

# Comprehensive Review on Concept and Recycling Evolution of Lithium-Ion Batteries (LIBs)

Kishore K. Jena, Akram AlFantazi, and Ahmad T. Mayyas\*



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**ABSTRACT:** Recycling of spent lithium-ion batteries (LIBs) is an emergent research area, which may contribute to a sustainable future with reduced waste. Current recycling strategies only generate recycled compounds rather than functional materials, and most of those strategies deal with cathodes rather than anodes. Developing an effective method to recover Co and Li from the spent LIBs has become a research area of great interest in the past decade and also a challenging job for the industry and researcher. Researchers have studied several methods to recycle valuable metals (Co, Li, Ni, and Mn) from spent lithium-ion batteries. Valuable metals such as cobalt (Co) and lithium (Li) are mainly used to prepare lithium cobalt oxide ( $\text{LiCoO}_2$ ) for applications in LIBs. The increasing demand of the LIBs for electronic devices and electric vehicles has created an additional problem to the initial and exclusive thought of finding good-performing and long-lasting batteries. In this present review, recovery of Co and Li from  $\text{LiCoO}_2$  powders of spent LIBs by a hydrometallurgical process is discussed and summarized to aid researchers and policymakers who are working on this area on the best recycling practices.



## 1. INTRODUCTION

Lithium-ion batteries (LIBs) are widely used in mobile phone, laptops, camera, and more<sup>1</sup> and are expanding their market in the area of rechargeable batteries. Due to excellent features such as small size, high power density, long cycle life, high voltage, and moderate self-discharge, LIBs have captured attention in the last two decades and left behind the nickel metal–hydride and nickel–cadmium rechargeable batteries, which lack such important characteristics needed in rechargeable batteries.<sup>2–5</sup> Limited resources, environmental issues, and strong demand for high energy densities in electric vehicles (EVs) have motivated many entrepreneurs to invest in recovering valuable metals (Co, Li, Ni, Mn) from spent LIBs and recycle them back to produce next-generation rechargeable LIBs and other rechargeable battery technologies (e.g., sodium-ion and lithium–sulfur batteries). The global demand for LIB raw materials and tactics in the resynthesis process along with the wide range of growing applications of spent LIB materials give more attention toward the recycling process.<sup>6</sup>

Cobalt (Co), nickel (Ni), and lithium (Li) are currently the state-of-the-art valuable metals in the cathode layer for most of the commercial LIBs. Different types of cathode-active materials such as  $\text{LiCoO}_2$  (LCO),  $\text{LiNiO}_2$  (LNO),  $\text{LiMn}_2\text{O}_4$  (LMO), and  $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$  (NMC)<sup>7,8</sup> have been recently recognized as significant materials due to the

predicted future market growth of lithium-ion batteries for EVs applications. It was found that Co, Ni, and Li could become critical materials in the near future for several major battery producers in the United States and members of the European Union which have no mining activities for Co and Ni. Recycling of valuable metals (Co, Li, Ni, Mn) from the spent LIBs is proposed as a potential solution to meet the future demand of the key elements in cathode materials. The world's LIBs production reached 2.05 billion in 2005 and 5.86 billion in 2012.<sup>9</sup> In China, the production of LIBs was 4.18 billion in 2012 and increased to 7.84 billion in 2016.<sup>10</sup> The current status and future demand of Co and Li in the market are discussed in this review.<sup>1,11–13</sup> Nowadays, the economics of LIBs recycling may be questionable as they contain only a small fraction of lithium carbonate which is inexpensive compared with Co and Ni, whereas Co and Ni recycling may

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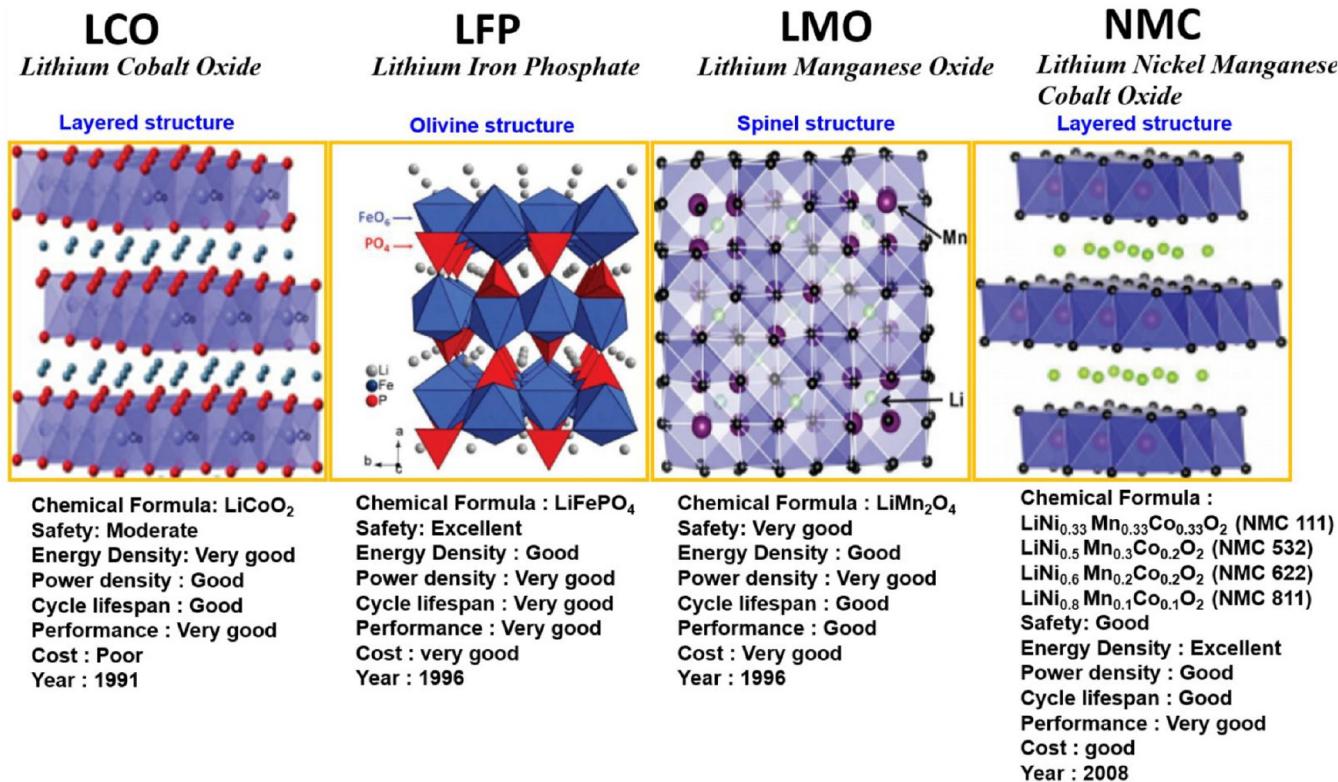


Figure 1. Summary of crystal structure and properties of different LIB cathodes.

be economically attractive. It is predicted that by 2030 the global LIB recycling market will reach \$23.72 billion.<sup>11,14,167</sup>

The materials recovered from the recycling process of spent LIBs give benefits to make new batteries and can lower the manufacturing cost. Recycling LIBs is not straightforward and associated with several challenges before and during the recycling process which can act as economic determinants to the adoption of some recycling processes. Fluctuations in the virgin material prices always put question whether recycling LIBs is a good business choice compared with manufacturing new batteries with virgin materials. Further, the recycling process of LIBs is complicated due to the wide variety of the battery structures and chemistries. In many cases, recyclers have to deal with compact, complex devices and unequal sizes and shapes, and some LIBs are not designed to be disassembled. As an example, in the early 1990s when Sony commercialized LIBs for the first time, researchers have repeatedly modified the cathode-active materials to reduce cost and enhance charging capacity, longevity, recharge time, and other performance parameters.<sup>15,16</sup> The cathode materials such as lithium nickel manganese cobalt oxide (NMC), lithium nickel cobalt aluminum oxide (NCA), and lithium iron phosphate (LFP) are used to improve the storage capacity and reduce the overall manufacturing cost of LIBs.<sup>17–19</sup> In this case, when the cobalt content in g/kWh in the LIBs is very low, recycling in the long term would be done mainly for ecological benefits and for adherence to environmental regulations in some countries.

Different recycling processes and changes in parameters were used to recover the metals from the LIBs. Lv et al.<sup>20</sup> reported a new methodology of advanced oxidation processes (AOPs) to get high concentrations of Li metal from spent LIBs during hydrometallurgical leaching. Li leaching was promoted

by the formation of a sulfate radical ( $\text{SO}_4^{\bullet-}$ ) and a hydroxyl radical ( $\text{HO}^{\bullet}$ ) from persulfate, and a  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  leaching process was prevented. Lin et al.<sup>21</sup> used a green chemistry to achieve a high concentration of Li and Co from spent LIBs. They reported that 99.3% Li and 98.7% Co were recovered from LIBs by using a conventional sulfation roasting process. Li et al.,<sup>22</sup> Fan et al.,<sup>23</sup> Chen et al.,<sup>24</sup> and Zheng et al.<sup>25</sup> used an organic acid leaching process for recycling LIBs. Li et al.<sup>26</sup> reported the leaching mechanism and morphology of a leaching process. Xu<sup>27</sup> reported interphasial chemistry and processes in LIBs. They reviewed about electrolyte components, degradation and stabilization of electrolytes, chemistry of interphase, and advanced characterization and imaging. Fan et al.<sup>11,28</sup> reported sustainable recycling technology for LIBs. Life-cycle assessment, perspectives of strategic resources, and economic demand are discussed to justify the sustainability of the recycling technology. Efficiency, economic return, environmental benefit, safety and new challenges, and future prospects for battery sustainability are also discussed.

In this review, the recycling of LIBs to recover Co, Ni, and Li by using a hydrometallurgy process is discussed. The current status such as leaching efficiency, application, cost, and environmental effect of  $\text{LiCoO}_2$  cathodes in the present recycling technologies of LIBs are discussed in this review. This review mainly deals with the lithium cobalt oxide (LCO) cathode. The limitation of current technologies and a new perspective toward the future concept of LIBs recycling are also pointed out. Possible research opportunities and challenges in recycling process are explained at the end of this review.

## 2. LI-ION BATTERY: TYPES, STRUCTURE, AND DEGRADATION MECHANISM

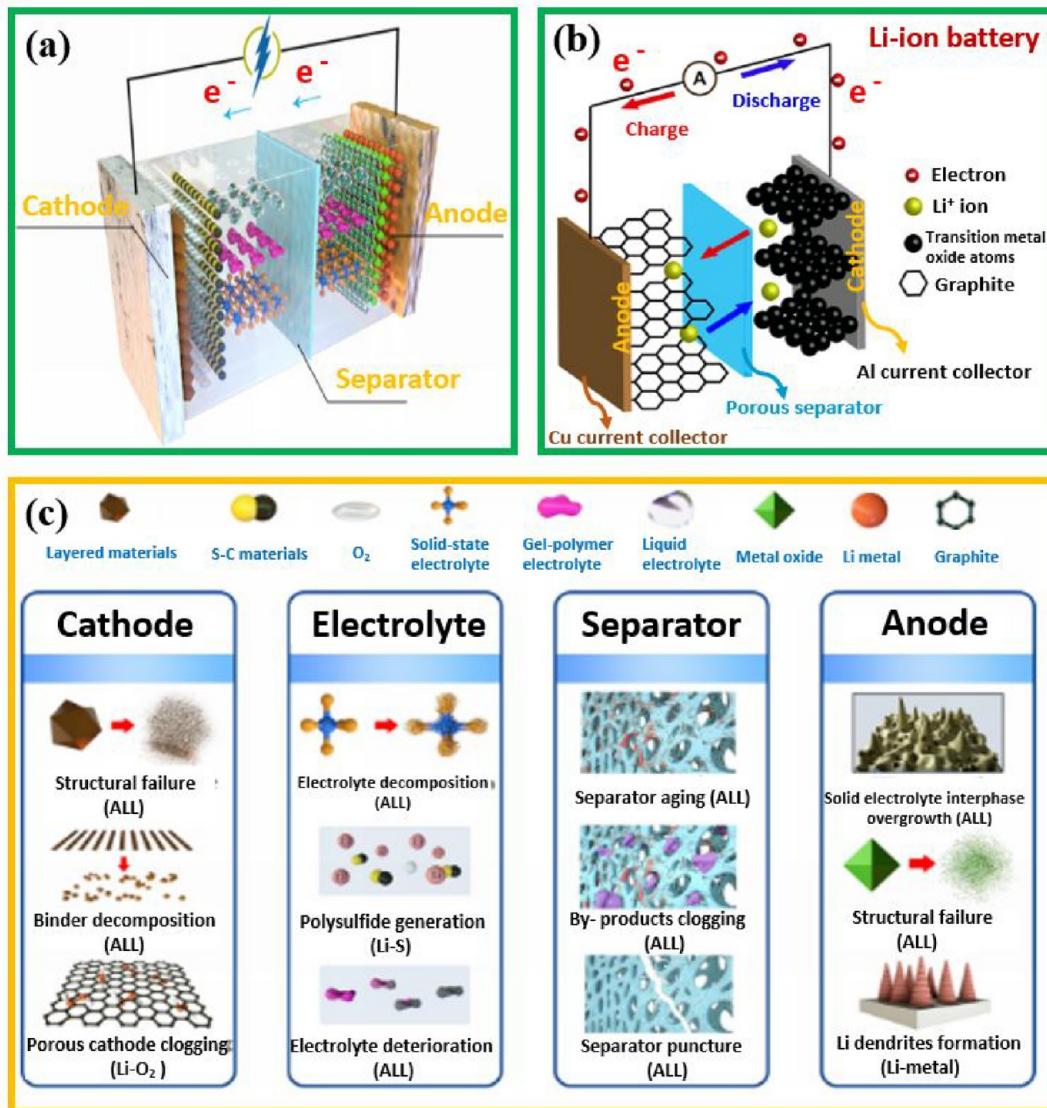
LIBs are rechargeable batteries that store energy through reversible intercalation of lithium ions. It does not involve full redox reactions and thus manages to avoid many of the lifetime and power limiting problems of fully chemical battery mechanisms. The ratio of ionization potential to atomic weight for lithium is higher than that for any other element, resulting in energy densities that will be difficult to match with any other electric storage technologies.<sup>29</sup> The lithium-ion battery is considered a powerful and high efficiency type of battery in comparison with Ni–Cd and Ni–MH batteries due to its high energy and power densities. As a result of these facts, most of the devices such as smart watches, laptops, digital cameras, calculators, and communication equipment have adopted LIBs as a main source for energy storage, with more installation capacity year after year in the last two decades.<sup>30–34</sup> This section explains six of the most common cathode materials of LIBs. Most of the LIBs are constructed with graphite in the anode and different metal oxides in the cathode, which have different chemistries and structures. In the process of charging and discharging, lithium ion can intercalate into and out of layers or tunnel structures. The performance of the LIBs depends on the structure and chemistry of the cathode materials. Figure 1 presents a summary of crystal structures and properties of the most common LIBs cathode. The different types of LIBs and their advantages and disadvantages are reported in Table 1.

