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Li-ion Batteries Waste Processing and Utilization Progress: A Review

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ABSTRACT: Li ion batteries (LIBs) are widely used as energy storage for electronic devices and electric vehicles. Due to its limited lifetime, its disposal can cause a serious environmental problem. Heavy metals are highly toxic and require serious handling. Moreover, the some of the heave metals are considered valuable to be directly discarded. In this review, LIBs waste processing techniques were discussed. The cathode material which contain high amount of heavy metals can be processed using metallurgical approach, such as: pyro-metallurgy, hydro-metallurgy and bio-metallurgy which have their own advances and disadvantages. The recovery of heavy metals can be performed by bottom-up process such as chemical precipitation, hydrothermal, and sol-gel process. In the end, the recovered valuable metals can be used as precursor to Li-ion batteries materials, thus reducing the exploitation of metals through mining process and reducing hazardous waste.

Keywords: Li-ion batteries waste, metallurgy, cathode, heavy metals.

1. Introduction

A battery is electrochemical cells that consist of an anode, a cathode, current collectors, a separator, liquid electrolyte, container and sealing parts. Due to can convert chemical energy into electrical energy, batteries have employed a common power source for many applications in household and industrial. The battery is classified into two types. There are primary battery and secondary battery (rechargeable). Lead-acid batteries, nickel-cadmium (Ni-Cd) batteries, nickel-metal hydride (NiMH) batteries, and lithium-ion batteries (LIBs) are examples of rechargeable battery. However, some lithium batteries have a higher energy density, higher cell voltage, less memory effect, low self-discharge, and very good cycle life than others [1].

Nowadays, many portable electronics use Lithium ion batteries (LIBs) as electrochemical power sources for example mobile telephones, personal computers, video-cameras and other modern-life appliances. Hence, the demand of LIBs has increased [2][3]. The usage of LIBs is not only for gadgets, but also in the next generation it will be chosen as the first category of dynamic batteries to supply power for electronic automobile [4] due to their great characteristics of light weight, high energy density and great performance[2][3].

The increasing of consumption LIBs can conduce a large quantity of spent LIBs because LIBs only have limited life span (1–3 years) [5]**.** In 2000, LIBs's fabrications reached about 500 million cells. Consequently, the waste of this consumption can be estimated at 200–500 MT [6]**.**

In terms of environmental and health, significant hazard can be generated by spent lithium batteries because they contain reactive materials, organic and inorganic compounds that can burst up at high temperature or can pollute the environment [7]. Therefore, researchers develop many recycling methods of the components of spent cells to be a favorable way to prevent environmental pollution and raw material consumption. The aim of this paper is to review how to recycle and repair the spent LIBs. LIBs contain heavy metals, organic chemicals and plastics in the proportion of 5–20% cobalt, 5–10% nickel, 5–7% lithium, 15% organic chemicals and 7% plastics, the composition varying slightly with different manufacturers [8]. Hazards and pollution in spent LIBs can be caused by the side reactions explained below : [9]

(a) Lithium has a low melting point (180^{o}C), if the metal lithium cells overcharge, molten lithium can be formed. However, this tends to occur in lithium-ion when metal lithium substituted by lithiated carbon materials.

(b) If the temperature of the cell increases, there will be reactions among the organic solutions and the electrode

Table 1. Potential Risk of Spent LiBs [10]

Components	Material	Potential Risk
Cathode Material	$LiCoO_2$	An acute reaction can occur when $LiCoO_2$ meets H_2O, acid or oxidant, and this can degrade into toxic cobalt or lithium-containing oxides
	$LiMn_2O_4$	Toxic gas can be released when this materials meets organic solvents or reductant, and oxygen can be also generated when the material is heated
	$LiNiO_2$	Li_2O, NiO, and O_2 can be generated when the material is heated
Anode Material	Carbon	A mixture of carbon dust and air can explode or burn, generating CO_2 or CO. A strong alkali solution can also be generated, or spontaneous combustion can occur, when inlaid lithium meets H_2O.
Electrolyte	$LiPF_6$	This is a strong corrosive, and can degrade into PF5 when heated, generating HF in the presence of H_2O, and combusting in the presence of P_2O_5
	LiBF4	This is a strong corrosive, and can release HF in the presence of H_2O or acid, or generate Li2O and B2O2 in the presence of combustion or heat.
	$LiClO_4$	This is a strong oxidant, and can combust in the presence of LiCl, O_2, and Cl_2
	$LiAsF_6$	This can dissolve in H2O, and can release HF in the presence of acid.
	$LiCF_3SO_3$	This can combust in the presence of CO, CO2,SO2, and HF, and generate HF in the presence of oxidants or acids.
Electrolyte Solution	PC, EC, DMC, DME, and EMC	This can combust in the presence of CO2 or CO, and can release aldehyde or alkone when heated.
Separator	PP and PE	This can combust in the presence of CO, aldehyde, and organic acid.
Binder	PVDF	This can generate HF when heated.

surface, especially when the solid-electrolyte interface is interrupted. The rising of the cell temperature above 70-100^{o}C will make the interface unstable and decomposes exothermically.

(c) Heat generation and thermal management are the key for secure operation of lithium-ion cells. Table 1 show the potential risks for various component in spent LiBs. Because spent LiBs's retain some of their electrical power, hazards like explosions can occur when their disposal is improper.

Beside the hazards of material contained in spent LiBs, major components of spent cell like copper, cobalt, lithium also include as valuable metals [11]. Table 2 give informations of the metal compositions for a cylindrical lithium cell and for a button lithium cell [12].

Table 2. Quantitative Analysis of Metallic Part of Lithium Cells

Elements	Composition of cylindrical cells of commercial LIBs (wt.% ± 0.2)	Composition of coin cells of LIBs (wt.% ± 0.2)
Li	1.5	1.8
Mn	9.6	16.4
Co	0.1	0.1
Fe	34	41.3
Ni	5.4	3.0
Cr	9.6	9.6
Mo	0.8	0.1

The most part of the batteries is the metallic part since the steel casing that almost represents 50% of the cell mass; the plastic part (external cover, joints, etc.) is evaluated in the range of: 27–40% of the mass [12].

Nowadays, the using of $LiCoO_2$ in LIBs is still dominant even if the cathode materials are quickly emerging [1]. The production of LiBs grow rapidly because of the high consumptions of LiBs [13]. Consequently, the increasing of LiBs's demand will be effect to the increasing mining of natural ores [14], and it leads to resource depletion [15]. Actually, there is still some power in the spent LIBs when the LIBs are disposed and the remaining power is still considerable as resources [1]. Therefore, effective recycling of major components in spent LiBs is required as the right solution to prevent environmental pollution and reduce the use of natural ores [16][17]. This approach will be thoroughly discussed in this review.

2. Recycle's Method

2.1. Pretreatment Processes

During the recycling process, LIBs often burst out because of the radical oxidation that is led by the mechanical shock of lithium metal generated from battery overcharge from exposure to the air [5]. Hence, it is important to implement a premilinary treatment such as physical process of spent LIBs before recycling. Meanwhile, this process can also diminish scrap volume, separate battery components and enrich valuable metals [18].

