [9].

4.2. *Pyrometallurgical recovery (Pyro.)*

Used LIBs are treated similarly to natural ores for the traditional pyrometallurgical recovery process [9]. First, larger battery packs are dismantled into individual cells to be sent into a high-temperature furnace with three temperature zones for smelting: the pre-heating zone, the plastics pyrolizing zone, and the smelting and reducing zone, respectively [9]. After that, the dismantled LIBs are heated below 300 °C in the pre-heating zone to release organic compounds from the electrolyte and avoid explosion [9]. Subsequently, they are sent into the plastic pyrolizing zone with temperature around 700 °C to incinerate the plastic parts, lowering the energy consumed in the next step [9]. In the final smelting and reducing zone, materials and components are smelted, and the metal oxides in the cells are reduced to metal alloys made of Cu, Co, Ni and Fe [9]. A slag with Li, Al, Fe, and Si is also produced [9]. The metal alloys obtained during the pyrometallurgical recovery process can be used as raw materials for battery manufacturing and applied to various fields, like cement processing units [5]. This process has a few advantages: low production costs, simple procedures, and reliable maintenance [9]. Nevertheless, this method only allows elements in the metal alloys to be recovered, which means significant amounts of Co and Li are wasted in the slag, leading to poor economic efficiency due to the high price of Co and the increasingly scarce Li storage [9]. Additionally, greenhouse (dioxins and furans) and toxic gases are exhaled during the burning of plastics and electrolytes, and colossal energy is needed to be consumed to heat the cells at high temperatures, which also causes serious safety hazards because of the cells and reductant contacted [9]. Therefore, alternative methods are developed to increase its economic efficiency and recovery rate.

A selective pyrometallurgical recovery method is investigated with the help of an electric arc furnace [11]. It converts used LIBs to Co alloys and lithium-containing concentrates [11]. The lithium-containing concentrates can then be transformed into Li_2Co_3 through hydrometallurgical metals reclamation [11]. Other metal fractions like Fe-Ni, Al, and Cu can also be separated individually [11]. Although this approach increases the efficiency of recycling used LIBs, it still faces drawbacks like the traditional process [11]. Hence, lowering the environmental hazards, increasing the recovery rates, and decreasing the energy consumption are still of great necessity.

4.3. *Hydrometallurgical metals reclamation (Hydro.)*

Hydrometallurgical metals reclamation is the most widely used way for recycling used LIBs [9]. It consists of many procedures (leaching, solvent extraction, chemical precipitation, electrochemical deposition, etc.) and results in a highly satisfactory recovery rate [9]. For instance, using bioleaching approaches with organic acids, 100% of Cu, 100% of Li, 75% of Al, and 54% of Ni can be recovered [9].

Leaching processes are classified into acid leaching and bioleaching [9]. For acid leaching, inorganic compounds like HCl, H_2SO_4, HNO_3 and organic compounds (citric acid and oxalate acid) filter the materials in the cathode of spent LIBs [9]. The leaching efficiency is affected by a few operational parameters, including temperature, concentration of H^+, time of leaching, and the additives added [9]. For example, Co (III) in the $LiCoO_2$ cathode of LIBs is reduced to Co(II) with H_2SO_4 and H_2O_2, acting as a reducing agent [12]. Since the Co (II) containing compound is readily soluble in aqueous mixtures, Co can be extracted efficiently after subsequent chemical precipitation and solvent extraction treatments [12]. In addition to the strong inorganic acids, with the help of organic acids like oxalic acid, Co can be directly obtained without any reducing agents or further treatment steps [9]. These acid-leaching processes have a higher recovery rate since the components in the $LiCoO_2$ cathode are highly soluble in acids compared with the pyrometallurgical recovery process [9].

In terms of bioleaching, metabolites produced by microorganisms like bacteria and fungi are used to dissolve components of $LiCoO_2$ cathode material and then separate metals out [9]. A type of haploid fungi called Aspergillus niger has been studied recently [9]. It is grown in mesophilic environments like soils or decaying fruits and vegetables, and it produces organic acids (oxalic acid, malic acid and gluconic acid) to donate the hydrogen ions and provide organic ligands, thereby separating Co and Li from $LiCoO_2$ [9]. However, the recovery rate of bioleaching is unstable since living organisms are utilized [9]. For example, it is investigated that the leaching efficiency for Co can drop from 52% to 10%, and for Li, it can drop from 80% to 37% due to the change in pulp density [9].