**2.1. Types of Lithium-Ion Batteries.** *2.1.1. Lithium Cobalt Oxide ( $\text{LiCoO}_2$ ), LCO.*<sup>35,168</sup> LCO is used in high specific energy batteries which consist of a cobalt oxide cathode and graphite anode and is used in most of the portable electronics such as mobile phones, laptops, and digital cameras. The cathode has a layered metal oxide structure, and lithium ions move from anode to cathode during the discharge mode and reverse flow from cathode to anode during the charging mode. Some common characteristics of the LCO include high charging rate (also called C-rate) which is in the range of 0.7–1C and discharge rate (C-rate) that could reach 1C.

*2.1.2. Lithium Nickel Manganese Cobalt Oxide ( $\text{LiNiMnCoO}_2$ ), NMC.*<sup>38</sup> NMC is the common cathode chemistry in electric vehicles, e-bikes, and electric scooters. Nickel provides high specific energy but poor stability, and manganese has the benefit of forming a spinel structure to achieve low internal resistance but offers a low specific energy. The strength of the lithium nickel manganese cobalt oxide is enhanced by the combination of the individual strength of nickel and manganese metals. One-third mole of nickel, one-third mole of manganese, and one-third mole of cobalt is used to make the NMC cathode, which is also known as 1–1–1 (some researchers also use 333 to refer to this NMC chemistry). Battery manufacturers recently started to change the combination of nickel, manganese, and cobalt to 5–3–2 due to the cost of the cobalt raw material, and the evolution of NMC is expected to go with lesser amounts of cobalt per kWh of storage capacity such as 6–2–2 and 8–1–1 cathode chemistries. The charge rate (C-rate) is 0.7–1C and charges to 4.20 V, with some going to 4.30 with a 3 h charge typical. Charge current above 1C may shorten the battery life. The discharge rate (C-rate) is 1C, with 2C possible on some cells, with a 2.50 V cutoff.

**Table 1. Different Electrode Materials of LIBs and Their Specific Capacities, Advantages, and Disadvantages**

Cathode Materials	Abbreviation	Voltage vs Li/Li <sup>+</sup>	Specific capacity (mAh/g)	Applications	Advantages	Disadvantages
$\text{LiCoO}_2$ ; cathode (~60% Co); LiCoO <sub>2</sub> anode, graphite	LCO	3.9	140	Mobile phones, tablets, laptops, cameras	High performance well understood	Short life span, low thermal stability, limited load capabilities, safety issues
$\text{LiNi}_{0.3}\text{Mn}_{0.3}\text{Co}_{0.3}\text{O}_2$ ; cathode, $\text{LiNiMnCoO}_2$ ; anode, graphite	NMC	3.8	160–170	E-bikes, medical devices, EVs, industrial services as hybrid cells	Better safety and better performance than LCO, high capacity and high power	High cost, nickel and cobalt (expensive and less abundant materials)
$\text{LiFePO}_4$ ; cathode, $\text{LiFePO}_4$ ; anode, graphite	LFP	3.4	170	Portable and stationary, need high load current and endurance	Excellent power, good lifetime and safety, abundant materials	Low energy density, elevated self-discharge
$\text{LiMn}_2\text{O}_4$ ; cathode, $\text{LiMn}_2\text{O}_4$ ; anode, graphite	LMO	4.1	100–120	Power tools, medical devices, electric powertrains	Cheap abundant materials and high power, safer than Li cobalt, high thermal stability, enhanced safety	Short lifetime, low energy density
$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ ; LiNiCoAlO <sub>2</sub> ; cathode (~9% Co); anode, graphite	NCA	3.8	180–200	Medical devices, industrial, electric powertrain (Tesla)	High capacity and voltage, high power densities, good life span	Safety issues, high cost
$\text{Li}_2\text{TiO}_3$ ; LMO or NMC cathode; anode, $\text{Li}_2\text{TiO}_3$ (titannate)	LTO	2.8	50–80 Wh/kg	Electric powertrain (Mitsubishi i-MEV, Honda Fit EV), solar-powered street lighting	Long life, fast charge, wide temperature range, safest Li-ion batteries	Low specific energy and expensive



**Figure 2.** (a) General battery structure. (b) Major components and operating mechanism of lithium-ion batteries (LIBs) (Or et al., reproduced with permission).<sup>42</sup> (c) Degradation mechanisms for rechargeable batteries (Fan et al., reproduced with permission).<sup>11</sup>

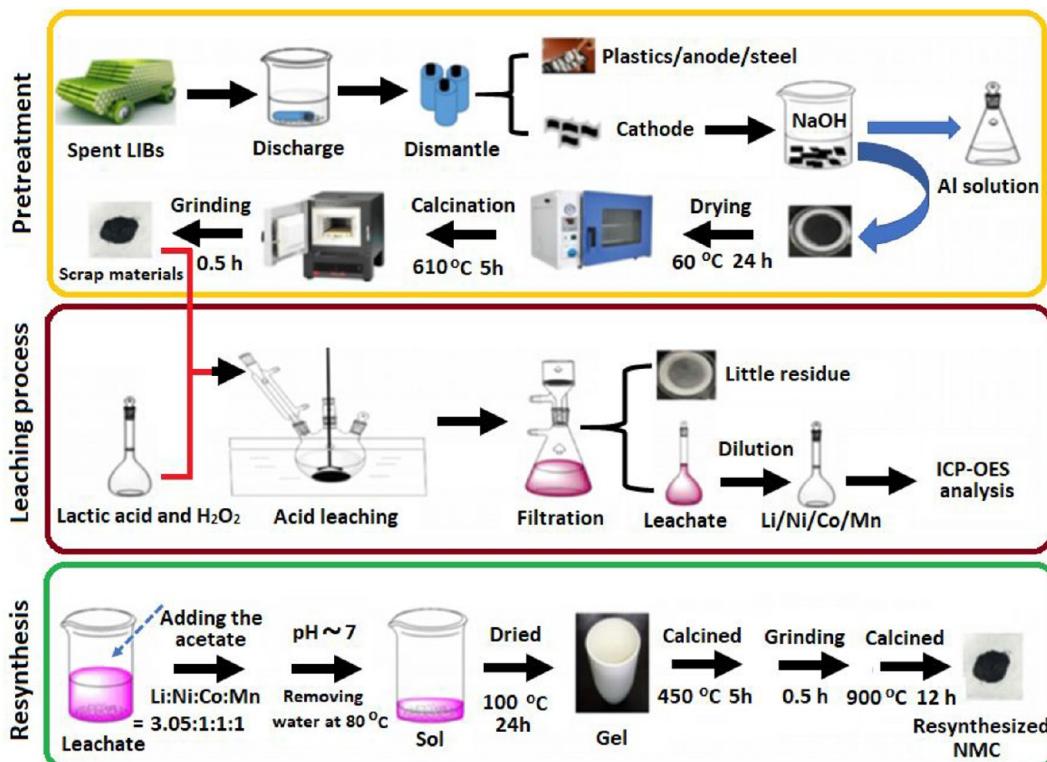
**2.1.3. Lithium Manganese Oxide ( $\text{LiMn}_2\text{O}_4$ ), LMO.**<sup>168</sup> LMO is a three-dimensional spinel structure (cubic close-packed oxides with eight tetrahedral and four octahedral sites per unit) of lithium manganese oxide as the cathode material that improves ion flow on the electrode, which results in lower internal resistance and improved current handling. To improve the specific energy and prolong the life span, most Li-manganese batteries are blended with lithium nickel manganese cobalt oxide (NMC). Most of the electric vehicle companies adopted this LMO and NMC combination for their new generation car development such as the Nissan Leaf, Chevy Volt, and BMW i3. In terms of charging and discharging rates, LMO has a typical C-rate in the range of 0.7–1C, with a maximum C-rate of 3C, and it charges to 4.20 V (most cells). The discharge rate (C-rate) is 1C, with 10C possible with some cells, with a 30C pulse (5s) and 2.50 V cutoff.

**2.1.4. Lithium Iron Phosphate ( $\text{LiFePO}_4$ ), LFP.** Phosphate as a cathode material for rechargeable lithium batteries was first discovered in 1996 by researchers from the University of Texas. Li phosphate offers good electrochemical performance such as a high current rating, long cycle life, good thermal

stability, and enhanced safety with low resistance. Li phosphate has a higher self-discharge than other LIBs. Li phosphate has excellent safety and a long life span but moderate specific energy and elevated self-discharge. A typical C-rate is 1C, and LFP charges to 3.65 V, with a 3 h charge time typical. The discharge rate (C-rate) is 1C, with some LFP cells reported to have 25C, with a 40A pulse (2s) and 2.50 V cutoff (lower than 2 V causes damage).

**2.1.5. Lithium Nickel Cobalt Aluminum Oxide ( $\text{LiNiCoAlO}_2$ ), NCA.** A lithium nickel cobalt aluminum oxide battery (NCA) offers high specific energy, good specific power, and a long-life span. The charge rate (C-rate) is 0.7C and charges to 4.20 V (most cells), with a 3 h charge typical, and fast charge possible with some cells. The discharge rate (C-rate) is 1C typically, with a 3.00 V cutoff; a high discharge rate may shorten the battery life.

**2.1.6. Lithium Titanate ( $\text{Li}_2\text{TiO}_3$ ), LTO.** Li titanate replaces graphite in the anode in the typical lithium-ion battery. The LTO layer forms into a spinel structure. LMO or NMC is used in the cathode, and Li titanate is used in the anode. LTO (commonly  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) has advantages over the conventional



**Figure 3.** Complete flowsheet of the recycling and regeneration process of the cathode-active material of LIBs (Li et al., reproduced with permission).<sup>46</sup>

cobalt-blended Li ion with the graphite anode by attaining zero-strain property, no solid oxide interface film formation, and no lithium plating when fast charging and charging at low temperature. Li titanate has excellent safety, long life span, and good performance at low temperatures. The charge rate (C-rate) is 1C typically, with a 5C maximum, and it charges to 2.85 V. The discharge rate (C-rate) is 10C possible, and it can reach a discharge rate of 30C in the form of 5 s pulses, with a 1.80 V cutoff on LCO/LTO.

Basically, the Li-ion battery compartment is covered with metal and plastic. At the cell level, LIBs consist of several stacked cells with active parts such as the cathode, anode, electrolyte, and separator (Figure 2(a)). The operating mechanism of LIBs is shown in Figure 2(b). The metals such as Co, Mn, Ni, and Li are present in the cathode part of LIBs in the form of metal oxide, such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub>,<sup>8,39</sup> and the anode is graphite or activated carbon. As per reported literature, cobalt, lithium, manganese, and nickel are dominantly available in cathode layers.

Recycling of Li and Co from LIBs is economically attractive and valuable metals for next-generation cathodes. Co is less abundant and more expensive than other transition metals such as Mn and Ni that are used in the cathode layer in the form of a metal oxide. Recycling of cobalt from LIBs is important due to the carcinogenic, mutagenic, and toxic effects to reproduction. Furthermore, recycling of nickel from LIBs is also equally important from health and environmental points of view.<sup>8,40,41</sup> The manganese quantity is negligible, and spot price does not make it one of the high-value materials. The importance of lithium metal has been increased due to the high demand on LIBs in portable electronic devices. The recycling of lithium from spent LIBs is a big advantage in the

development of next-generation electric vehicles since the demand on lithium may surpass the supply if not enough investment in lithium extraction is made in the near future.

Today, recycling of LIBs is an important and major task for recyclers in industry and research institutes, not only because of the battery's short service life but also because of other factors such as environmental concerns and having a potential source to recover expensive valuable materials. The big question is when the battery is considered at its end of the life. First, we need to know that degradation mechanism of the batteries happens because of structural failure and particle cracking, corrosion of the current collector, binder decomposition, dissolution, dendritic formation in both electrode materials (cathode and anode), decomposition and deterioration of the electrolyte and aging, puncture, and clogging of the separator.<sup>11,42</sup> The schematic diagram of the degradation mechanism of the cathode, anode, electrolyte, and separator of a rechargeable battery is shown in Figure 2(c). Many LIBs are considered at the end of their life when their storage capacities faded by 20%–30% of the original storage capacity.<sup>43,44</sup>

### 3. RECYCLING PROCESS OF LI-ION BATTERIES

The recovery of valuable cathode-active materials from spent lithium-ion batteries has been done using four different methods, namely, mechanical process, pyrometallurgy, hydrometallurgy, and direct physical recycling. These methods are used alone or in combination such as in the the pyrometallurgy process which needs a hydrometallurgical means to recover high-value elements such as cobalt and nickel.<sup>12</sup> Out of these four general recycling classes, hydrometallurgy is considered unique and the most effective recycling process due to several advantages it possesses such as being ecofriendly, having low energy consumptions, effective rate of reaction, ability to reuse

**Table 2. Recovered Materials and Advantages and Disadvantages of Different Recycling Processes<sup>43,44,47</sup>**

Recycling methods	Recovered materials	Advantages	Disadvantages	Examples (Companies)
Mechanical process <sup>32,48,49</sup>	$\text{Li}_2\text{CO}_3$	<ul style="list-style-type: none"> <li>1. Applicable to any battery chemistry and configuration.</li> <li>2. Lower energy consumption</li> <li>3. Enhanced leaching efficiency</li> </ul>	<ul style="list-style-type: none"> <li>1. Mechanical process alone not sufficient to recover materials</li> <li>2. Should be combined with hydrometallurgical process</li> </ul>	<ul style="list-style-type: none"> <li>1. SNAM (France)</li> <li>2. Taxco process</li> </ul>
Pyrometallurgy (smelting) <sup>47,50</sup>	Cathode: cobalt nickel copper iron; recoverable from molten alloys, more than 90% Anode: not possible to recover	<ul style="list-style-type: none"> <li>1. Highly effective at recovering nickel, cobalt, copper</li> <li>2. High recycling efficiency</li> <li>3. Ability to remove toxicity</li> <li>4. Potential to scale it for larger scales and simplified logistics</li> <li>5. Already exists at industrial scale and mature metallurgical technique</li> </ul>	<ul style="list-style-type: none"> <li>1. Inherent chemistry of smelter traps, other elements in the slag</li> <li>2. Recovering lithium from the slag expensive and inefficient</li> <li>3. Other chemicals in the battery lost</li> <li>4. Suboptimal from lifecycle perspective</li> <li>5. Energy intensive, toxic gas emissions</li> </ul>	<ul style="list-style-type: none"> <li>1. Accurec (Germany)</li> <li>2. Batrec (Switzerland)</li> <li>3. Umicore (Belgium)</li> <li>4. Nippon Mining and Metals (Japan)</li> </ul>
Hydrometallurgy <sup>50,51</sup>	Cathode: cobalt, lithium, nickel, aluminum, copper, $\text{Li}_2\text{CO}_3$ ; recoverable as salt, more than 95% Anode: destroyed	<ul style="list-style-type: none"> <li>1. Easy recycling and simplified procedures to reuse as battery material</li> <li>2. Almost any material recovered at high efficiency</li> <li>3. Chemistry and procedures fairly mature</li> <li>4. Low emission of gases</li> <li>5. Energy consumption less</li> </ul>	<ul style="list-style-type: none"> <li>1. Environmental and revenue issues in large scale due to use of hot water, acid, solvents</li> <li>2. Source material needs known (e.g., battery chemistry) to tailor efficient process</li> <li>3. Potential revenue and costs that make hydrometallurgy approaches promising are highly dependent on scale</li> <li>4. Retriev Technologies (Canada)</li> </ul>	<ul style="list-style-type: none"> <li>1. Eurodieuze (France)</li> <li>2. G&amp;P Batteries (UK)</li> <li>3. Recupyl (France)</li> <li>4. On To Tech (USA)</li> </ul>
Direct Recycling <sup>52,53</sup>	Almost all components except separators	<ul style="list-style-type: none"> <li>1. Potential recovery of all battery materials in a reusable form</li> <li>2. Higher revenues and lower environmental impacts</li> <li>3. Process not dependent on scale as pyrometallurgy or hydrometallurgy approaches</li> </ul>	<ul style="list-style-type: none"> <li>1. Recently demonstrated at a workable scale and quality</li> <li>2. Process depends on knowing battery composition and battery chemistry</li> <li>3. Old cathode chemistries may not be desired to be reused in new generation LIBs</li> <li>4. Manual approach to breaking the cell and extracting its contents may be difficult to scale</li> </ul>	

some leaching chemicals after filtration and purification, low emission of gases, and high concentration metal recovery. To recover the high concentration of leaching solution (leachate), the nature of the metal and the acid efficiency are the main factors in the recycling process.<sup>45</sup> Li et al.<sup>46</sup> presented a complete flowsheet of the recycling and regeneration process of the cathode material in Figure 3. The advantages and disadvantages of the different recycling process are reported in Table 2.