2.1.1. Mechanical Separation Process

2.1.1.1. Discharging & Dismantling

As same as other electronic waste, mechanical operation like dismantling and separating of spent LIBs will required for further treatment. It is because the metals in LIBs are covered with or encapsulated by plastic or iron shell [1].

There is a discharging pretreatment step to prevent short-circuiting and self-ignition before dismantling the cells [19]. Then, the cell were dismantled using manual procedure to detach their plastic and steel cases. First, the plastic case of spent LIBs were detached using a small knife and a screwdriver. Second, the battery was immersed into liquid nitrogen for 4 min and fixed in a lathe in order to detach the metallic shell that covers it. Such a cryogenic method was employed for safety precautions. Third, the metallic shell was then cut using a saw; the ends of the metallic shell were detached firstly and a longitudinal cut was done in order to access the internal material of the battery which was detached using pliers. Fourth, anode and cathode that uncurled manually were separated and dried for 24 h at 60°C All steps in the experimental procedure were carried out using glasses, gloves and gas masks for safe operation [20].

2.1.2. Crushing & screening

Mechanical treatment like crushing and screening was used to enlarge the efficiency. When the spent LIBs from Laptop employed crushing and screening, the 12 mm aperture screen was excellent to guarantee that $LiCoO_2$ is served in the larger products in minimal amounts, to gain 28% Co and 2% impurities in the recovered electrodes[21].

There was mechanical separation process consisting of a two-step crushing studied by Shin et all. Step one is primary crushing with a sieve of 20 mm size and step two is fine crushing with a sieve of 10 mm size, then both of that step were followed by a hydrometallurgical procedure for lithium and cobalt recovery. Fine crushing is employed to reach a complete elimination of aluminum foil from the lithium cobalt oxide particles although it is not required for the leaching process with a high concentration leaching agent. In order to separate aluminum and copper electrodes, steel casing and plastic packaging, Vibration sieving and magnetic separation were followed. A magnetic separator detached pieces of steel casing after large pieces of the materials were separated. The active material of the cathode which contained in the bulk of non-magnetic particles is generated from the magnetic separator. Fine crushing is used to remove small pieces of aluminum foil attaching to the particles of lithium cobalt oxide. The second vibration sieving separates the pieces of aluminum foil completely [8].

2.1.3. Thermal Treatment

Thermal treatment has several purposes depending on temperature. The binder material PVDF will decomposed at low temperature (<380°C) [22] and oxidation of carbon can be achieved. Decomposition of hazardous solvents could also be the target for temperatures lower than 350°C. The incineration of plastics and solvents or pyrolysis is allowed at higher temperatures if the atmosphere is controlled [23][24][25].

The treatment is employed for safety reasons since the electrolyte is extracted and maybe existing metallic lithium is turned to more stable and safer compounds. Moreover the treatment sustain a great separability of the active materials from the electrode foils by the decomposition of the binder [26].

Thermal treatment such as incinerating and pyrolysis can be used to eliminate the undesired materials. Fouad et al. [27] presented that in order to burn binder and organic additives, the cathode part separated by shredding could be heated at 150–500°C for 1 hr. Then, the unclean cathode material could be incinerated at 700–900°Cfor 1 hr to eliminate carbon and residual unburned organics if present. $LiCoO_2$ was separated to be recycled during the process.

Sun and Qiu [28] developed a novel process involving vacuum pyrolysis and hydrometallurgical technique for the combined recovery of cobalt and lithium from spent LIBs. Pyrolysis process would make the organic materials (including electrolyte and binder) were evaporated or decomposed to low molecular weight products. Hence, most of the cathodic active materials could not bind aluminium foil heavily and could be separated easily. The results of the research using vacuum pyrolysis technique presented that the cathode powder composing of $LiCoO_2$ and CoO indicate complete removal from aluminum foils under the following experimental conditions: temperature of 600℃, vacuum evaporation time of 30 min, and residual gas pressure of 1.0 kPa.

Nevertheless, it often had a drawback on the following chemical leaching process. For example Shin et al. [8] investigated that incineration of lithium cobalt oxide particles at 900℃ for 1 h to eliminate carbon and organic binder before chemical leaching significantly lead the leaching efficiency lower.

2.2. Secondary Treatment

During physical process, only few cathode material or anode material can be peeled. Most cathode material or anode material is still attached to the foil since the electrodes in the spent LIBs consists of electron-conducting carbon, binder and Al current collector. Therefore, there are many alternatives processes have been tested to separate $LiCoO_2$ from Al foil and recovery valuable components. Figure 7 illustrates the systematic secondary treatment process of the spent LIBs that Cu foil and Al foil can be extracted for Cu or Cu solution, Al or Al solution, Li solution, Co solution, and C [1].

2.2.1. Ultrasonic Treatment

Ultrasonic treatment was attested to be effective to helpfully separate the cathode material from the Al foil [20][29][30]. The use of agitation alone will make the electrode materials still stuck to the foils. Then, using ultrasonic washing alone will make only part of the electrode materials could be eliminated. However, when the agitation and the ultrasonic washing were used simultaneously, nearly all electrode materials could be separated from Al foil. Hence, ultrasonic treatment is often regarded as assisting way[21]. Li et all studied about the leaching of Co and Li from spent $LiCoO_2$ with the assistance of ultrasonic agitation and the increased leaching efficiency was mainly ascribed to the unique cavitation action of ultrasonic waves. Because of the cavitation action of ultrasonic, the dissociation of H^+ and chelating with Co^{2+} is supremely fast. Consequently, with the ultrasonic-assisted technology and citric acid, more than 96% Co and 98% Li obtained in the spent LIBs were leached at relatively low temperature in a short time. The application of ultrasonic agitation advanced the leaching efficiency of both metals[31].

Temperature also influenced the processing efficiency. Applying ultrasonic washing and agitation at 55℃, 92% of the electrodes was eliminated, but the elimination ratio mitigated to 76% at 85℃, and the electrodes could not be completely separated from the Al foils (Fig. 4a). This is mainly because at higher temperatures the force lead by the collapse of the ultrasonic cavitation bubble is relatively small, and it cannot completely ruin the binding agent between electrode materials and Al foils [21].

The cavitation effect of the ultrasonic wave can produce greater pressure to ruin insoluble substances and distribute them in the water. The flushing effect agitation then facilitates the process of separating electrode materials from Al foils[21]. The products can be obtained after crushing and ultrasonic treatment [20].

2.2.2. Dissolution process

The dissolution process proposes a larger efficiency in the recovery of valuable components of spent batteries. The adhesion of the PVDF that holds the active materials (anode and cathode) to the current collectors would weakened by this process. However, the right organic solvent influence the dissolving of the polyvinylidene fluoride (PVDF) or the polytetrafluoroethylene (PTFE) to support a successful dissolution process. N, N-dimethylformamide (DMF), N, Ndimethylacetamide (DMAC) and N-methylpyrrolidone (NMP) can used as organic solvents for separation of active materials from cathodes. All reagents can employed without any further purification[32].