Regarding the last stage of the hydrometallurgical metal's reclamation process, solvent extraction, chemical precipitation, and electrochemical deposition are the three main ways [9]. In the solvent extraction process, different extractants are used to separate various metals (Co, Li, Cu, Mn and Fe) in the leaching liquor obtained from spent LIBs [9]. Extractants involved in this liquid-liquid extraction process include di-(2-ethylhexyl) phosphoric acid (D2EHPA), trioctylamine (TOA) [9]. The main advantages of this process are low energy disspation, excellent isolation outcomes and simple operation environments [9]. In contrast, it is costly due to consuming large amounts of extractants [9]. Chemical precipitation involves a series of precipitation reactions with the help of precipitation agents to adjust the pH values of the solution after leaching, helping obtain valuable metals [9]. For instance, dissolved

DOI: 10.54254/2755-2721/58/20240695

Li is separated by pumping carbon dioxide gas into the liquor, converting it into lithium carbonate [9]. Chemical precipitation has the advantages of a high recovery rate and low energy consumption [9]. It was investigated that about 80% of Li can be recycled after chemical precipitation [9]. However, due to the difficulties in separating metals from complicated solutions and the low speed of delamination [9], it is not an ideal choice applied to the industry. Regarding electrochemical deposition, metals are separated effectively from the leaching solution directly as pure metal or their hydroxide [9]. For example, the $LiCoO_2$ cathode materials are recycled to obtain Co as $Co(OH)_2$ [9]. The purity of metals separated is exceptionally high, and the recovery rate is also better [9]. In contrast, the energy used is massive [9].

4.4. Direct recycling (Dir.)

The direct recycling process is achieved by recycling materials in used LIBs without any complicated chemical procedures [9]. This process is typically used for $LiMn_2O_4$ cathode in used LIBs [9]. First, LIB packs are discharged and disassembled into individual cells [9]. Then, supercritical CO_2 is used to separate the electrolytes from other parts of the cells by reducing the temperature and pressure [9]. Subsequently, the remaining parts of the cells are crushed and dismantled, followed by separating with physical treatments [9]. In the end, the electrolytes and other components collected from LIB cathodes can be used for the reproduction of LIBs [9]. This process has the strengths of fewer recycling steps, minor environmental damage, and higher energy efficiency and recovery rate [9]. However, LIBs made of recycled materials are more likely to have poor long-term performance than fresh ones [9].

4.5. Comparison of the Pyro., Hydro. and Dir. recycling technologies

The selection of three recycling methods according to their advantages and performance is influenced by several aspects: processing cost, energy utilization, waste production, reliability, maintainability [5]. It is investigated that Pyro. has the highest reliability and maintainability, and the lowest production cost [5]. However, its energy utilization and waste production are the largest [5]. This is opposite to Dir. which has the lowest energy utilization and waste production, but the worst reliability and maintainability, and the highest production cost [5]. The performances of these aspects for Hydro. are between Pyro. and Dir. [5].

In order to obtain a direct conclusion of which method is the best with respect to these aspects, their ratings are converted into quantified data ranging from 0-10, so that different values can be assigned to the three methods [5]. After posting suitable deals, processing these values with mathematical expressions, and weighting them according to the degree of importance for these aspects, the resultant performance code of each approach is finally obtained (Pyro.: 0.5990, Hydro.: 0.6680, Dir.:0.4545) [5]. This means Hydro. has the best performance among them and hence, can be applied to the most expansive fields and various circumstances.

5. Conclusion

EVs have been widely popularized in protecting the natural environment and resources due to the development and application of LIBs, which are considered a crucial constituent to provide electrical energy. However, the use of LIBs still has several issues. Two prominent aspects among them are low energy density and how to recycle after retirement. Li-S battery is a promising rechargeable device developed recently to address their low energy density. It is likely a potential alternative to traditional LIBs because of its higher energy density, lower manufacturing cost and higher safety level. However, the fade of battery capacity and high current of discharging lead to its relatively short cycle life, inhibiting its large-scale prevalence. Hence, further research should be carried out to increase the scale of production and alleviate the pressure of recycling. For their recycling approaches, it is investigated that the performance of Hydro. is better than Pyro. and Dir. by considering various aspects, such as processing cost, energy utilization, waste production, reliability and maintainability.

DOI: 10.54254/2755-2721/58/20240695

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