**3.1. Pretreatments.** The importance of a pretreatment process is to get electrode materials from spent LIBs and then proceed in the subsequent hydrometallurgy process. The lithium-ion battery contains different metals, plastics, and polymers; these should be removed before further processing. The recovery of expensive cobalt metal, which is present in high concentrations in battery cathodes (e.g., LCO and NMC) is really challenging work. Therefore, direct processing without pretreatment may lead to losing high concentration valuable metals. In this section, different pretreatment process such as discharging, mechanical separation, dissolution, ultrasonic washing, and heat-treatment methods are explained.

**3.1.1. Discharging.** The main objective of this process is to reduce the chance of short circuiting and self-ignition of spent LIBs. LIBs should initially be discharged to release any remaining stored energy in the battery. Ku et al.<sup>54</sup> discussed the process of discharging the spent LIBs to less than 0.1 V by using a discharger. He et al.<sup>55</sup> used 5% NaCl solution to discharge the LIBs completely. The duration of discharging batteries is an important factor to speed up the recycling process and proceed to the next step. Shaw-Stewart et al.<sup>56</sup> used different saline and basic solutions and studied the discharge characteristics of fully charged LIBs. Li et al.<sup>57</sup> studied the discharge efficiency by using different concentrations of NaCl solutions and at different discharging times. They observed a 72% discharge efficiency with a 10 wt % NaCl solution in 358 min. Lu et al.<sup>58</sup> studied the effect of different NaCl solution concentration (1%, 5%, and 10%) for discharge of new batteries. At a high concentration of NaCl solution, the cell voltage was dropped significantly. Recently, Li et al.<sup>59</sup> and Ojanen et al.<sup>60</sup> studied the cell discharge phenomenon by using sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) other than NaCl salt. The first work was reported on cell discharge by using sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) salt by Li et al. Ojanen et al. used different salts (NaCl,  $\text{NaSO}_4$ ,  $\text{FeSO}_4$ , and  $\text{ZnSO}_4$ ) as aqueous electrolytes in "electrochemical discharge".

**3.1.2. Mechanical Separation (Dismantling and Separating).** After completely discharging, LIBs are manually dismantled to separate the cathode, anode, organic separator, steel, and plastic from the battery compartment. However, it is very difficult to separate the different parts of LIBs manually, when considering large-scale recycling processes. Therefore, a mechanical process such as crushing, sieving, magnetic separation, and classification may be more economic from cost and effectiveness perspectives.<sup>4,61</sup> Zhang et al.<sup>62</sup> reported a crushing method for pretreatment of spent LIBs. They reported that aluminum foil, copper foil, and plastics were removed as coarse particles from the ground parts and a mixture of fine particles of graphite and  $\text{LiCoO}_2$  electrode materials. Then, this mixture undergoes several steps to recover the high-value elements such as cobalt and lithium.

**3.1.3. Dissolution.** Electrode materials are strongly adhered to copper and aluminum current collector surfaces. The cathode part is prepared with cathode-active materials,

polyvinylidene fluoride (PVDF), and activated carbon; then, the slurry is coated on the aluminum surface. Nowadays, research focuses on separation of cathode-active materials from an Al foil surface by using a simple and efficient dissolution process. N-Methylpyrrolidone (NMP) is usually employed to separate the cathode-active materials from Al foils, which follows the mechanism of "like dissolves like". The polarity of PVDF and NMP plays major role in the dissolution process, where NMP easily dissolves the PVDF polymer and separates the cathode-active materials from the Al foil surface.<sup>63–67</sup> Li et al.<sup>68</sup> reported that the cathode-active materials were easily separated from an aluminum support in a NMP solution in 1 h at 100 °C. An ultrasonic-assisted dissolution process was reported by Yao et al.<sup>69</sup> Initially, they immersed the cathode in a NMP solution for 1 h at 80 °C and then treated it in an ultrasonic bath for 20 min. It was reported that the separating efficiency and yield were significantly improved.

Yang et al.<sup>70</sup> used ultrasonic treatment to separate cathode-active materials from an Al surface at room temperature. Many researchers have used other organic solvents such as *N,N*-dimethylacetamide (DMAc),<sup>25</sup> *N,N*-dimethylformamide (DMF),<sup>71</sup> dimethyl sulfoxide (DMSO),<sup>72</sup> and ionic liquid<sup>73</sup> for the separation of the cathode-active materials. The complete removal of cathode-active materials by a dissolution process is not possible, which needs further processing such as a thermal treatment process (calcination process) to burn off the carbon and PVDF residues. Additionally, for scaled up recycling processes, organic solvent is not suitable due to its high cost and lack of availability as per the polar and nonpolar nature.

**3.1.4. Ultrasonic Washing.** The explosion of small bubbles during ultrasonic washing produces an impact force, which helps remove the cathode-active materials from aluminum foil. In this technique, LIBs are crushed and sieved to smaller sizes then go through ultrasonic washing. This complete process is continued at room temperature in a short duration of time and thus requires low energy consumptions, without noticeable environmental pollutions and with higher levels of operational safety.

**3.1.5. Heat-Treatment Method.** The thermal treatment method is an important process to remove PVDF polymers and carbon black from the cathode-active materials. In this process, the cathode is chopped into small pieces and then treated at high temperature in the furnace to complete the burn off of the carbon and organic polymers.<sup>40,74,75</sup> In this process, high toxic gases and smoke are released due to the combustion of carbon and organic polymers. To avoid the release of toxic gases during thermal treatment, many researchers<sup>76–78</sup> have introduced vacuum pyrolysis for the separation of cathode-active materials. In the pyrolysis process, high molecular weight polymers degrade to low molecular weight products, and then, the adhesion between the cathode materials and Al foil becomes weak, which subsequently helps separate cathode-active materials from Al foil. Yao et al.<sup>77</sup> used a vacuum furnace at 600 °C for 2 h to peel out the cathode-active materials from aluminum foil. Sun et al.<sup>78</sup> extracted cathode materials by a vacuum pyrolysis process in which pressure was maintained at less than 1.0 kPa and the temperature at 600 °C. In this process, volatile gases and noncondensable gases were collected by a condenser and gas collector, respectively. After complete pyrolysis process, metal oxide (lithium cobalt oxide) was easily peeled from Al foil.

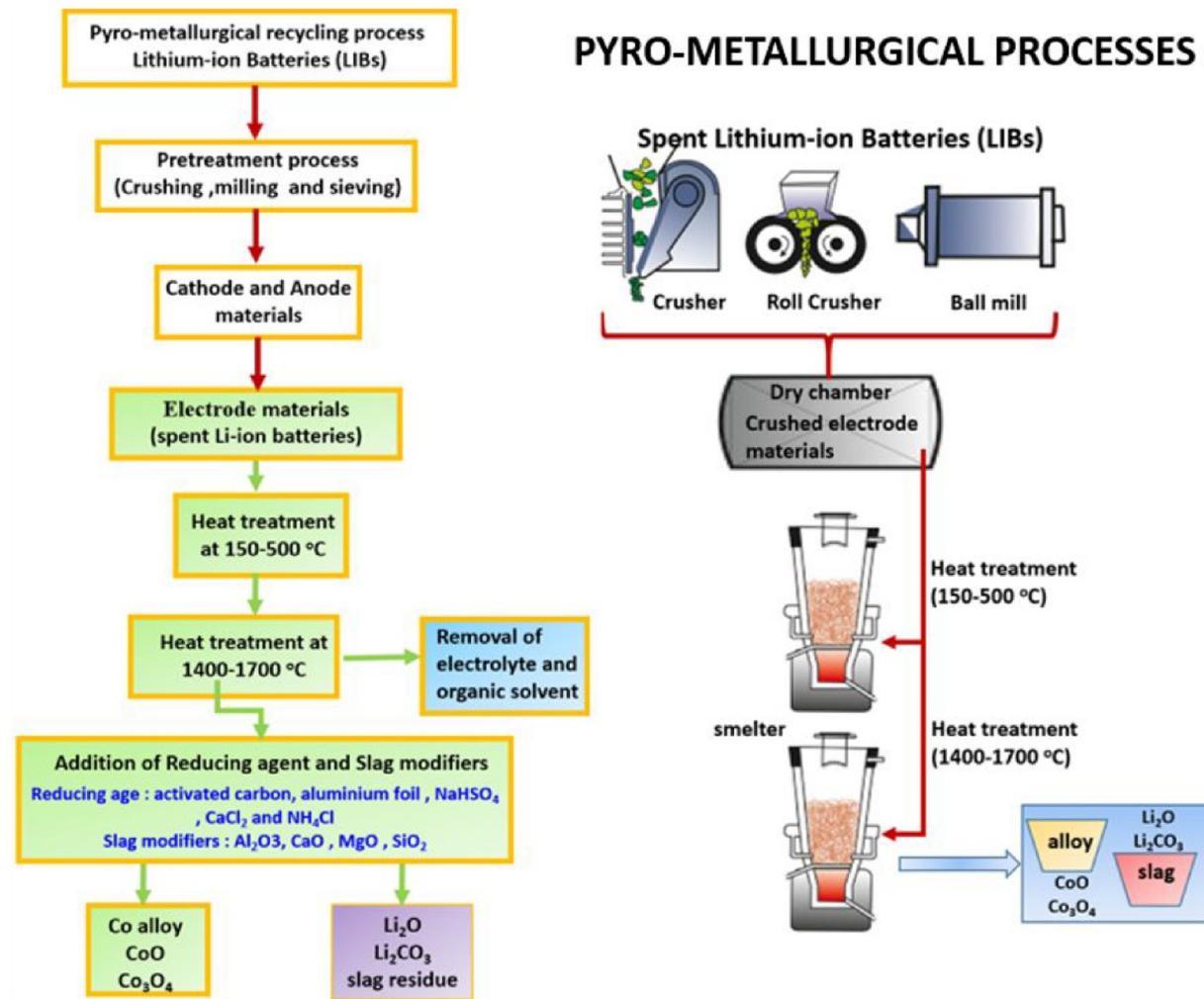


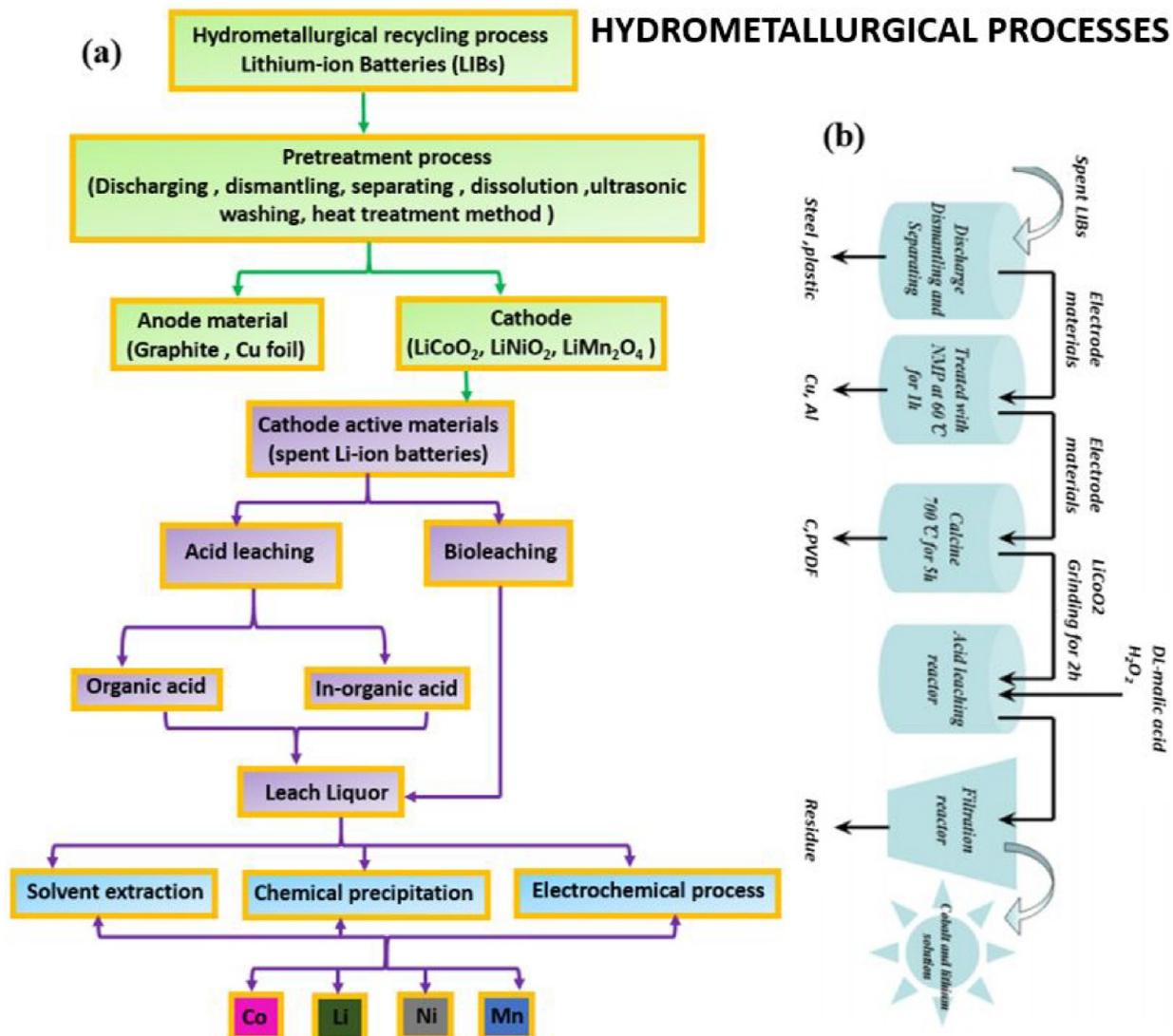
Figure 4. Pyrometallurgical process flowchart of spent LIBs.