Contestabile et al. [21] studied recycling process of spent LIBS in a laboratory scale. They used N-methylpyrrolidone (NMP) to dissolve PVDF in the spent LIBs recycling since NMP is a good solvent (solubility around 200 g/kg of solvent) for PVDF, i.e. for the binder used to hold the electrode films on the substrate, and that its boiling point is high (about 200°C). The experiment using NMP was treated at 100℃for 1 hour and recovery of both copper and aluminum in their metallic form was obtained [5].

Li et al. also investigated the separation of the electrode materials from the current collector using ultrasonic vibration then treated using NMP at 40°C for 15 min to set free the active materials from current collectors [30]. Chen and Zhou also performed that the cathodes foils were immersed in NMP in an ultrasonic washing container as assist for 30 min at 80 ℃ (ultrasonic frequency of 40 Hz at 100 W) then calcined at 800 °C for 2 h to eliminate carbon, binder, and other impurities[33].

Zhou et al. presented the experiment about the solubility of PVDF in DMF, DMAC and NMP tested at different temperature to determine the optimal operating condition for recovering $LiCoO_2$ from cathodes by dissolution method. The result of the experiment can be seen in figure 4. The author chose DMF as the decent solvent because of the solubility and costs. In this experiment, cathodes are immersed into DMF for 2h at 60℃ because of the low boiling point of DMF and the results showed that solubility of DMF for PVDF could reach 176g/L at 60℃[32].

2.3. Acid Leaching

Leaching is a common technique of recycling. This process will extract one or more solutes from a solid using a liquid solvent. Both phase get into close contact and the solute or solutes used can diffuse from the solid to the liquid phase, causing to a separation of the original components of the solid[34]. H_2SO_4 [35][36], HCl [37][5] and HNO_3 [12][38] usually utilize as leaching agents for $LiCoO_2$ leaching process.

Zhang et al. presented a study of various leachates to leach the $LiCoO_2$ such as sulfurous acid, hydroxylamine hydrochloride and hydrochloric acid. Hydrochloric acid offer the optimum performance among the three leachates tested. The high efficiency used 4 M HCI solution at 80 °C for 1 hour, and could be obtained more than 99% of cobalt and lithium [37]. Subsequently, hydrochloric acid was applied for the leaching of lithium and cobalt by other researchers such as Contestabile et al.[5].

Castillo et al. used nitric acid compared to hydrochloric acid in the lithium leaching processes. The results showed that dissolution in hydrochloric acid, even for very small concentrations (typically 0.1 mol/L), only can recovered 80% lithium after 2 h. When using nitric acid under the same time conditions with concentration is ranging between 1 and 2 mol/L, it approximately recovered 100% lithium [12].

A new procedure for the nitric acid leaching of $LiCoO_2$ from lithium-ion batteries was submitted by Lee and Rhee i.e. reductive leaching of the cathodic active material with H_2O_2 addition in a nitric acid[6]. Kim et al. proposed a leaching process using sulfuric acid to recover lithium and cobalt. The effects of the leaching agent, particle size and incineration during acid leaching were tested in order to obtain the optimum condition for metal recovery[39]. Kang et al. performed reductive acid leaching process of the fine fraction (36.4% −16 mesh) that contains most of the cobalt as $LiCoO_2$ for 1 h at 60 °C with 2 M H_2SO_4 and 6 vol.% of H_2O_2 recovered 98% cobalt and 97% lithium [40]. Jha et al. developed the experiments were carried out to optimize the process parameters for the recovery of lithium and cobalt by varying the concentration of leachant, pulp density, reductant volume and temperature. The optimum conditions of leaching used 2 M sulfuric acid with the addition of 5% H_2O_2 (v/v) at a pulp density of 100 g/L and 75 ^{o}C for 1 hour resulted in the recovery of 99.1% lithium and 70.0% cobalt. H_2O_2 in sulfuric acid solution represents as an effective reducing agent, which enlarge the percentage leaching of metals [19].

Wang et al. investigated a novel recovery process with various concentrastions of HCL and the optimum leaching conditions are chosen to be 4 M HCL concentration, 80 °C leaching temperature, 1 hour leaching time and 0.02 gml^{-1} solid-to-liquid ratio, as a result 99.5% Co, 99.9% Li, 99.8% Ni and 99.8% Mn in the mixture are readily leached out[21].

The procedure includes the mechanical separation of lithium cobalt oxide particles, can be applicable in the commercial recycling of lithium-ion battery waste. Li et al. utilized citric acid and hydrogen peroxide ($C_6H_8O_7.H_2O$ and H_2O_2) as leaching reagents to investigate reaction conditions. Co and Li were recovered from the leaching solutions as their respective citrates. More than 90% Co and nearly 100% Li were obtained experimentally by varying the concentrations of leachate, time and temperature of the reaction as well as the starting solid-to-liquid ratio[41].

Sun and Qiu used organic oxalate as leachant and precipitant to leach and precipitate with $LiCoO_2$. The efficiency of $LiCoO_2$ was increasing by the increasing of the concentration of oxalate, the reaction temperature and time, however the influence of H_2O_2 added was found to be not significant for the metal reaction conditions. The highest reaction efficiency of 98% of $LiCoO_2$ was achieved under the optimum conditions. Wang 2012 developed reductive leaching process using H_2SO_4 and $Na_2S_2O_3$ as leaching agent and reducing agent. The best condition in this study scope was 3 mol/L H_2SO_4, 15: 1 of liquid/solid, 0.25 mol/L $Na_2S_2O_3$ at temperature 90 ℃ for 3 h, indicated that the recycling rates of Co and Li are 99.95% and 99.71% respectively [42].

Nayl et al. performed a procedure for dissolving and recovery Al, Cu, Mn, Co, Ni, and Li served in the powder obtained from crushing, and mixing of different spent LIBs. The conditions of leaching were 4.0 M NH_4OH with a L/S mass ratio of 15/1 at 60 °Cfor 60 min, then the recovery efficiency were 97.8% Al and 64.7%. Subsequently, about 97.8% Mn, 99.4% Ni, 99.6% Co, and 98.8% Li have been leached from the alkali residue of spent LIBs using 2.0 M H_2SO_4 with 4.0% H_2O_2 at 70^{o}C for 120 min with a L/S mass ratio of 10/1[43].

Li et al. developed the leaching of Co and Li from spent $LiCoO_2$ with the assistance of ultrasonic agitation for sulfuric acid, hydrochloric acid and citric acid with the conditions. From the experiment was found that citric acid was more effective and environmentally friendly than H_2SO_4 and HCl inorganic acids in the leaching process. The leaching conditions were 2 M citric acid with 0.55 M H_2O_2, an S/L ratio of 25 g/L at 60 ℃ for 5 hours using ultrasonic power of 90 W then obtained more than 96% Co and nearly 100% Li[31].

Zeng et al. developed recovery process, only combined with oxalic acid leaching and filtering. The results from theory and experiments showing that $LiCoO_2$ can be leached utilizing oxalic acid without an assistance from hydrogen peroxide solution. The recovery efficiency of lithium and cobalt from spent LIBs can reach about 98% and 97%, the conditions at 150 min, 95 °C, 15 g/L solid–liquid ratio, and 400 rpm rotation rate[44].

Joulie et al. studied the leaching of NCA cathode using sulfuric, nitric and hydrochloric acids as leaching solvent. At The optimum leaching conditions have been obtained at 4 mol/L hydrochloric acid, 90 °Ç 18 h with 5% (w/v) solid to liquid ratio. For the cobalt, it has been recovered by oxidative precipitation. The recovery efficiencies of cobalt and nickel are respectively 100% and 99.99%. The purity of cobalt hydroxide and nickel hydroxide are resulted respectively at 90.25 wt.% and 96.36 wt.% [45].

Bertuol et al. investigated the effectiveness of supercritical fluids for the leaching of cobalt contained in spent LIBs which performed with supercritical CO_2 and co-solvents under conventional conditions. In both cases, sulfuric acid and H_2O_2 are used as reagents. Then, to recover the cobalt, the solution obtained from the supercritical leaching is processed using electrowinning. The results of electrowinning using a leach solution achieve a current efficiency of 96% and a deposit with cobalt concentration of 99.5 wt%[46]. Guo et al. (2016) studied the acid leaching process to recycle lithium from anode electrodes of spent LIBs. At leaching temperature of 80^oC, 3 M hydrochloric acid and S/L ratio of 1:50 g/ml for 90 min produced the highest leaching recovery of 99.4 wt% Li[47].

2.4. Bio Leaching

Bioleaching is a process of mineral bio-oxidation utilizing microorganisms as assistance which transforms insoluble metal sulfates into water-soluble metal sulfate [48]. Microorganisms (bacteria and fungi) make numerous physiologically important reactions that allow them to grow and reproduce. The formations of metabolic products such as inorganic and organic acids by microbial activities assist in the leaching of metals from wastes and minerals [49].

Mishra et al. studied bioleaching of metals from spent lithium ion secondary batteries using *Acidithiobacillus ferrooxidans.* The results showed that it is potential to dissolve metals from spent cathode material of LIBs by the use of acidophilic bacteria. These cells are able to grow in the medium containing elemental sulfur and iron as their energy source, and the results showed that a culture of A. ferro oxidans can generate sulfuric acid to leach metals indirectly from the LIBs. It was found that Cobalt was leached faster than lithium. The utilize of Fe(II) ion in the leaching experiments was to multiply the cell growths in the lixiviant: the higher the Fe(II) ion concen tration, the slower the metal dissolution. It was caused by co-precipitation of Fe(III) which formed during the course of the investigation with the metals in the leach residues. Solid/liquid ratio would influenced bacterial activity, found that higher solid/liquid ratios prevented bacterial activity in the process as higher metal concentrations are considered to be toxic for cells.(49) in this experiment using 5 g/L of solid/liquid ratio, cobalt dissolution was about 65% and at 10 g/L it was about 56% [49].

Xin et al. developed the bioleaching mechanism of Co and Li from spent LIBs through a mixed culture of sulfur-oxidizing and iron-oxidizing bacteria. The dissolution of Co and Li from the spent LIBs mainly depended on the non-contact mechanism, but not on the contact mechanism. This experiment used bioacidic dissolution as the bioleaching mechanism of Li in three bioleaching systems; Li displayed the maximum extraction efficiency in the S system due to its having the lowest pH. During bioleaching, the Oxidation–Reduction Potential (ORP) value of the solutions was observed for reflecting the generation of Fe^{3+}/Fe^{2+} and their transformation, the pH value was evaluated for reflecting the balance between the biogenetic sulfuric acid and its consumption, then concentration of Co and Li was assigned for reflecting the bioleaching efficiencies. Nevertheless, the different energy materials would distinguished the dissolution mechanisms. Acid dissolution was the sole mechanism for Co release in the S system, a combined action of acid dissolution and Fe^{2+} mediated reduction accounted for Co release in the S + FeS_2 or FeS_2 system. The maximum leaching efficiencies of this experiment was 90% Co and 80% Li [50].

During spent LIBs recycling process using A. ferrooxidans, wastewater was produced. Yoo et al. treated wastewater biologically then recirculate the treated water in the recycling process. From the treatment, it could be known that the bacteria can maturate in solutions with high metal concentrations such as 8000 g m^{-3} of Cr and 13,000 g m^{-3} of Ni, but the Fe^{2+} oxidation activity of the bacteria is significantly suppressed by Li concentration of 5000 g m^{-3} in a pure 9 K medium. Even though a low Fe oxidation ratio is observed, the pH and Fe concentration respectively decrease to 1.8 and 21,633 g m^{-3} in the case of a 90 vol.% real wastewater solution. This result proposed that wastewater treated by the bacteria can be re-utilized in the recycling process [51].

Horeh et al. also developed the fungal bioleaching of spent mobile phone batteries in laboratory-scale using *Aspergillus niger* through one-step, two-step and spent medium bioleaching. It was indicated that the recovery efficiencies of spent medium bioleaching methods was higher than that in others, obtained 100% Cu, 95% Li, 70% Mn, 65% Al, 45% Co and 38%. In one-step bioleaching methods, 100% Li, 58% Al, 11% Cu and 8% Mn were recovered with Ni and Co having negligible leaching. Using two-step bioleaching methods could recovered 100% Li, 61% Al, 10% Mn, 6% Cu and 1% Co (the amount of leached Ni was negligible). Furthermore, the results also showed that citric acid had an important role in the effectiveness of bioleaching using A. niger, compared with other detected organic acids (gluconic, oxalic and malic acid). The results of FTIR, XRD and FE-SEM analysis of battery powder before and after bioleaching process affirmed that the fungal activities were quite effective.Furthermore, according to the results, citric acid was the major lixiviant among the other determined organic acids produced by the fungus [52].

Because of the slow kinetics of bioleaching, commercial application of this method in metal extraction is relatively limited [49][50]. Therefore it is required different methods to tested, such as improving bacterial cultivation, adhesion of metal-ions, and the addition of tensioactive agents in order to improving bioleaching rates [53]–[55]. Various authors [56]–[59], have presented that the rate of metal dissolution during the bioleaching process can be improved by adding catalytic ions to the solution. Authors such as Hu et al. [60]and Carranza et al. [61], utilized metals such as Ag, Bi, Ru and Hg, as catalysts. So that, It is necessery to utilize metal catalysts which are efficient while being cheap enough to enable application during the bioleaching process on an industrial scale.

Along these lines, Zeng et al., investigated a process ofcopper-catalyzed bioleaching to recycle cobalt in spent lithium-ionbatteries (mainly $LiCoO_2$). The authors investigated the effect of copper ions on the bioleaching of $LiCoO_2$ using Acidithiobacillus ferrooxidans (A.f). They attested that almost all of the cobalt (99.9%) after 6 days turned into the solution in the presence of 0.75 g/l of copper ions, while only 43.1% of cobalt dissolution was obtained after 10 days without the use of copper ions [62].