**3.2. Pyrometallurgical Process.** In this pyrometallurgical process, metal species like Co, Ni, and Cu are recovered from LIBs in the form of alloys, and Li, Al, Si, Ca, and Fe are formed as a slag.<sup>79,80</sup> After the initial mechanical process like the dismantling of the battery pack, the batteries are directly processed in a high temperature smelting furnace without the need to separate cathode or anode layers, especially for the small-sized batteries. This treatment goes through two different heat treatment processes. At low temperature treatment (150–500 °C), electrolytes and organic solvent are slowly removed from the batteries, and in the second step, the batteries are subject to high temperature treatment (1400–1700 °C), which produces (Co, Ni, and Cu alloys) and slag (Li<sub>2</sub>O or Li<sub>2</sub>CO<sub>3</sub>). Figure 4 shows the pyrometallurgical process flowchart of spent lithium-ion batteries.

Today, a few companies such as Sony, Umicore, Accurec, and Inmetco<sup>81,82</sup> have adopted the thermal process to obtain alloys and slag which go into further processing by hydrometallurgical means. Pyrometallurgical or thermal processing approaches bring several advantages to the recycling system such as easier scalability and using fewer chemicals, and at the same time, there is lot of disadvantages associated with this process such as failure to recycle materials in the electrolyte, the loss of valuable Li metal and graphite in the anode, emission of harmful gases, and also high consumption of

energy. Battery recycling using thermal treatment is mainly the addition of reducing agents to spent battery materials in order to directly produce alloy and metal oxides.<sup>83</sup> Further, the decreasing content of Co in the lithium-ion batteries of EVs makes pyrometallurgy less favored from the economic perspective.<sup>84</sup>

**3.3. Hydrometallurgical Process.** Hydrometallurgical process have gained more interest in research and development in research institutes and industry due to high recovery rates of Co, Ni, and Li (>98%), low energy consumption, greater selectivity, low impurities, and because it is relatively considered a low cost process at low production volumes.<sup>10</sup> The acid leaching and solvent extraction process opened the eyes of many researchers to extract high purity cobalt from LIBs at low cost and by using simple techniques. The hydrometallurgical technique deals with four different steps: (1) acid leaching, (2) chemical precipitation, (3) solvent extraction, and (4) electrochemical separation. Initially, the cathode-active materials such as LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiNi<sub>0.33</sub>Mn<sub>0.33</sub>Co<sub>0.33</sub>O<sub>2</sub> are dissolved by acid solutions, and then, the process proceeds to extract Co, Li, Ni, and Mn metals from the solution by a suitable method. A hydrometallurgical process flowchart of spent LIBs and flow sheet for the recovery of Co and Li from spent LIBs using D,L-malic acid as a leachant are shown in Figure 5(a) and (b).

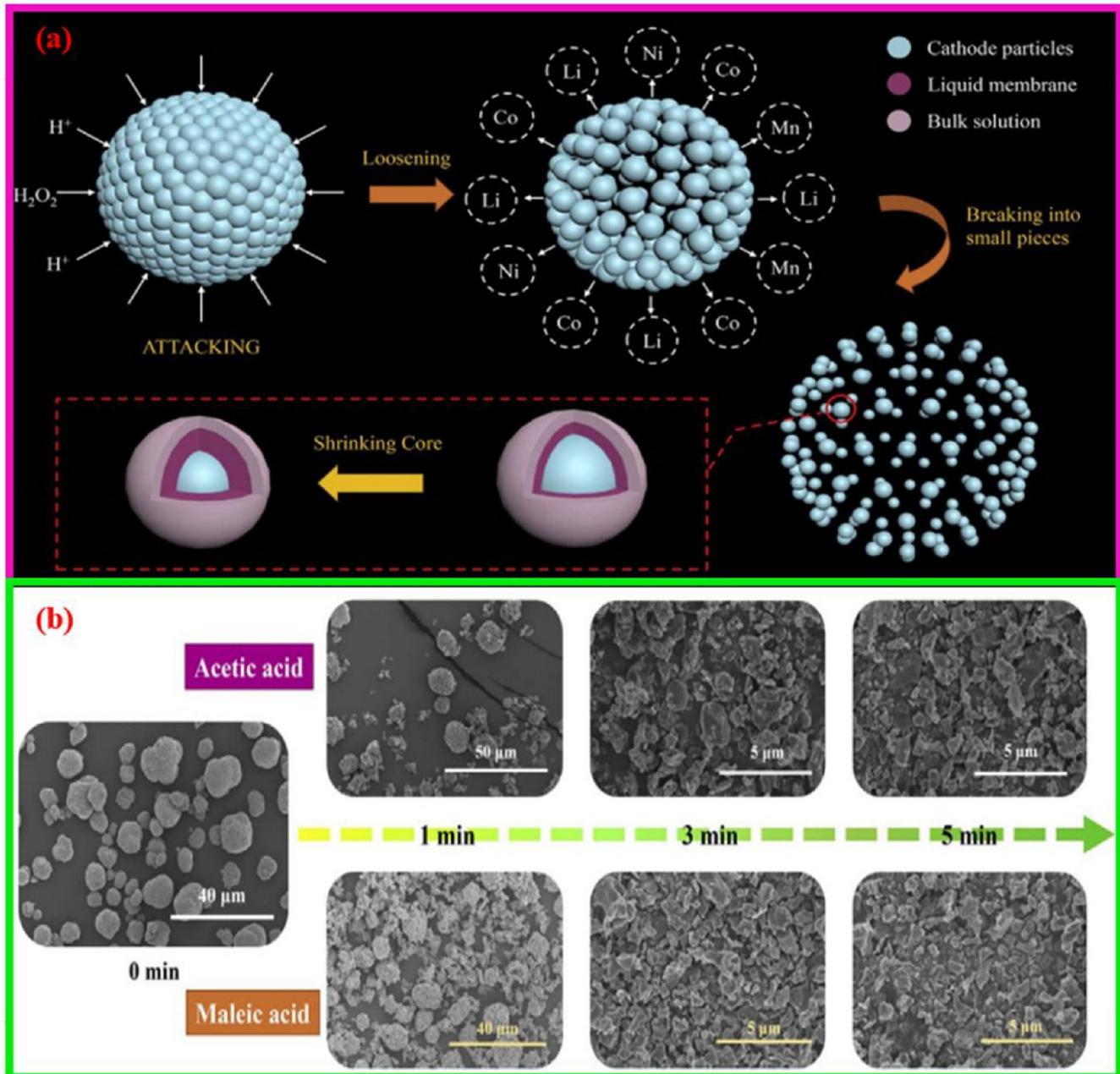


**Figure 5.** (a) Hydrometallurgical process flowchart of spent LIBs. (b) Flow sheet for the recovery of Co and Li from spent Li-ion batteries using D,L-malic acid as a leachant (Li et al., reproduced with permission).

**3.3.1. Acid Leaching.** Acid leaching is considered as one of the most effective and widely used methods to extract valuable metals from the spent LIBs. In the recent years, many researchers have worked on the acid leaching process to extract metal from spent LIBs using different inorganic acids like HCl,<sup>86,87</sup> HNO<sub>3</sub>,<sup>40</sup> and H<sub>2</sub>SO<sub>4</sub>.<sup>81,88</sup> Organic acids such as citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>),<sup>23,25</sup> oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>),<sup>74,76</sup> D,L-malic acid (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>),<sup>83,89</sup> L-tartaric acid (C<sub>4</sub>H<sub>6</sub>O<sub>6</sub>),<sup>55,90</sup> and mixed acid<sup>91,92</sup> have been also used to extract high-value metals from spent LIBs. The details of the acid leaching process by using inorganic acid, organic acid, and mixed acid are discussed extensively in the literature. A lot of work has been done in this domain since the past decade which has been a landmark for the recycling of LIBs.<sup>10</sup> In acid leaching process, the leaching efficiency of cobalt, lithium, nickel, and manganese depends on the different parameters such as acid concentration, reducing agent concentration, reaction temperature, reaction time, and solid to liquid (S/L) ratio. In the leaching process, the molecular structure of LiCoO<sub>2</sub> is broken down in the presence of an acid solution to form cobalt ion. This is a heterogeneous reaction where the reactant of acid initially is diffused to the surface of LiCoO<sub>2</sub> from the bulk phase to form a cobalt acid

complex on the surface of LiCoO<sub>2</sub>, and then, the leaching product of the cobalt acid complex leaves the solid–liquid interface by diffusion. Li et al.<sup>26</sup> explained the leaching mechanism and morphology of the leaching process very nicely. The leaching process goes through three steps which include particle loosening, breaking, and core shrinking. These steps are diagrammatically presented in Figure 6(a). The mechanisms of the leaching processes with the aid of SEM (scanning electron microscope) analyses of both acetic acid and maleic acid are explained in Figure 6(b). The cathode-active materials appear as aggregated spherical particles before the leaching process, but after few minutes, the large crystal particles start to loosen and break. The next sections summarize the leaching process using inorganic, organic, and mixed acids.

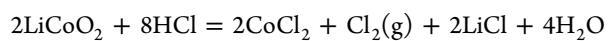
**3.3.1.1. Inorganic Acid Leaching Process.** Inorganic acids like sulfuric acid,<sup>78,88,93</sup> hydrochloric acid,<sup>86,87</sup> nitric acid,<sup>94</sup> phosphoric acid,<sup>95,96</sup> and hydrofluoric acid<sup>97</sup> as leaching reagents have been used and studied extensively in the literature. These acids are strong acids which facilitate a fast leaching reaction and give high recovery rates of metals from the spent LIBs. Inorganic acids are less costly, but they are also



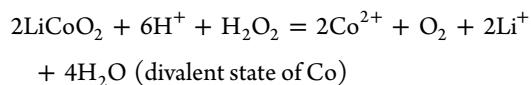
**Figure 6.** (a) Diagrammatic sketch of particle loosening, breaking, and core shrinking (reaction mechanism) in the leaching process. (b) SEM images of residual powders in acetic acid and maleic acid leaching process after 1, 3, and 5 min reaction (Li et al., reproduced with permission).<sup>26</sup>

associated with some concerns about their environmental impacts. As an example, when HCl reacts with LiCoO<sub>2</sub> during the leaching process, it produces Cl<sub>2</sub> gas due to the oxidation of HCl. Leaching agents such as H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, and H<sub>3</sub>PO<sub>4</sub> with reducing agents such as ethanol, hydrogen peroxide, sodium hydrogen sulfite, and glucose were used by many researchers to enhance the leaching efficiency.<sup>98,10,78,94,99–102</sup> The main concern of the reducing agent is to reduce the oxidation state of the metal and make it suitable to soluble in the acid solution. The metals like cobalt and manganese immediately turn to the Co(III) and Mn(IV) oxidation states, which are difficult to dissolve in acid solution; however, divalent states of Co(II) and Mn(II) are easily and quickly soluble in acid solutions.

The following reactions summarize the reactions that involve HCl and reducing agent (H<sub>2</sub>O<sub>2</sub>) with LiCoO<sub>2</sub>:



(oxidation of HCl, Cl<sub>2</sub> gas)



Chen et al.<sup>103</sup> reported recovery of valuable metals using leaching agent H<sub>2</sub>SO<sub>4</sub> and reducing agent H<sub>2</sub>O<sub>2</sub>. They reported high reaction yields of 98.5% for Co, 99.8% for Li, 99.8% for Ni, and 98.6% for Mn. The leaching reaction solution was prepared using 2 M H<sub>2</sub>SO<sub>4</sub>, 10v% H<sub>2</sub>O<sub>2</sub>, and a liquid to solid mass ratio of 30 mL/g and maintained the

**Table 3.** Summary of Some Research Results for Leaching of Spent LIBs in Inorganic Acids

Cathode materials	Leaching agent + reducing agents	T (°C)	S/L ratio(g/L)	Time (min)	Leaching rate (%)	Literature
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 10 vol % H <sub>2</sub> O <sub>2</sub>	70	30	60	98.5% Co 99.8% Li	Chen and Ho <sup>103</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 5.0 vol % H <sub>2</sub> O <sub>2</sub>	80	50	60	>99% Co >99% Li	Sun and Qiu <sup>78</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	25	20	240	98.3% Co	Takahashi et al. <sup>93</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> O <sub>2</sub>	50	20	240	98.4% Co	Takahashi et al. <sup>93</sup>
LiCoO <sub>2</sub>	5 M HCl	95	10	70	~99% Co 98% Li	Guzolu et al. <sup>87</sup>
LiCoO <sub>2</sub>	3 M HCl + 3.5v % H <sub>2</sub> O <sub>2</sub>	80	5	60	>89% Co >89% Li	Shuva and co-worker <sup>86</sup>
LiCoO <sub>2</sub>	1 M HNO <sub>3</sub> + 1.7 vol % H <sub>2</sub> O <sub>2</sub>	75	10	30	~99% Co ~99% Li	Lee and Rhee <sup>94</sup>
LiCoO <sub>2</sub>	H <sub>3</sub> PO <sub>4</sub> (2%v/v) + 2 vol % H <sub>2</sub> O <sub>2</sub>	60	8	90	99% Co 88% Li	Pinna et al. <sup>95</sup>
LiCoO <sub>2</sub>	HF (15% (v/v))	95	20	120	98% Co 80% Li	Suarez et al. <sup>97</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 2.0 vol % H <sub>2</sub> O <sub>2</sub>	60	33	120	96.3% Co 87.5% Li	Zhu et al. <sup>104</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 5.0 vol % H <sub>2</sub> O <sub>2</sub>	75	100	60	70.0% Co 99.1% Li	Jha et al. <sup>105</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 8 vol % H <sub>2</sub> O <sub>2</sub>	75	50	60	98% Co	Bertuol et al. <sup>106</sup>
LiCoO <sub>2</sub>	1 M H <sub>2</sub> SO <sub>4</sub>	95	50	240	66.2% Co 93.4% Li	Meshram et al. <sup>81</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 6 vol % H <sub>2</sub> O <sub>2</sub>	60	100	60	98% Co 97% Li	Jingu et al. <sup>107</sup>
LiCoO <sub>2</sub>	4.0 M HCl	80	—	120	99% Co 97% Li	Li et al. <sup>31</sup>
LiCoO <sub>2</sub>	0.7 M H <sub>3</sub> PO <sub>4</sub> + 4 vol % H <sub>2</sub> O <sub>2</sub>	40	50	60	99.7% Co 99.9% Li	Nayaka et al. <sup>108</sup>
LiCoO <sub>2</sub>	6 vol % H <sub>2</sub> SO <sub>4</sub> + 5 vol % H <sub>2</sub> O <sub>2</sub>	65	20	60	95% Li 80% Co	Dorella and Mansur <sup>34</sup>
LiCoO <sub>2</sub>	2 M H <sub>2</sub> SO <sub>4</sub> + 5 vol % H <sub>2</sub> O <sub>2</sub>	75	100	30	94% Li 93% Co	Swain et al. <sup>109</sup>