3. Deep Recovery

In pretreatment stage, only a few metals as Cu and Al can be achieved, but more metals will be transformed into leaching solutions in secondary treatment stage when the cathode material or anode material is leached. Hence, to develop some processes should be necessary so that the leaching solutions can be recovered for Co, Li, Cu, and Al. Based on the latest status, the deep recovery process is summarized in Figure 10. The combining process of solvent extraction, precipitation, electrowinning has been developed for high purity products[1].

3.1 Solvent Extraction

Solvent extraction has been widely used as a method to recover and separate metals from the leach liquor, effluents, and the waste [34]. In order to recovery of metal from waste $LiCoO_2$, solvent extraction is possible thru different routes and using different extractants such as PC-88A [63], D2EHPA [63], and Cyanex 272[35][3].

Swain et al. [64], investigated a hydrometallurgical process (acid leaching, solvent extraction, scrubbing and stripping) for the recovery of a pure and marketable form of cobalt sulfate solution/ salt from the waste produced by the LiB industry. The results can be showed below:

- It was found that the best condition for leaching cobalt from the waste $LiCoO_2$ 2 M H_2SO_4 at 75 °C, pulp density of 100 g/L, and 5 vol% of H_2O_2 for 30 min. Under these conditions, the leaching efficiencies of cobalt and lithium were obtained 93 and 94%, respectively.
- By using a Cyanex 272 concentration of 1.5 M, an initial pH of 5 and an O/A ratio of 1.6 in a single stage, the quantitative recovery of cobalt with a minimum lithium co-extraction was achieved.
- Subsequently, the residue of the cobalt was extracted at a Cyanex 272 concentration of 0.5 M, an initial pH of 5.35 and an O/A ratio of 1 in a single stage.

Lupi et al. [24], performed a hydrometallurgical process to recycle Li-ion and Li-polymer batteries containing both $LiCoO_2$ and $Li\text{-}Co_xNi_{(1x)}O_2$ as cathode materials. The operations used in the process were: cathodic paste leaching, cobalt–nickel separation by solvent extraction with modified Cyanex 272 in kerosene, Co and Ni metal recovery by galvanostatic electrowinning, Co and Ni recovery by potentiostatic electrolysis presented on partially depleted electrolytes. The results were summarized below: The electrowinning process conditions of the metallic Ni was at 250 A/m^2, pH 3–3.2 and temperature process at 50 °C, obtained 87% current efficiency and 2.96 kWh/kg specific energy consumption. Current efficiency of Ni Powder which generated by Potentiostatic electrolysis was changing from 70% to 45%, depend on Ni concentration in the electrolyte. By using a solution containing manganese and $(NH_4)_2SO_4$ at 250 A/m^2, pH 4–4.2 and 50 °C can be achieved 96% current efficiency and 2.8 kWh/kg specific energy consumption for Co. The Co powder, generated in potentiostatic conditions (0.9 V vs. SCE, pH 4, room temperature) emerge mainly appopriate for recycling Co as cobaltite in new batteries.

Kang et al.[40] recommended the system for selective extraction of cobalt from nickel and lithium were 50% saponified 0.4 M Cyanex 272 at optimum equilibrium pH 5.5–6.0, achieved 95–98% Co extraction and ~1% Ni extraction. Extraction and separation of Mn(II), Co(II), Ni(II) andLi(I) from the leach liquor spent LIBs was proposed by Nayl et al.[65]. The Precipitate conditions of Mn(II), Co(II), Ni(II) and Li(I) were at 20% Acorga M5640 in kerosene with agitation for 5 min at 30 °C at equal phase ratio of unity, achieved more than 99% purity.

Chen et al.[66], investigated a combined hydrometallurgical process (selective precipitation and solvent extraction) in order to recover metal values from the leaching liquor of spent LIBs. First, precipitation of nickel used dimethylglyoxime reagent after purification operation. Recycled dimethylglyoxime could be re-utilized as precipitant for nickel and showed similar precipitation performance compared with fresh dimethylglyoxime. After that, the separation of manganese and cobalt was conducted by solvent extraction method using cobalt loaded D2EHPA. Finally, $CoC_2O_4.2H_2O$ and Li_2CO_3 were resulted from precipitation and recovering of cobalt and lithium using ammonium oxalate solution and saturated sodium carbonate solution, respectively. Recovery efficiencies could be achieved as follows: 98.7% Ni; 97.1% Mn, 98.2% Co and 81.0% Li under optimized experimental conditions.

3.2 Chemical precipitation

Compared with solvent extraction method, chemical precipitation has simpler operation and relatively higher recoveries of metals from spent LIBs. This method, employed during recovery and recycling of spent LiBs, utilize precipitation agents in order to precipitate valuable metals in spent LiBs like cobalt [67].

Contestabile et al.[5], studied the treatment and recycling of spent LiBs under laboratory conditions. The process implicated the following stages: classification, trituration and sieving, selective separation of the active materials, lithium cobalt dissolution and cobalt hydroxide precipitation. By addition equivalent volume of a 4 M NaOH solution, the cobalt which dissolved in a chlorhydric solution was recovered as cobalt hydroxide $Co(OH)_2$.

Zhu et al.[68], combined method of acid leaching and chemical precipitation to recover y Co and Li in spent Libs. The component separated from the cathode of LiBs were dissolved in 2 mol/L H_2SO_4 and 2.0% H_2O_2 (volume fraction) solution, then by addition of $(NH_4)_2C_2O_4$, with the conditions 1.2:1.0 molar ratio of ammonium oxalate to Co^{2+}, an initial pH of 2, at 50 °C for 1 h, would be precipitated as $CoC_2O_4{\cdot}2H_2O$ microparticles. After collection of the $CoC_2O_4{\cdot}2H_2O$ product by filtration, the Li_2CO_3 precipitates were achieved by addition of Na_2CO_3 in the rest filtrate, the molar ratio of sodium carbonate to Li^+ is 1.1:1.0, equilibrium pH is 10, lithium-ion concentration is 20 g/L, reaction time is 1 h at 50 °C, and agitation speed is 300 r/min. The results showed that 96.3% of Co (mass fraction) and 87.5% of Li can be dissolved in the solution, 94.7% of Co and 71.0% of Li can be obtained respectively in the form of $CoC_2O_4{\cdot}2H_2O$ and Li_2CO_3.

The precipitate can be obtained by centrifugation or filtration. The benefit of the precipitation reaction is the re-utilize of the material if a appropriate solidifying agent was used. A disadvantage is a possible left solubility of the connection and the soiling of the metal connections which require to employ an additional cleaning step [4].