leaching process at 70 °C for 120 min. Sun et al.<sup>78</sup> recovered cobalt and lithium from spent LIBs by using both vacuum pyrolysis and a hydrometallurgical technique. More than 99% of cobalt and lithium were recovered under experimental conditions of 2 M H<sub>2</sub>SO<sub>4</sub> at 80 °C and a solid/liquid ratio of 50 g/L for 60 min. They also state that this technology is an environmental friendly process that is also cost competitive and feasible to be scaled up. Takahashi et al.<sup>93</sup> reported all three steps such as grinding, leaching, and solvent extraction with different leaching agents such as H<sub>2</sub>SO<sub>4</sub>, HCl, and HNO<sub>3</sub> and reducing agent H<sub>2</sub>O<sub>2</sub> to enhance cobalt recovery from LIBs. The reaction condition was maintained at pH 3–5, temperature of 25 and 50 °C, time of 240 min, and a solid–liquid ratio of 1/5. Recovery rates of 98.3% for Li and 98.4% for Co were reported at pH 3, S/L = 1/5, and 25 and 50 °C. The Co leaching efficiency was increased to 98.8% in the oxidative medium. The energy consumption and pollution during the recovery of Li and Co from spent LIBs were reduced by ultrasonic washing, acid leaching, and the precipitation method. Guzolu et al.<sup>87</sup> recovered 98% of Li and nearly 99% of Co under optimum conditions of a 5 M HCl solution, temperature of 95 °C, reaction time of 70 min, and solid to liquid ratio S/L of 10 g/L. The precipitation reaction was conducted using NaOH at pH 12.5 for 1 h at 55 °C. It was found that Co and Li were recovered at rates that exceed 99%. Shuva and co-woker<sup>86</sup> used HCl and H<sub>2</sub>O<sub>2</sub> as leaching and

reducing agents to recycle the spent LIBs. The optimum conditions for leaching of lithium and cobalt was found to be 3 M HCl, S/L ratio = 1:20 mg/mL, 80 °C, 60 min, and H<sub>2</sub>O<sub>2</sub> 3.5 vol %. It is reported that 89% of Co and Li were leached at optimized conditions. The dissolution efficiency of LiCoO<sub>2</sub> increased with increasing the temperature, concentration of HCl, time, and solid/liquid (S/L) ratio. Lee and Rhee<sup>94</sup> reported that the leaching efficiency increases with increasing temperature and leaching agent HNO<sub>3</sub> concentration, and Li and Co were leached with over 95% recovery rate with the addition of 1.7 vol % H<sub>2</sub>O<sub>2</sub>. The optimum condition to recover Co and Li was found to be 1 M HNO<sub>3</sub>, 10–20 g L<sup>-1</sup> initial S/L ratio, 75 °C temperature, and 1.7 vol % H<sub>2</sub>O<sub>2</sub> addition. The dissolution process was explained on a reduction mechanism of Co<sup>3+</sup> to Co<sup>2+</sup>. They also calculated the activation energies of Co and Li and found them to be 12.5 and 11.4 kcal/mol, respectively. Pinna et al.<sup>95</sup> studied the dissolution process of LiCoO<sub>2</sub> metal oxide using phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and reducing agent hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The optimum condition to recover Co and Li from spent LIBs was found to be H<sub>3</sub>PO<sub>4</sub> (2%v/v), H<sub>2</sub>O<sub>2</sub> (2 vol %), solid–liquid (S/L) ratio = 8 g/L, 90 °C, and 60 min. It was reported that 88% Li and 99% Co were recovered due to efficient dissolution of LiCoO<sub>2</sub> to form high purity Co<sub>2</sub>O<sub>4</sub> and Li<sub>3</sub>PO<sub>4</sub> as final products. The effect of changing certain parameters such as reaction time, leaching temperature, solid–liquid ratio, and concentrations of

the leaching agent ( $H_3PO_4$ ) and the reducing agent ( $H_2O_2$ ) were discussed in this paper. They found that the dissolution of the sample increased with increasing phosphoric acid concentration up to 2% (v/v), above which the  $LiCoO_2$  dissolution remains constant. Suarez et al.<sup>97</sup> used hydrofluoric (HF) acid leaching to recover Li and Co metals. The dissolution parameters such as temperature, reaction time, solid–liquid ratio, stirring speed, and concentration of HF were studied in this experiment. The results indicated that an increase in the HF concentration, temperature, and reaction time can favor the leaching reaction of the  $LiCoO_2$ . The recovery rates of Co and Li reached 98% and 80%, respectively.

The chemical behavior of the metal in different oxidation states plays a major role in obtaining high purity cobalt and lithium products from the cathode material of LIBs. Zhu et al.<sup>104</sup> separated cobalt and lithium by acid leaching cathode-active materials in 2 M  $H_2SO_4$  and  $H_2O_2$  (2 vol %) and precipitated as cobalt(II) oxalate dihydrate ( $CoC_2O_4 \cdot 2H_2O$ ) microparticles by addition of di-ammonium oxalate  $(NH_4)_2C_2O_4$ . Results showed that up to 96.3% of Co and 87.5% of Li can be recovered in this process. Acid leaching with 2 M  $H_2SO_4$  with the addition of 5 vol %  $H_2O_2$  reducing agent at a S/L ratio 100 g/L at 75 °C resulted in the recovery of 99.1% lithium and 70.0% cobalt in 60 min as per the reported results by Jha et al.<sup>105</sup>

Recently, researchers started to look at supercritical fluids for leaching cobalt. Bertuol et al.<sup>106</sup> performed leaching tests with supercritical  $CO_2$  and cosolvents, as well as under conventional conditions. It was reported that more than 95% Co can be extracted using supercritical conditions with the reduction of reaction time. Meshram et al.<sup>81</sup> recovered nickel and manganese along with lithium and cobalt by a sulfuric acid leaching process. Results showed that 93.4% Li, 66.2% Co, 96.3% Ni, and 50.2% Mn were recovered when the cathode-active material was leached in 1 M  $H_2SO_4$  at 95 °C and a 50 g/L pulp density (S/L ratio) for 240 min. Kang et al.<sup>107</sup> recovered cobalt sulfate by reductive leaching and solvent extraction with Cyanex 272. Cobalt was reductively leached in 60 min by stirring with 2 M  $H_2SO_4$  and 6 vol %  $H_2O_2$ , at 60 °C using a S/L ratio of 100 g/L. Here, 98% Co and 97% Li were recovered using the above-mentioned optimal conditions.

Recovering cobalt from spent LIBs can be done by a combination of pretreatments such as crushing, ultrasonic washing, acid leaching, and precipitation to improve the recovery efficiency and reduce energy consumption and pollution. For example, Li et al.<sup>31</sup> used a combined recovery process to recover Co metal from LIBs. They prepared a leaching solution with 4 M HCl and continued the leaching reaction for 120 min at 80 °C. Results showed that 97% Li and 99% Co can be recovered at these conditions. Nayaka et al.<sup>108</sup> recovered the valuable metals using a sustainable recycling process and mild phosphoric acid. It was reported that 99.7% Co and 99.9% Li were recovered when the cathode-active material was leached in 0.7 M  $H_3PO_4$  and 4 vol %  $H_2O_2$  at 40 °C for 60 min. The leaching kinetics and activation energy were calculated for Co and Li and estimated to be 7.3 and 10.2 kJ/mol, respectively. Table 3 reports a few works on acid leaching using inorganic acids as leaching agents.

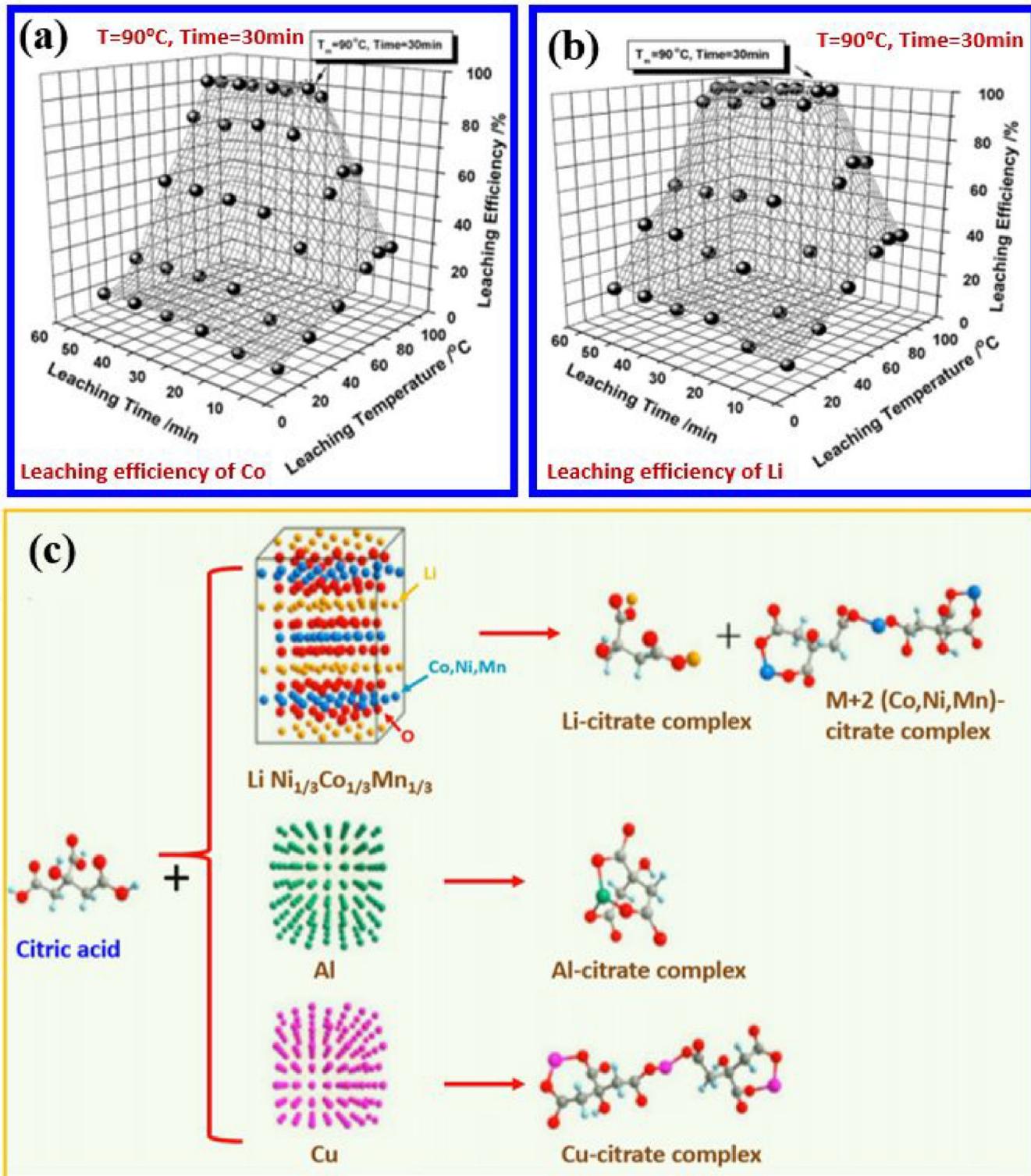
**3.3.1.2. Organic Acid Leaching Process.** Research has been diverted toward the organic acid leaching process due to the negative impact on the environment like generation of toxic gases such as  $CO_2$ ,  $SO_2$ ,  $Cl_2$ , ethane, phosphorus, and  $NO_x$  that form during the inorganic acid leaching process. Additionally,

due to the low pH of the solution, the extraction of metal from solution may be difficult in some cases. Environmentally friendly and green recycling processes have been of great interest in the recent years.<sup>110</sup> Organic acids such as citric acid,<sup>59,69</sup> malic acid,<sup>77</sup> lactic acid,<sup>46</sup> and maleic acid<sup>26</sup> can be used as leaching or chelating agents and have similar leaching efficiencies like inorganic acids/mineral acids. Today, organic acids play key roles in the leaching process due to biodegradable properties, ease of processing, and since they do not emit toxic gases. The leaching efficiency of the organic acids depends mainly on the acidic nature and unique chelating coordination properties. Acidity of the organic acid depends mainly on their functional groups and acid dissociation constant ( $pK_a$  value).<sup>11</sup>

Chen and co-workers<sup>111,112</sup> and Horeh et al.<sup>113</sup> reported the advantages of organic acids such as being ecofriendly and efficient leaching agents, no harmful gases emitted, and recycling the remaining acid after the leaching process. Additionally, Deng<sup>29</sup> in his comparative study between organic and inorganic acids claimed that organic acids are thermally stable, have no significant negative impacts on the environment, and are strong chelates, but they are considered weak oxidants compared to inorganic acid. Li et al.,<sup>22</sup> Fan et al.,<sup>23</sup> Chen et al.,<sup>24</sup> and Zheng et al.<sup>25</sup> revealed that organic acids show the same leaching efficiency like inorganic acids and additionally are less harmful to the environment. This section attempts to discuss the reported work on recycling processes using organic acids as efficient leaching agents.

**Citric Acid:** Citric acid is a weak organic acid that is difficult to dissolve fully in water; thus, this may limit its leaching capabilities. The reaction between citric acid and  $LiCoO_2$  produce  $Co^{3+}$ , which is very difficult to dissolve in water and decrease the efficiency of the leaching process of cobalt metal. Therefore, many researchers<sup>22,25</sup> used  $H_2O_2$  as a reducing agent with citric acid to form  $Co^{2+}$  ions in water, which can easily dissolve in water and increases the leaching efficiency.

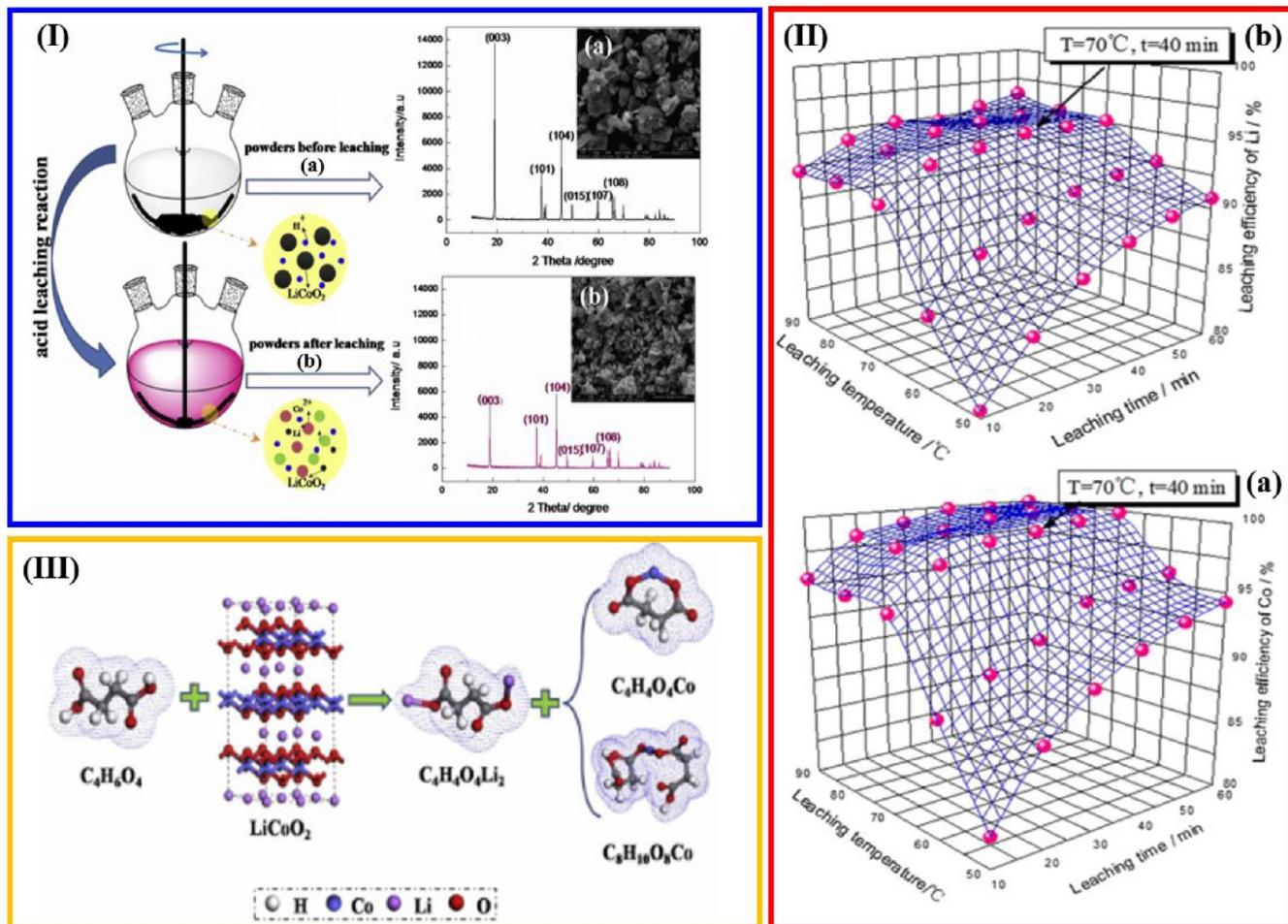
Zheng et al.<sup>25</sup> studied the leaching process using organic citric acid and the kinetic process of cobalt leaching. The leaching reaction was conducted using citric acid, water, spent  $LiCoO_2$  powder, and  $H_2O_2$  solution in a reactor. Leaching efficiency was investigated by changing certain parameters such as the mole ratio of  $LiCoO_2$  to citric acid,  $H_2O_2$  concentration, solid-to-liquid ratio, temperature, and time. It was reported that 99.07% of cobalt was recovered using citric acid (4M), S/V ratio of 15g/L, and  $H_2O_2$  (1.0 vol %) in 5 h at 90 °C. They concluded that the leaching process using citric acid at 90 °C represents the optimum temperature for extraction of cobalt and lithium from spent LIBs. The SEM analysis showed irregular and agglomerated morphology of the spent  $LiCoO_2$ . XRD analysis showed two different phases,  $LiCoO_2$  and  $Co_3O_4$ , which indicates the decomposition of  $LiCoO_2$ . Li et al.<sup>22</sup> also used citric acid and hydrogen peroxide as leaching and reducing agents, respectively, to recycle the lithium and cobalt from spent LIBs. In this work, both the mechanical separation process and acid leaching process were done consecutively to extract cobalt and lithium. The metal leaching process was conducted by changing the citric acid concentration, S/L ratio, temperature, and  $H_2O_2$  concentration. The results showed that up to 90% Co and 100% Li can be recovered by varying the concentration of citric acid, time, and temperature as well as the S/L ratio. The effect of temperature and time on leaching efficiency of cobalt and lithium was studied at 1.25 M citric acid, 1.0 vol % hydrogen peroxide, and



**Figure 7.** Effect of leaching temperature and leaching time on the leaching of waste  $\text{LiCoO}_2$  with 1.25 M citric acid ( $\text{H}_2\text{O}_2 = 1 \text{ vol } \%$ , S: L = 20 g  $\text{L}^{-1}$  and agitation speed = 300 rpm). (a) Leaching efficiency of Co and (b) leaching efficiency of Li (Li et al., reproduced with permission). (c) Systematic structure design of leaching reaction and possible complex formation during leaching process of metal in Citric acid solution (Meng et al., reproduced with permission).<sup>114</sup>

a S/L of 20 g  $\text{L}^{-1}$ . Figure 7(a) and (b) shows the increase of metal leaching efficiency with increasing temperature and time, but a significant effect was not observed after a 30 min reaction time. Results also indicate that cobalt (8%)/lithium (15%), cobalt (74%)/lithium (84%), and cobalt (91%)/lithium (99%) were leached at 25, 80, and 90 °C, respectively. However, at

100 °C, the efficiency of leaching Li and Co showed almost no change. This could be partially linked to the dissociation process of citric acid. It was observed that 100% Li and 90% Co were recycled from the spent LIBs using 1.25 M citric acid, 1.0 vol % hydrogen peroxide, and a S/L ratio of 20 g/L at 90 °C and for 30 min. Meng et al.<sup>114</sup> reported a simple and

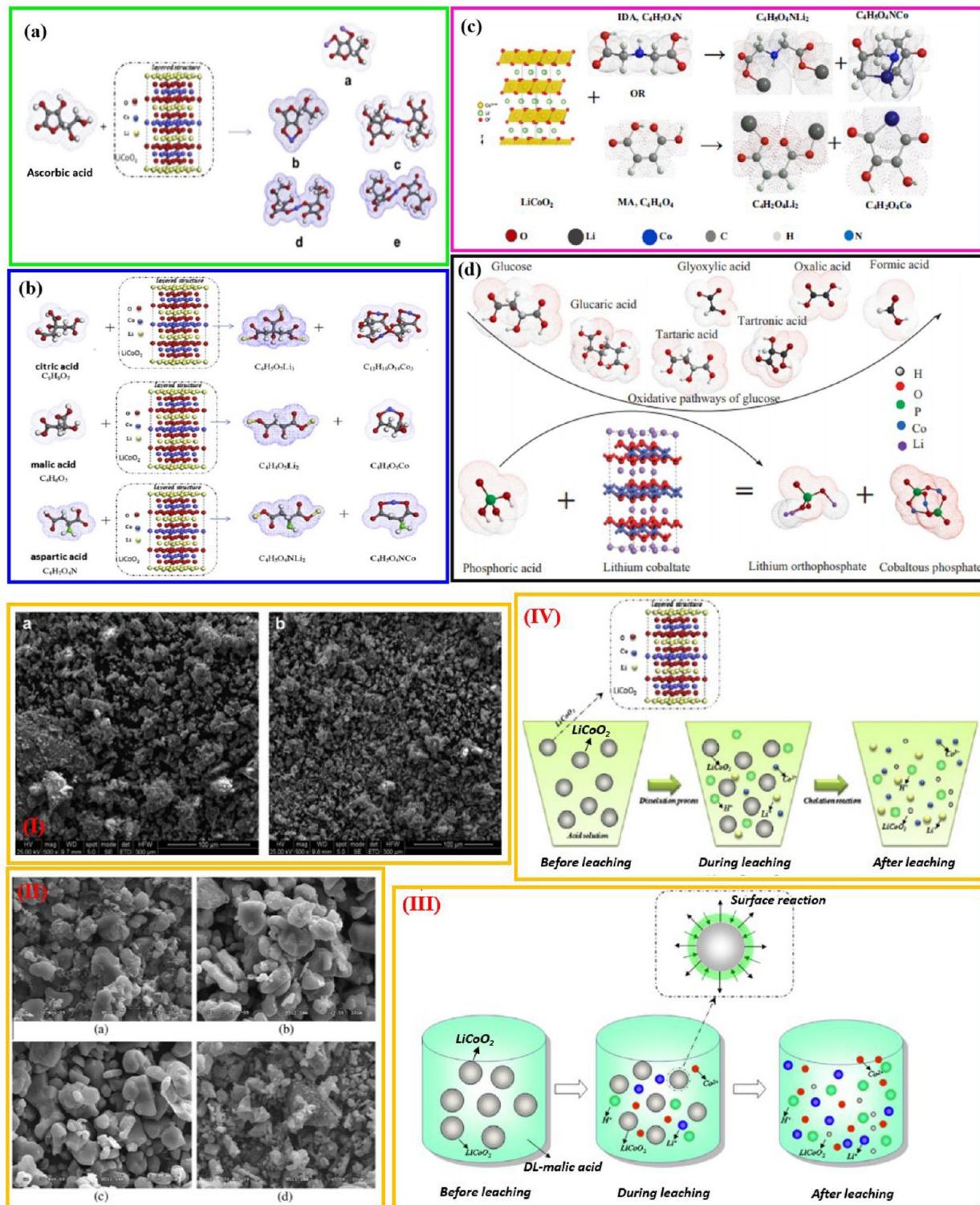


**Figure 8.** (I) XRD patterns of (a) cathodic materials after calcination and grinding but before leaching and (b) black residues after leaching. (II) Effect of reaction time and temperature on leaching efficiency of (a) Co and (b) Li. (III) Leaching reaction and possible reaction products in the succinic acid leaching process (Li et al., reproduced with permission).<sup>9</sup>

economical leaching process to recycle the cathode materials from industrial waste LIBs. The leaching experiment was conducted using citric acid with the addition of reductants H<sub>2</sub>O<sub>2</sub> and ascorbic acid (AA). The concentration of citric acid (0.25–2.0 mol/L), S/L ratio (20–100 g/L), reaction time (5–180 min), and temperature (50–90 °C) were used in the recycling process. SEM and XRD were used to study the morphology and crystal structure of leaching residues. The leaching process and different complex structure formation at the time of the citric acid reaction with different metals are shown in Figure 7(c). Effects of temperature and time, acid concentration, S/L ratio, H<sub>2</sub>O<sub>2</sub> concentration, and ascorbic acid during leaching process are well described in this paper. In addition, the kinetic study was performed to understand the relationship between the metal leaching and leaching parameters. Authors were able to recover 91.0% of Li, 90.9% of Co, 94.1% of Ni, 88.6% of Mn, 19.5% of Cu, and 26.9% of Al using citric acid (0.5M) and a S/L ratio of 80 g/L at 90 °C in 80 min without reductant. They also found that there was no significant increase in the metal leaching efficiency by addition of H<sub>2</sub>O<sub>2</sub>.

Almeida et al.<sup>115</sup> used citric acid (2M) as leaching agents and H<sub>2</sub>O<sub>2</sub> (0.25M) to evaluate the chemical composition in cathode-active materials of different spent Li-ion batteries. The use of 2.0 mol L<sup>-1</sup> citric acid as an environmentally friendly

alternative for metal leaching showed good results. A new green recycling process is now on demand to recycle cobalt and lithium from the cathodes of spent batteries by using citric acid as a leaching agent and also to study the photocatalytic effect of synthesized Co<sub>3</sub>O<sub>4</sub> and LiCoO<sub>2</sub> mixtures. Santana et al.<sup>116</sup> used citric acid to develop an ecofriendly recycling route for spent LIBs. The main contribution is to produce valuable materials through an effective recycling process with photocatalytic properties from spent Li-ion batteries without disturbing the environment. A simple and efficient method was investigated by Yu et al.<sup>117</sup> to recover the valuable cathode-active materials from spent LIBs by a direct leaching process in citric acid solution without a pretreatment process. This work discussed the effect of citric acid concentration, H<sub>2</sub>O<sub>2</sub> concentration, reaction temperature, reaction time and solid-to-liquid ratio on the leaching efficiency. It was observed that about 99% of Co and 99% of Li were recovered using 1 M citric acid in the presence of 8 vol % H<sub>2</sub>O<sub>2</sub> and 40 g/L S/L ratio in 70 min at 70 °C. The results showed that the leaching efficiency increased substantially when the citric acid concentration increased from 0.1 to 1.0 M and immediately declined after reaching 2M. Further, the authors also noticed that the leaching efficiency increased with the increasing concentration of the hydrogen peroxide, reaction temperature, solid–liquid ratio, and reaction time. Aaltonen et al.<sup>118</sup>



**Figure 9.** (a) Possible products of leaching reaction of waste  $\text{LiCoO}_2$  with ascorbic acid (Li et al., reproduced with permission).<sup>67</sup> (b) Possible products observed during leaching reaction of  $\text{LiCoO}_2$  with citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ), D,L-malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ), and L-aspartic acid (Li et al., reproduced with permission).<sup>123</sup> (c) Possible complexation of Li and Co with IDA and MA during dissolution (Nayaka et al., reproduced with permission).<sup>108</sup> (d) Possible leaching process of  $\text{LiCoO}_2$  materials in glucose and phosphoric acid solution (Meng et al., reproduced with permission).<sup>125</sup> (I) SEM micrographs of (a) dismantled cathode material from spent LIBs and (b) leach residues, (Li et al., reproduced with permission).<sup>67</sup> (II) SEM images of different cathode materials: (a) dismantled cathodic material from a spent LIB, (b) cathodic material after treatment with NMP, (c) cathodic material after dismantling and calcination at  $700^\circ\text{C}$  for 5 h, and (d) leach residues (Li et al., reproduced with permission).<sup>85</sup> (III) Possible multiphase reaction of the D,L-malic acid acid solution and  $\text{LiCoO}_2$  particles (Li et al., reproduced with permission).<sup>123</sup> (IV) Possible multiphase leaching reaction of  $\text{LiCoO}_2$  particles and organic acid solutions (Li et al., reproduced with permission).<sup>123</sup>

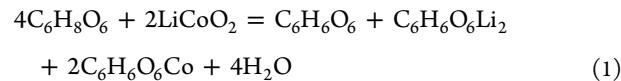
investigated leaching process at room temperature using citric acid (1M) and 1 vol %  $H_2O_2$ , with 50 g/L pulp density in 24 h. This process allows for recovery up to 97% of Co, 89% of Li, 98% of Mn, and 93% of Ni.

Citric acid is an excellent acid for selective metal dissolution compared to sulfuric acid. Ma et al.<sup>119</sup> observed from the experiment they conducted on spent LIBs that the citric acid with reducing agent  $H_2O_2$  shows a significant Co and Ni metal leaching process but slows dissolution of other metals such as Mn, Fe, and Zn. Musariri et al.<sup>120</sup> studied a 1–1.5 M citric acid solution for the leaching process to recover lithium, cobalt, and nickel from LIBs. The increase of citric acid concentration from 1 to 1.5 M strongly influences the metal leaching rate. It was reported that 98% of Co, 96% of Li, and 99% of Ni were recovered using 1.5 M citric acid and 2 vol %  $H_2O_2$  at 95 °C in 30 min. Fan et al.<sup>23</sup> reported an economical and environmentally friendly leaching process using 1.25 M citric acid and 1 vol %  $H_2O_2$  solution to recover metals from  $LiCoO_2$  cathode-active materials. Nearly 90.2% and 98% recovery rates for Co and Li, respectively, were achieved using citric acid (1.25 M) and 0.9 vol %  $H_2O_2$ , with a 60 g L<sup>-1</sup> S/L ratio in 35 min at 90 °C.

**Succinic Acid:** Succinic acid, a natural weak organic acid, has been used for recycling of Co and Li metals from LIBs due to low energy consumption, no air emissions, complete recovery of valuable components with high purity, and for being among the most cost-effective leaching processes. Li et al.<sup>9</sup> discussed the recycling process of valuable Co and Li metals from LIBs using succinic acid as a leaching agent and  $H_2O_2$  as a reducing agent. After several trials, the experiment was conducted under optimal conditions, 1.5 M succinic acid, 4 vol %  $H_2O_2$ , and a 15 g/L S/L ratio at 70 °C for 40 min. The morphology and structural integrities of the cathode-active materials before and after the leaching experiment were well reported in Figure 8(I). Leaching efficiencies of cobalt and lithium were studied with the increase in temperature and time and showed remarkable leaching of Co and Li in succinic acid (1.5M), S/L of 15g/L, and  $H_2O_2$  (4 vol %) at 70 °C. The graph (Figure 8(II(a, b))) indicates that the Co and Li leaching efficiencies reached 82.27% and 80.55%, respectively, at 50 °C and 10 min and further increased to 99.83% and 94.65% for cobalt and lithium, respectively, with increasing temperature and time (70 °C for 40 min), and finally maintained a negligible change with further increases in the reaction time. The stepwise leaching reaction of  $LiCoO_2$  in succinic acid leachant is shown in Figure 8(III). They identified theoretically two possible leaching products containing Co(II) that was  $C_4H_4O_4Co$  and  $C_8H_{10}O_8Co$ . However, Xu et al.<sup>121</sup> and Li et al.<sup>67</sup> reported thermodynamic calculations of the leaching product and showed that  $C_4H_4O_4Co$  is the only product that forms during the leaching reaction. They further explained the nature of the reaction of the symmetrical structure of  $C_4H_4O_4Co$ ; this molecule is more stable and easier to generate, which leads to the increase in the leaching efficiency.