3.3 Electrocemichal proses

Electrowinning can be employed to extract metal components out of solution and achieved the necessary reduction. In electrowinning, two electrodes are applied to serve energy to the solution and yields oxidation and reduction of ions in the solution. The method need differing reductive and oxidative potentials for the metals present in the solution. Solvent extraction can be employed to separate metals into different solutions thereby allowing for electrochemical deposition to generate very high purity metals [4].

Myoung et al. studied an electrochemical deposition and suitable thermal treatment to set up cobalt oxide from Co (III) of waste LiCoO2 cathodes. Under suitable pH conditions, island-shaped cobalt hydroxide is precipitated on the titanium substrate and heat treatment of the cobalt hydroxide results in the formation of cobalt oxide [69].

Freitas and Garcia investigated the recovering of cobalt from spent cellular telephone Li-ion batteries using electrochemical techniques. In line with X-ray diffraction, the composition of cathodes of spent Li-ion batteries consists of $LiCoO_2$, Co_3O_4, C, and Al. The Co_3O_4 present in the cathode obtains from the transformation of the active material (LiCoO2). In the electrochemical recycling of cobalt, charge efficiency increases with increasing pH. The higher charge efficiency obtained was 96.90% at pH 5.40. The application of the nucleation models to the initial electrodeposition stages indicates that the nuclei grow progressively at pH 5.40 (progressive nucleation). SEM represented a three dimensional nucleus growth. The nucleation process becomes instantaneous (instantaneous nucleation) with the decrease in pH to 2.70. For electrodeposits formed at − 1.00 V the resistant to corrosion increase with the increase of pH. This fact is proved by the decrease in adsorbed hydrogen in electrodeposits. In pH 5.4 the cobalt electrodeposition begins from $Co(OH)_2$. This mechanism does not result in hydrogen inclusion in the electrodeposits [70].

Compared to other hydrometallurgical processes, electrolysis can achieve a highly pure cobalt compound from spent LiBs since it does not introduce other substances and therefore avoid introduction of impurities. However, the disadvantage of this process is consuming too much electricity[4].

4. RENOVATION & RESYNTHESIS ELECTRODE MATERIAL OF SPENT LIBS

Some LIBs can be renovated for reuse again. Re-synthesis of electrode materials from the recycled spent LIBs is developed by many researchers. Some combination technique of renovation & resynthesis electrode materials of spent LiBs will be explained the following.

4.1. Combined Processes of Mechanical, Thermal, Hydrometallurgical and Sol–gel steps

Lee and Ree[38], investigated a combined recycling process involving mechanical, thermal, hydrometallurgical and sol–gel steps to recover cobalt and lithium from spent LiBs and synthesize $LiCoO_2$ from leach liquor as cathodic active materials.

Mechanical and thermal treatment was employed to concentrate the electrode active materials in a powder form, under the conditions: first thermal treatment at 100–500 ^oC for 30 min, high-speed shredding to 5–20 mm, second thermal treatment at 300–500 ^oC for 1 h, vibrating screening, calcination at 700–900 ^oC for 1 h. The results shows that the carbon and binder were incinerated by calcination above 800^o C. Then, acid leaching was carried out to dissolve Co and Li from cathodic active materials. Before leaching, the active material was ground in a ball mill then dried in an oven at 60 ^oC for 48 h. The mean particle size is about 15 μm. Addition of hydrogen peroxide to the nitric acid in leaching would enhanced Co extraction 40–85% and Li extraction 75–85%. The extraction of Co and Li is enhanced with increasing HNO_3 concentration, temperature and the amount of hydrogen peroxide and with decreasing S:L ratio. It was found that the optimum leaching conditions are 1 M HNO_3, 20 g/l initial S:L ratio, 75^{o}C, 1.7 vol.% H_2O_2 and 1 h[38].

Of the many possible processes to produce $LiCoO_2$, the amorphous citrate precursor process (ACP) has been employed to produce powder with a higher surface-area that gave a higher performance. Subsequent to leaching, the molar ratio of Li to Co in the leach liquor is set to 1.1 by adding a fresh $LiNO_3$ solution. In order to prepare a gelatinous precursor in a rotary vacuum dryer at 65°C for 2 h, 1 M citric acid solution at a 100% stoichiometry is added. When the precursor is calcined at 950 °C for 24 h, purely crystalline $LiCoO_2$ is successfully achieved. The particle size and specific surface-area of the resulting crystalline powder were 20 mm and 30 cm^2/g, respectively[38].

Then, the cathodes were prepared with a mixture of $LiCoO_2$, 15 wt.% acetylene black and 5 wt.% binder pasted on an aluminum foil current-collector for electrochemical performance tests. The results indicated that initial charge and discharge capacities of the $LiCoO_2$ powder are 165 and 154 mAh/g, respectively[38].

4.2. Combined Processes of Ultrasonic treatment, Acid dissolution, Precipitation

Li et al. [30] studied separation the electrode materials from the current collector by assisting of ultrasonic vibration. In order to release the active materials from current collectors, the electrode material was immersed in NMP solution at 40°C for 15 min, then filtered them out from the NMP solution. H_2SO_4 and H_2O_2 are selected to dissolve Co and Li from the separated electrode powders, under the conditions 3M H_2SO_4 and 1.5M H_2O_2 at 70°C for 1 h. By addition of a 1M $Na_2C_2O_4$ solution, the 99.5% cobalt that dissolved in the H_2SO_4 and H_2O_2 solution is precipitated as CoC_2O_4 at 50°C. Lithium is left in the surplus filtrate after the elimination of cobalt. The filtrate is concentrated to be about 3 M of Li, and then treated with a saturated Na_2CO_3 solution. The Lithium can be recovered till 94.5% when adding 100% excess saturated Na_2CO_3 solution. The recovered of Li_2CO_3 and CoC_2O_4 are utilized as precursors to prepare $LiCoO_2$. The CoC_2O_4 is baked, and mixed uniformly with a Li/Co molar ratio of 1.05:1 by grinding. $LiCoO_2$ is achieved by heating the mixtures at 600°C for 6 h, grinding, and heating at 900°C for 10 h, successively. The electrochemical perfomance is tested in a coin cell, which consists of a cathode with the composition of 88 wt% $LiCoO_2$, 6 wt% carbon black, and 6 wt% PVDF. The results indicated that the morphologies of the synthesized $LiCoO_2$ particles are close to spherical with particle size of about 10 μ m and its electrochemical perfomance presents a specific capacity of 153 mAh/g and good cycleability at 0.2 °C.