**Ascorbic Acid:** Ascorbic acid can act as both leaching agent and reducing agent at the same time to dissolve metals and reduce high-valent metals like Co(III) to Co(II) oxidation states. Li et al.<sup>67</sup> executed a recycling process using a combination of ultrasonic washing, calcination, and ascorbic acid leaching. Cobalt and lithium recovery efficiency was improved substantially using organic acid and a reducing agent. The leaching reaction was conducted under a condition of ascorbic acid (1.25M), temperature of 70 °C, time of 20 min,

and a solid-to-liquid ratio of 25 g L<sup>-1</sup>. They proposed this reaction method which can be scaled up at industrial scale to recycle Co and Li from spent LIBs. The detailed structural information, reaction mechanism, and possible structure formation of the leaching product are presented theoretically and thermodynamically in Figure 9(a). The valuable information was observed in the morphology analysis (SEM images, Figure 9(I(a, b))). Xu et al.<sup>121</sup> predicted product (b) in Figure 9(I), i.e.,  $C_6H_6O_6Co$  which is more stable during leaching process. The leaching reaction is as follows:



It was reported that 94.8% Co and 98.5% Li were recovered by using 1.25 M ascorbic acid concentration with a S/L ratio of 25 g/L at 70 °C for 20 min. Additionally, it was reported that the efficiency of the acid leaching process was affected by several factors, such as leaching temperature and time, acid concentration, and S/L ratio.<sup>121</sup>

**D,L-Malic Acid ( $C_4H_6O_5$ )/Oxalic Acid ( $C_2H_2O_4$ ):** Many researchers have reported a leaching process using oxalic acid and D,L-malic acid due to their strong acidity and reducibility properties. de Oliveira Demarco et al.<sup>50</sup> focused on an ecofriendly and effective leaching process using three organic acids such as malic acid, citric acid, and formic acid at concentrations of 2 M to recover cobalt, lithium, and manganese metals from spent LIBs. They used mechanical, thermal, and leaching processes in their experiment. They carried out several experimental conditions, but the effective one was D,L-malic acid (2M), 6 vol %  $H_2O_2$ , S/L ratio 20 g/L, 95 °C, and reaction time of 60 min. In this condition, Co (90.57%), Li (93.22%), and Mn (99.53%) were recovered. Additionally, citric acid and formic acid showed good leaching efficiencies at 65 °C. Li et al.<sup>85</sup> used a biodegradable, environmental friendly, and efficient leaching agent (D,L-malic acid) to recover Co and Li from spent LIBs. The leaching process was conducted under variable conditions and different concentrations of D,L-malic acid (0.5–3.0 M),  $H_2O_2$  (0–2.5 vol %), solid/liquid ratio (33–17 g/L), temperature (20–100 °C), and reaction time (10–50 min). They concluded that more than 90% of Co and nearly 100% Li can be recovered at 1.5 M D,L-malic acid, 2.0 vol % hydrogen peroxide, a leaching temperature of 90 °C, a S/L ratio of 20 g L<sup>-1</sup>, and a time interval of 40 min. Different steps involved in the recycling process, morphology of cathode materials before and after leaching, and reaction mechanism between  $LiCoO_2$  and D,L-malic acid are presented in Figure 9(II) and (III).

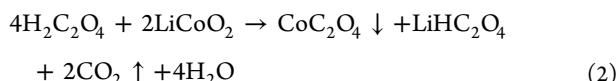
Sun et al.<sup>76</sup> reported vacuum pyrolysis, oxalate leaching, and a precipitation process to recover Co and Li and reported that this process is environmentally friendly. They used oxalate as the leaching reagent and precipitant which leaches and precipitates cobalt from  $LiCoO_2$  and CoO directly as  $Co_2O_4 \cdot 2H_2O$ . The optimal condition was achieved with 1.0 M oxalate solution, a S/L ratio 50 g/L, temperature of 80 °C, and leaching time of 120 min. The authors reported that more than 98% of  $LiCoO_2$  was obtained under this optimum condition.

Most of the organic acids present a similar reaction mechanism to citric acid, but oxalic acid follows a different reaction mechanism. Due to the complication in the conventional process combined with leaching, precipitating, and filtering to recover cobalt and lithium from spent LIBs,

**Table 4.** Summary of Some Research Results for Leaching of Spent LIBs Using Organic Acids

Cathode materials	Leaching agent	T (°C)	S/L ratio (g/L)	Time (min)	Leaching rate (%)	Literature
LiCoO <sub>2</sub>	4 M citric acid + 1 vol % H <sub>2</sub> O <sub>2</sub>	90	15	300	99% Co 90% Li	Zheng et al. <sup>25</sup>
LiCoO <sub>2</sub>	1.25 M citric acid + 1 vol % H <sub>2</sub> O <sub>2</sub>	90	20	30	100% Li	Li et al. <sup>22</sup>
LiNiCoMnO <sub>2</sub>	0.5 M citric acid	90	80	80	90.9% Co 91.0% Li	Meng et al. <sup>114</sup>
LiCoO <sub>2</sub>	2 M citric acid + 0.25 M H <sub>2</sub> O <sub>2</sub>	80	20	120	~99% Co ~99% Li	Almeida et al. <sup>115</sup>
LiCoO <sub>2</sub>	1 M citric acid + 8 vol % H <sub>2</sub> O <sub>2</sub>	70	40	70	99% Co 99% Li	Yu et al. <sup>117</sup>
LiCoO <sub>2</sub>	1 M citric acid + 1 vol % H <sub>2</sub> O <sub>2</sub>	RT	50	1440	97% Co 89% Li	Aaltonen et al. <sup>118</sup>
LiCoO <sub>2</sub>	1.5 M citric acid + 2 vol % H <sub>2</sub> O <sub>2</sub>	95	—	30	98% Co 96% Li	Masariri et al. <sup>120</sup>
LiCoO <sub>2</sub>	1.25 M citric acid + 0.9 vol % H <sub>2</sub> O <sub>2</sub>	90	60	35	90.2% Co 98% Li	Fan et al. <sup>23</sup>
LiCoO <sub>2</sub>	1.5 M succinic acid + 4 vol % H <sub>2</sub> O <sub>2</sub>	70	15	40	100% Co <96% Li	Li et al. <sup>9</sup>
LiCoO <sub>2</sub>	1.25 M ascorbic acid	70	25	20	94.8% Co 98.5% Li	Li et al. <sup>67</sup>
LiCoO <sub>2</sub>	1.5 M D,L-malic acid (C <sub>4</sub> H <sub>5</sub> O <sub>6</sub> ) + 2 vol % H <sub>2</sub> O <sub>2</sub>	90	20	40	<90% Co ~100% Li	Li et al. <sup>85</sup>
LiCoO <sub>2</sub>	2 M D,L-malic acid + 6 vol % H <sub>2</sub> O <sub>2</sub>	95	20	60	90.5% Co 93.2% Li	de Oliveira Demarco et al. <sup>50</sup>
LiCoO <sub>2</sub>	1.5 M oxalate + H <sub>2</sub> O <sub>2</sub>	80	50	120	<98% Co <98% Li	Sun and Qiu <sup>76</sup>
LiCoO <sub>2</sub>	1.0 M oxalate	95	15	150	97% Co 98% Li	Zeng and Shen <sup>74</sup>
LiCoO <sub>2</sub>	2 M citric acid + 1.25 vol % H <sub>2</sub> O <sub>2</sub>	60	30	120	81.5% Co 92.5% Li	Golmohammadzadeh et al. <sup>122</sup>
LiCoO <sub>2</sub>	2 M citric acid + 1.25 vol % H <sub>2</sub> O <sub>2</sub>	60	30	300	96.4% Co 99.8% Li	Golmohammadzadeh et al. <sup>122</sup>

Zeng et al.<sup>74</sup> proposed a novel recovery process, only combined with oxalic acid leaching and filtering. The oxalic acid was used as the reductant and leachant, and the leaching efficiencies of Co and Li were achieved at 97% and 98%, respectively. The reaction mechanism is described as



The optimal condition for leaching process is controlled at 150 min, 95 °C temperature, 15 g/L solid/liquid ratio, and 400 rpm rotational speed. Golmohammadzadeh et al.<sup>122</sup> studied four different organic acids (D,L-malic, oxalic, citric, and acetic acids) and found that the best sequence is citric acid > D,L-malic > acetic > oxalic acid in terms of their efficiency to recover Co and Li from spent LIBs. They reported that 81.5% of Co and 92.5% of Li were recovered at the optimum leaching condition of 60 °C, S/L 30 g/L, 2 M citric acid concentration, 1.25 vol % H<sub>2</sub>O<sub>2</sub> concentration, and 120 min leaching time. Furthermore, ultrasonic agitation enhanced the recovery of Li and Co. These recovery rates can be increased to 96.4% for Co and 99.8% for Li when the leaching time increased to 300 min, while maintaining the other conditions at their levels discussed above. Table 4 reports few works on acid leaching using organic acid as leaching agents.

**3.3.1.3. Mixed Acid Leaching Process.** Li et al.<sup>68</sup> reported that the leaching efficiency of Co in citric acid is higher than HCl and H<sub>2</sub>SO<sub>4</sub>, and the leaching efficiency of Li is almost

constant in all leaching media. The ultrasonic-assisted leaching process with organic acid was adopted to increase the effectiveness of the process and to mimic the friendly nature of the leaching environment. They used both inorganic and organic acids such as sulfuric acid, hydrochloric acid, and citric acid along with H<sub>2</sub>O<sub>2</sub> as a reducing agent in the leaching process. It was reported that leaching of Co and Li is more efficient with organic acid (citric acid) than inorganic acid (H<sub>2</sub>SO<sub>4</sub>, HCl). More than 96% of Co and nearly 100% Li were recovered in citric acid leaching condition, whereas less than 80% Co was recovered in inorganic acid leaching condition. However, Li leaching was maintained above 90% with inorganic acids. The optimal citric acid leaching condition was 0.5 M citric acid with 0.55 M H<sub>2</sub>O<sub>2</sub>, solid-to-liquid ratio of 25 g/L, temperature of 60 °C, leaching time of 5 h, and ultrasonic power of 90 W. The high leaching efficiency was observed in the citric acid optimal condition, and ultrasonic-assisted technology could be due to the unique cavitation action of the ultrasonic waves. Using citric acid, malic acid, and aspartic acid along with H<sub>2</sub>O<sub>2</sub> reducing agent to recover Co and Li from spent LIBs was reported by Li et al.<sup>123</sup> XRD diffraction and SEM were used to analyze the complete structure and morphology of leaching materials. They varied the parameters such as temperature, time, leachant, H<sub>2</sub>O<sub>2</sub> concentrations, and S/L ratio to understand the Co and Li optimal recovery conditions. It was reported that citric acid and malic acid showed leaching efficiency of 90% for Co and

**Table 5.** Summary of Some Research Results for the Leaching of Spent LIBs in Mixed Acids

Cathode materials	Leaching agent	T (°C)	S/L ratio (g/L)	Time (min)	Leaching rate (%)	Literature
LiCoO <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.55 M H <sub>2</sub> O <sub>2</sub>	60	25	300	47.6% Co 97.2% Li	Li et al. <sup>68</sup>
LiCoO <sub>2</sub>	0.5 M HCl	60	25	300	76.4% Co 95% Li	Li et al. <sup>68</sup>
LiNiCoMnO <sub>2</sub>	0.5 M citric acid + 0.55 M H <sub>2</sub> O <sub>2</sub>	60	25	300	96.1% Co 98.4% Li	Li et al. <sup>68</sup>
LiCoO <sub>2</sub>	0.1 M citric acid + 0.02 M ascorbic acid	80	—	360	80% Co 100% Li	Nayaka et al. <sup>92</sup>
LiCoO <sub>2</sub>	0.4 M tartaric acid + 0.02 M ascorbic acid	80	—	300	97% Co 100% Li	Nayaka et al. <sup>91</sup>
LiCoO <sub>2</sub>	0.1 M iminodiacetic acid + 0.02 M maleic acid + ascorbic acid	80	—	360	91% Co 99% Li	Nayaka et al. <sup>108</sup>
LiCoO <sub>2</sub>	0.5 M glycine + 0.02 M ascorbic acid	80	—	360	95% Co	Nayaka et al. <sup>124</sup>
LiCoO <sub>2</sub>	(0.5–2.0 M) citric acid/malic acid/aspartic acid + (1.0–6.0) vol % H <sub>2</sub> O <sub>2</sub>	90	20	30	100% Li	Li et al. <sup>123</sup>
LiCoO <sub>2</sub>	3 M H <sub>2</sub> SO <sub>4</sub> + 0.4 g/g cellulose	95	25	120	90% Co 54% Co 100% Li	Chen et al. <sup>88</sup>
LiCoO <sub>2</sub>	3 M H <sub>2</sub> SO <sub>4</sub> + 0.4 g/g sucrose	95	25	120	96% Co 100% Li	Chen et al. <sup>88</sup>
LiCoO <sub>2</sub>	3 M H <sub>2</sub> SO <sub>4</sub> + 0.4 g/g glucose	95	25	120	98% Co 96% Li	Chen et al. <sup>88</sup>
LiCoO <sub>2</sub>	1 M tartaric acid + 30 g/L ascorbic acid	80	—	90	84.3% Li 47.3% Co	Cheng et al. <sup>90</sup>
LiCoO <sub>2</sub>	1 M tartaric acid with 20 g/L glucose	80	—	90	82.7% Li 46.6% Co	Cheng et al. <sup>90</sup>
LiCoO <sub>2</sub>	1.5 M phosphoric acid + 0.02 M glucose	80	—	120	Co: 98% ~100% Li	Meng et al. <sup>125</sup>
LiCoO <sub>2</sub>	1.5 M H <sub>2</sub> SO <sub>4</sub> + 30% H <sub>2</sub> O <sub>2</sub> /glutaric acid	90	10	120	87.85% Co 99.91% Li 1.46% Ni	Urbanska. <sup>126</sup>

Li, whereas aspartic acid showed low recovery efficiency. The mechanism of the leaching process initiates, in conjunction with the dissolution of LiCoO<sub>2</sub>, an active material in the presence of H<sub>2</sub>O<sub>2</sub> followed by chelation of Co(II) and Li with organic acids. The reduction reaction of Co(III) to Co(II), dissolution of spent LiCoO<sub>2</sub>, and chelation reaction of CO<sup>2+</sup> and Li with citrate, malate, and aspartate are shown in Figure 9(IV). The possible products were observed during the leaching reaction of LiCoO<sub>2</sub> with citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), and D,L-malic acid (C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>) and L-aspartic acid are reported in Figure 9(b). They found that 90% of Co and nearly 100% of Li were recovered in 1.25 M citric acid, 1 vol % H<sub>2</sub>O<sub>2</sub>, and a 20 g/L S/L ratio in 30 min at 90 °C experimental conditions.