4.3. Hydrothermal method

Kang et al. [71],reported that separation and renovation of LiCoO2 cathode material simultaneously using a single synthetic step by the hydrothermal treatment. $LiCoO_2$ phase can be achieved by the hydrothermal reaction [2][3][8][73][74]. Therefore, the reaction mechanism is fully based on "dissolution–precipitation" mechanism [8][73][74]. The simultaneous separation and renovation of $LiCoO_2$ cathode material was employed in a laboratory-made stainless steel autoclave with two polytetrafluoroethylene (PTFE) vessels. One of the PTFE vessels is adjusted to the pressure vessel of the autoclave and the other is a small PTFE vessel with a lid that has a lot of holes 1 mm in diameter to make the possible exchange of the inside and outside solutions. The spent $LiCoO_2$ electrodes were put in the small PTFE vessel, then the small PTFE vessel was immersed in 5.0 M LiOH solution during the hydrothermal reaction. The conditions of hydrothermal experiment was at 200◦ C for 20 h with an approximate heating rate of 3.0 ◦ C/min and the subsequent isothermal process followed by the cooling process. No external pressure and gas injection were added during the hydrothermal reaction and the pressure in the autoclave is just ascribed to water evaporation at 200 °CThe dark gray colored powder was precipitated on both of the bottom of two PTFE vessels. In order to remove residual LiOH solution, the precipitate in the large PTFE vessel was rinsed several times using doubly distilled water with assisting ultrasonic cleaner, and then dried at 80◦ C for 10 h. The renovated $LiCoO_2$ powders were mixed with 10 wt.% super-P carbon black and 10 wt.% polyvinylidene fluoride (PVDF) binder dissolved in NMP until a slurry was achieved. The estimated properties show the renovated LiCoO2 phase to be proposing as a cathode material for lithium rechargeable batteries eventhough the separation of $LiCoO_2$ is not completely attained. The results of the electrochemical performance for the first discharge capacity was 144.0 mAh/g and the discharge capacity retention was 92.2% after 40 cycles [71].

4.4. Combined Processes of Detachment with NMP, Acid leaching, Electrochemical

Li et al. [74], perfomed a new process for recovering and regenerating lithium cobalt oxide from spent lithium-ion by a combination of detachment with N-methylpyrrolidone (NMP), acid leaching and resynthesis of $LiCoO_2$ using electrochemical deposition technology. After discharging & dismantling, black pastes were separated from the cathode by assisting ultrasonic energy together with NMP. Then cathode active material was achieved by calcination of carbon and residual binder at 800 °C for 2 h. After the calcination process, the resulting $LiCoO_2$ powder was leached at 80 °C for 1 h with 1 M HNO_3 containing 1.0 vol.% H_2O_2 in a reactor, in which the ratio of S:L (Solid: Liquid) was 20 g/L. Synthesis of $LiCoO_2$ films was presented in a hermetically sealed 80 ml polytetrafluoroethylene vessel. The electrochemical deposition experiments were employed with a nickel plate as the anode and platinum as cathode. The electrolyte was an alkaline solution consist of 20 ml leaching liquor which pH was adjusted to 11 with 30 ml LiOH solution. During the electrolysis process, the current was preserved at 1.0 mA/cm^2, the temperature was 100 °C for 20 h. After that, the $LiCoO_2$ samples were rinsed with doubly distilled water, then dried at 80 °C for 24 h. Electrochemical properties of the samples were tested in CR2025 coin type cells. The results showed that the initial charge and discharge capacity were 130.8 and 127.2 mAh/g, respectively, and the capacity had decreased by less than 4% compared with the first cycle after 30 cycles. The particle size and layer thickness of the regenerated $LiCoO_2$ crystalline powder were 0.5 μm and 0.2 mm.

4.5. Combined Processes of Vacuum-assisted Heat-treating and Solid state reaction

Lu et al. [75] developed a simple process combination of vacuum-assisted heat-treating and solid state reaction to re-synthesize $LiCoO_2$ from spent lithium ion batteries. For discharging, the spent batteries were placed into a 1 wt.% NaCl solution, then the discharged batteries was heat-treated at 600 °Cin vacuum condition for 3 hours to eliminate the organic solvent and carbonize the binder. After that, the battery was cut, ground and sieved to separate the metallic composite and powder. The powder that mainly contains cathode and anode active materials then heat-treated at 800°C to eliminate the carbon and the final obtained product (denoted as Co-A) was evaluated by atomic absorb spectroscopy to analyze the contents of Co and Li. The $LiCoO_2$ was synthesized by direct reaction of the recycled Co_3O_4 and Li_2CO_3 with Li:Co=1.05:1, then the reactants were mixed in ball-mill for 2 hrs. After that the mixture was sintered at 750 °Cfor 15 hrs to produce the LiCoO 2 (denoted as LCO). The slurry of

$LiCoO_2$ as cathode material was processed by ball-milling a mixture of 10 wt.% Super P (TIMCAL) carbon as conductive regent, 80 wt.% $LiCoO_2$ as active materials and 10 wt.% PVdF as binder with an adequate amount of N-methyl-2-pyrrolidone (NMP) solvent for 2 hrs. The $LiCoO_2$ slurry was coated onto Al foil with an area of 1 cm^2, then the electrodes were dried at 100 °C under vacuum for more than 10 hrs to obtain an electrode. The re-synthesized $LiCoO_2$ indicates a reversible capacity of 106.8 mAh/g and nearly no capacity degradation after 20 charge/discharge cycles.

4.6. Combined Processes of Ultrasound-assisted Hydrothermal

Zhang et al. [76], investigated renovation of $LiCoO_2$ using Ultrasound-assisted Hydrothermal. After dismantling and physically separating of Spent LiBs into their different parts, the cathode plates were put into muffle and heated at 500 ºC for 60 min to separate $LiCoO_2$ powder from aluminum foil. $LiCoO_2$ powder at 10 g was put in a beaker and then 2.0 mol/L of LiOH solution was added to make 600 mL of mixed solution, and was renovated by way of ultrasound radiation under hydrothermal method in a concentrated LiOH solution at temperature 80 ºC, ultrasonic power 600 W, ultrasonic method “work 5s-stop 2s”, ultrasonic radiation for 6 h and then cooled to room temperature. Ultrasonic wave can make cavitation effect and acceleration effect in liquid to increase the probability of stripping of PVDF from the surface of $LiCoO_2$. The ultrasonic shearing effects also encouraged the mass transfer process of Li^+, and consequently the average content of Li^+ from the spent $LiCoO_2$ was enhanced. The residue was rinsed several times with deionized water and dried at 80 °C until constant weight. The achieved sample was collected for next testing. In order to electrochemical performance tests, renovated $LiCoO_2$ was assembled into button battery. The charge capacity in the first cycle is 134.2mAh/g and the discharge capacity is 133.5mAh/g, and the discharge capacity is still 132.9mAh/g after 40 cycles.

4.7. Carbothermal reduction process

Bian et al.[77], demonstrated a novel process to recycle spent LiFePO4 for synthesizing LiFePO 4 /C hierarchical microflowers. After dismantling and separating operations, the cathodes, anodes, separator and other components could be separated respectively. Particularly, elimination of aluminum foil from $LiFePO_4$ cathode materials was in a way by immersing the cathode in NaOH aqueous solution (10 mol/L) with ultrasound-assistance. The aluminum foil could be recovered in its metallic form and the spent $LiFePO_4$ materials were collected through filtering, washing sequentially with deionized water and ethanol, and drying at 80℃ in air. LiFePO 4 powder at 1 g was dissolved into 40 mL, 0.5 mol/L phosphoric acid (H_3PO_4) solution in a beaker at room temperature with continuous stirring for 1 h. Afterwards, the acid leaching solution was filtered to eliminate impurities such as carbon powder,polymeric substance and others, and a transparent solution was achieved. The transparent solution was then refluxed for 9 h at 85℃in a 250 mL three-necked flask with a vapor condenser and $FePO_4.2H_2O$ precipitates were generated. The precipitate was collected by filtering, washing several times with distilled water and ethanol respectively, and drying at 80℃in air.

Generating of $LiFePO_4$ /C samples were via a carbothermal reduction method using the recovered $FePO_4.2H_2O$ hierarchical microflowers as precursors. The mixture of $FePO_4.2H_2O$ and Li_2CO_3 (molar ratio of 1:1.05) was initially dispersed into distilled water, then glucose in a 20:100 weight ratio to $LiFePO_4$ product was also added to the suspension with forceful stirring to form a uniform slurry. In order to make dry mixture, the slurry was heated at 80℃ sequentially it was milled in mortar and heated at 350°C for 4 h and at 650°C for 9 h in a tube furnace in N_2 atmosphere which heating rate is 5°C min^{-1}. The product was called as Re-synthesized LFP. It can be observed that Re-synthesized LFP sample presents a discharge capacity of 159.3 mAh/g at a low rate of 0.1 C, corresponding to 93.7 % of the theoretical capacity of $LiFePO_4$, and eventhough the current density is enhanced to 20 C, it can present a discharge capacity of 89.33 mAh/g and has high discharge platform too, showing that Re-synthesized LFP is appropriate for cathode materials of high-power lithium batteries[77].

4.8. Using an Aqueous Pulsed Discharge Plasma

Zhu et al.[78], developed that renovation of Lithium Cobalt Oxide from Spent LiBs by an Aqueous Pulsed Discharge Plasma in a laboratory-made plexiglas cylinder. The reactor has dimensions of ϕ60 mm×130 mm and was fitted with an needle-plate reactor and a positive needle electrode (see Fig. 2). The positive needle electrode was consist of five stainless steel acupuncture needles (ϕ0.30 mm×75 mm, Hefei medical instruments Co., Ltd.), which were placed approximately 1.5 cm above the bottom of the reactor, and were associated with five microtubes. Since the gas bubbled by way of the microtubes into the reactor, the gas surrounded the needle tip and formed gas bubbles to homogenize the solution with ultrasonic effect from shock waves in a pulsed discharge to stabilize $LiCoO_2$ suspension.

The spent $LiCoO_2$ cathode material was soaked in 0.1 M LiOH solution for 30 min. Afterwards the renovated $LiCoO_2$ in the reactor was filtered and rinsed three times using doubly distilled water to eliminate residual LiOH solution, and dried at 80 °C for 8h. The renovated $LiCoO_2$ was made as cathode then assembled into button battery. The cycling test (at 5/C rate) indicated that the initial discharge capacity and capacity retention after 50 cycles are 131.9 mAh g-1 and 97.2 %, respectively[78].

4.9. Combined Processes of Green recycling and Solid state reaction

Nie et al.[79], presented a green and efficient recycling process to recycle spent $LiCoO_2$ batteries. It is different from the conventional recycling processes. During the recycling process, only the binder (PVDF) and conductive carbon (acetylene black) are eliminated, the structure of recycled $LiCoO_2$ is not destroyed then the obtained $LiCoO_2$ is produced by solid state synthesis with Li_2CO_3. The spent batteries were immersed in Na_2SO_4 saturated solution with iron powders for 24 h, totally discharged by electrolyzing water and short circuit, and then dismantled in a sealed glove box. The electrolyte waste gas in sealed box was liberated to air after three-stage spray purification with DMF, dilute alkaline solution and water in turn, and the electrolyte liquid remaining in the dismantled batteries was extracted and collected by centrifuging. After manual separation, washing and drying, the clean diaphragms and batteries outer shells were directly recycled, the clean cathodes and anodes required to be further demolished. In order to eliminate PVDF, the cathodes were calcined in air at 400 °C for 1 h, and the powders were separated from Al foils after sieving (50 mesh screen). The Al foils were recycled after further washing. After ball-milling and sieving (400 mesh screen), the cathode powder required to be further calcined in air at 800 °C for 2 h in order to eliminate acetylene black. The C, Li and Co mass contained in the cathode powders were respectively 0.3 %, 6.4 % and 59.2 % (ICP), and the molar ratio of Li/Co was 0.92 after calculating. In accordance with the data, 100 g cathode powders were mixed with additional Li_2CO_3 powders (molar ratio of Li/Co was 1.05:1), calcined in air at 850-950 °C for 12 h, ball-milled, and sieved (400 mesh screen). Finally, the regenerated $LiCoO_2$ was achieved, then assembled into button battery.

It can be observed that the particle size of regenerated $LiCoO_2$ is in the range of 5-20 and after regeneration at 900 °C, the discharge capacity could attain about 152.4 mAh/g (commercial $LiCoO_2$:140-155 mAh/g , coin cell) and the attenuation rate of capacity during every cycle is only 0.0313 mAh/g.

4.10. Solid Phase Sintering Method

Song et al.[80] proposed a direct regeneration of cathode materials from spent $LiFePO_4$ batteries using a solid phase sintering method. Firstly, the spent battery is dismantled to separate the cathode and anode plate, then the cathode plate is immersed in DMAC organic solvent to separate the cathode materials and Al foil (the optimal conditions : 30 min at 30 °Cand solid liquid ratio of 1 : 20 g/ml). The solution is filtered to obtain the powder and dried at 60° C for 24 h. The spent $LiFePO_4$ powder was placed in porcelain boat, and quickly put into a tube heating furnace. The furnace was sealed and bubbled into N_2 for 15 min, then adjusting the volume of N_2 until maintaining constant. By solid phase sintering, the spent materials were obtained at different temperatures for 8 h with the heating rate of 5 °C/min. After sintering, the samples were taken out with natural cooling. This experiment investigated high temperature regenerations (600 °C, 700 °C, 800 °C) with doping of new $LiFePO_4$ powder at the ratio of 1:9, 2: 8, 3:7. The result showed that the initial discharge of regenerated $LiFePO_4$ can attain over 120 mAh/g at 0.1 C, particularly with the highest value of 144 mAh/g with a doping ratio of 3 : 7 at 700 °C

5. Conclusion

The development of Li-ion batteries waste processing technology has increased rapidly due to the presence of significant amount of spent Li-ion batteries. The used batteries can be handled by series of metallurgical process. Heavy metals can either be leached directly using acids or indirectly using acids produced by microorganism. The solution obtained from leaching process contain valuable metals that can be recovered through various techniques such as chemical precipitation, electrochemical precipitation, heat treatment and reduction process. The various option can provide similar solution of waste handling. In addition, a close loop process is potentially beneficial since it does not require fresh materials to obtain new cathode materials. Thus, the exploitation of metal from mining process can be reduced which is also important for the sustainability of LIBs technology.

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