Nayaka et al.<sup>92</sup> reported 100% lithium and 80% cobalt dissolution of LiCoO<sub>2</sub> using a mixture of citric acid and ascorbic acid at 80 °C for 6 h. The experiment was conducted using citric acid as the chelating agent and ascorbic acid as the reducing agent. Another work was presented by Nayaka et al.<sup>91</sup> where they used a tartaric acid and ascorbic acid mixture for leaching process. Experiment was conducted using different concentrations of tartaric acid (0.1–0.5M) with constant concentration of ascorbic acid (0.02M). The experiment condition was maintained at 80 °C for a duration of 5 h, and samples were collected at different time periods to study the leaching percentage of cathode-active materials (LiCoO<sub>2</sub>). It was reported that more than 95% dissolution occurred by using a 0.4 M tartaric acid and 0.02 M ascorbic acid mixture at 80 °C in 5 h. Recently, one more work was published from

Nayaka et al.,<sup>108</sup> where they used iminodiacetic acid (IDA) and maleic acid (MA) and organic acid with a reducing agent (ascorbic acid) to recover Co and Li metals from LIBs. They also found similar observations like those they got in their previous work,<sup>91,92</sup> where 100% lithium and less than 95% Co dissolution occurred at 80 °C in 6 h. In their articles, Nayaka et al.<sup>108</sup> discussed the reductive complexing dissolution mechanism. Figure 9(c) shows the possible complex formation in cobalt and lithium with iminodiacetic acid (IDA) and maleic acid (MA). Nayaka et al.<sup>124</sup> introduced a mixture of glycine and ascorbic acid as leaching regents and observed effective Co recovery when both glycine and ascorbic acid were used. They recovered more than 95% Co by varying the concentration of leachant and reaction time. According to the findings of this study, the optimal condition for highly efficient recovery of Co was achieved with 0.5 M glycine and 0.02 M ascorbic acid in 6 h at 80 °C. Many studies have been reported since the past decade on leaching of LiCoO<sub>2</sub> cathode-active materials using mild organic acids such as citric acid, malic acid, oxalic acid, aspartic acid, and succinic acid with hydrogen peroxide as the reducing agent, and we arranged a complete reported work in organic acid and mixed acid sections. Environmentally friendly and satisfactory results were observed using these mild organic acids. Many researchers used hydrogen peroxide as a reducing agent to improve the leaching efficiency. However, hydrogen peroxide is unstable in the acid leaching process; hence, it is important and essential to find an efficient and stable alternative to hydrogen peroxide. Meshram et al.<sup>99</sup> and Nayaka

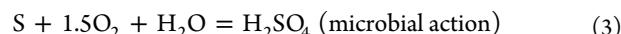
et al.<sup>124</sup> recently used sodium hydrogen sulfite and an ascorbic acid reducing agent as alternatives for hydrogen peroxide. Meng et al.<sup>125</sup> recently focused on glucose as a reducing agent in the leaching process of cathode-active material with phosphoric acid. During the leaching process, glucose can be successively oxidized and decomposed with the formation of monocarboxylic acids, including gluconic acid, tartaric acid, oxalic acid, and formic acid. A possible leaching process of LiCoO<sub>2</sub> materials in the glucose and phosphoric acid solution are shown in Figure 9(d). Meng et al.<sup>125</sup> reported that about 98% Co and nearly 100% Li were leached in 1.5 M phosphoric acid and 0.02 M glucose at 80 °C in 2 h.

Chen et al.<sup>88</sup> investigated the leaching efficiency of Co and Li using three different leaching systems: sulfuric acid + glucose, sulfuric acid + sucrose, and sulfuric acid + cellulose. H<sub>2</sub>SO<sub>4</sub> + glucose leaching system: 98% Co and 96% Li were leached in H<sub>2</sub>SO<sub>4</sub> (3 M), 0.4 g/g glucose, and a 25g/L S/L ratio in 120 min at 95 °C. H<sub>2</sub>SO<sub>4</sub> + sucrose leaching system: 96% Co and 100% Li were leached in H<sub>2</sub>SO<sub>4</sub> (3 M), 0.4 g/g sucrose, and a 25g/L S/L ratio in 120 min at 95 °C. H<sub>2</sub>SO<sub>4</sub> + cellulose leaching system: 54% Co and 100% Li were leached in H<sub>2</sub>SO<sub>4</sub> (3 M), 0.4 g/g glucose and a 25g/L S/L ratio in 120 min at 95 °C. In a similar work, Cheng et al.<sup>90</sup> prepared a leaching solution using tartaric acid and three different reducing agents ((glucose, ascorbic acid, and hydrogen peroxide) to recover lithium and cobalt from LIBs. They studied the leaching efficiency of cathode-active materials using different reducing agents with one leaching agent (tartaric acid). They calculated that 82.4% of Li and 53.2% of Co were recovered using 1 M tartaric acid with 10% H<sub>2</sub>O<sub>2</sub> at 80 °C in 90 min, and 84.3% of Li and 47.3% of Co were recovered using 1 M tartaric acid with 30g/L ascorbic acid at 80 °C in 90 min. Also, 82.7% of Li and 46.6% of Co were recovered using 1 M tartaric acid with 20 g/L glucose at 80 °C in 90 min. Urbanska<sup>126</sup> recovered Co, Li, and Ni from spent LIBs using organic and inorganic reducing agents such as H<sub>2</sub>O<sub>2</sub> and glutaric acid with 1.5 M sulfuric acid as the leaching agent. The recovery rates of Co, Li, and Ni in both reducing agents were analyzed. They found that the highest recovery degrees of the investigated metals (Co, 87.85%; Li, 99.91%; Ni, 91.46%) were obtained in the presence of both H<sub>2</sub>O<sub>2</sub> and glutaric acid (C<sub>5</sub>H<sub>8</sub>O<sub>4</sub>) reducing agents. Natarajan et al.<sup>127</sup> recovered valuable metals such as Li, Co, and Mn by using acetic acid (CH<sub>3</sub>COOH) and water as lixivants. The leaching reaction was conducted using 3 M acetic acid and 7.5 vol % H<sub>2</sub>O<sub>2</sub> at 70 °C and a pulp density of 20 g/L for 40 min to recover 99.9% Li, 98.7% Co, and 99.5% Mn from the spent LIBs. In summary, the dissolutions of LiCoO<sub>2</sub> in different mixed acids are reported in Table 5.

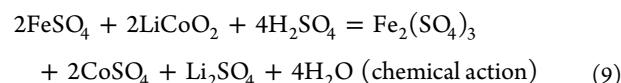
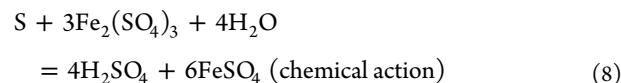
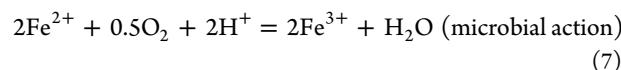
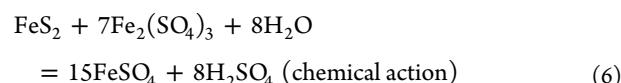
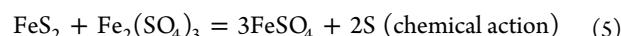
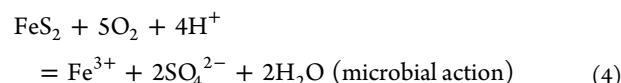
**3.3.1.4. Bioleaching Process.** Apart from direct acid leaching, bioleaching is an interesting process to recover valuable cathode-active materials from spent LIBs. In this process, metabolic products such as inorganic acids and organic acids were released by microbial activities that are involved in the leaching process. The leaching process can proceed through mineral acid and organic acid depending on the ability of bacteria and fungi. Some bacteria possess the ability to produce inorganic acids, and some types of fungi metabolites can produce organic acids that promote leaching processes.<sup>128–131</sup> Brandl and Faramarzi,<sup>132</sup> Rohwerder et al.,<sup>133</sup> and Cerruti et al.<sup>134</sup> reported that bioleaching processes have gradually replaced hydrometallurgical recycling due to their higher efficiency, lower costs, and few industrial requirements.

Mishra et al.<sup>135</sup> investigated a bioleaching method to recycle Co and Li from spent LIBs using chemolithotrophic and acidophilic bacteria and *Acidithiobacillus ferrooxidans*. Elemental sulfur and ferrous ions were utilized to produce metabolites like H<sub>2</sub>SO<sub>4</sub> and ferric ions in the leaching medium to improve the efficiency. The formation of metabolites in the leaching medium helps dissolve LiCoO<sub>2</sub> metal oxide. It is reported that a culture of *A. ferrooxidans* can produce H<sub>2</sub>SO<sub>4</sub> to leach some metals indirectly from LIBs and Co was leached faster than Li.<sup>135</sup> Xin et al.<sup>136</sup> reported the different mechanisms for bioleaching of LiCoO<sub>2</sub> electrodes. The mechanism of Li and Co dissolution in three different energy materials systems such as elemental sulfur (S), pyrite (FeS<sub>2</sub>), and a S + FeS<sub>2</sub> mixed system are presented in the reactions below:

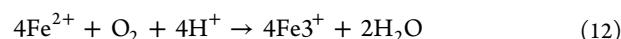
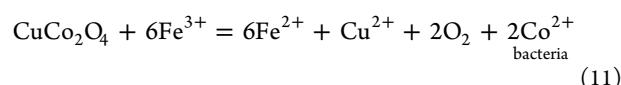
Li dissolution in Sulfur system:



Co dissolution in S + FeS<sub>2</sub> mixed system:



The authors claimed that bioleaching of Li occurs due to biogeneration of H<sub>2</sub>SO<sub>4</sub>, whereas Co dissolution is due to acid leaching and redox reactions involving iron and sulfur. In the presence of iron and sulfur, the metabolism of the energy source generates H<sub>2</sub>SO<sub>4</sub> and Fe<sup>3+</sup> that cause direct acid dissolution of Co<sup>2+</sup> and redox reactions leading to the formation of Fe<sup>2+</sup> which promotes the reduction dissolution of insoluble Co<sup>3+</sup>. Recently, some researchers started to improve the bioleaching efficiency using copper ions and silver ions as catalysts. Zeng et al.<sup>137</sup> reported a bioleaching process by *Acidithiobacillus ferrooxidans* using copper ions and silver<sup>138</sup> ions as a catalyst. They observed 99.9% and 98.4% of Co dissolution at a copper concentration of 0.75 g/L after 6 days and Ag<sup>+</sup> concentration of 0.02 g L<sup>-1</sup> after 7 days, respectively. The catalytic mechanism of the copper ion is reported in eqs 10 and 11 and the reducing effect of iron ion in eq 12

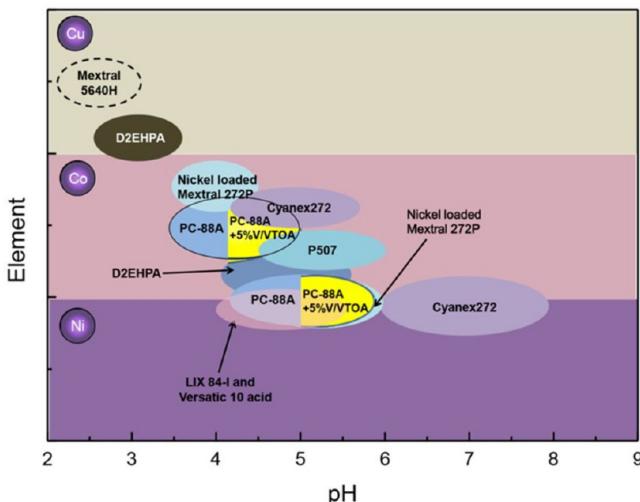


*Aspergillus niger* fungus produces organic acid metabolites such as oxalic acid, citric acid, tartaric acid, and malic acid to

dissolve metals from spent LIBs. Bahaloo Horeh et al.<sup>113</sup> used *Aspergillus niger* for the bioleaching process of spent LIBs which helps secrete organic acid metabolites such as malic, gluconic, oxalic, and citric acids. Citric acid was found to be an effective metabolite in bioleaching process. Here, 95% of Li and 45% of Co were recovered at a pulp density of 1% in a spent medium bioleaching for 16 days. The industrial application of the bioleaching process is really difficult and also not satisfactory due to the slow leaching process, longer treatment period, slow microbial culturing, and use of low concentrations of metal ions, although it has considerable advantages in terms of energy savings and environmental protection.<sup>10</sup>

**3.3.2. Solvent Extraction.** Solvent extraction is a liquid–liquid extraction method, where two immiscible liquids are separated from each other. Solvent extraction is used to recover Co, Li, and Cu from spent LIBs after the leaching process of cathode-active materials. Here, di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis(2,4,4-trimethyl-pentyl) phosphinic acid (Cyanex 272), trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA), or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) were used as extractants in the hydrometallurgy recycling process. This process recovered high percentages and high purities cobalt, nickel, lithium, and copper metals at easy operational conditions and low energy consumption. Cyanex272 is an excellent selective agent in extracting Co; therefore, it has been widely investigated as an extractant for valuable materials in the LIBs. Swain et al.<sup>109</sup> used Cyanex 272 as an extractant with 5 vol % tributyl phosphate (TBP) as a phase modifier and kerosene as a diluent and reported 85.42% Co extraction at pH 5. A similar type of work was reported by Jha et al.,<sup>139</sup> where they used Cyanex 272 as an extractant and isodecanol as a phase modifier. They got 99.9% Co extraction efficiency at pH 5. For example, copper and manganese ions are extracted in good amounts using di(2-ethylhexyl) phosphoric acid (D2EHPA) and extractant, but its selectivity in extracting Co is poor at pH 2.2–3.0.<sup>140</sup> Joo et al.<sup>141</sup> reported that the extraction efficiency of Co with cationic extractant D2EHPA was improved with increasing pH of leachate. Kang et al.<sup>107</sup> reported reductive leaching and solvent extraction with Cyanex 272 to extract Co from the spent LIBs. They initially precipitated the metal ion impurities (copper, iron, and aluminum) to hydroxide form by adjusting the pH (6.5) and then extracted Co from the purified aqueous phase by equilibrating with 50% saponified 0.4 M Cyanex 272 at pH ~ 6. Granata et al.<sup>142</sup> used 2 g/g of H<sub>2</sub>SO<sub>4</sub> and glucose as a reducing agent (excess of 50%) to perform the leaching process. Iron, aluminum, and copper (partially) were removed by precipitation as hydroxides at pH 5.0. Solvent extraction and crystallization methods were used to recover Co and Li. The suitable scales of pH of different extraction reagents are summarized in Figure 10.<sup>141,143–146</sup> Cyanex 272 and P507 present good choices to separate Co and Ni at a pH range between 3 and 5 to avoid the corrosion of the reactors. The additive can change the optimal pH of solvent extraction, which was reported and explained in Figure 10 by Joo et al.<sup>141</sup> The pH reduced to 3.5–4 when only PC-88A was used to extract Co, but after addition of the phase modifier trioctylamine (TOA), the pH scale shifted between 3.5 and 5.

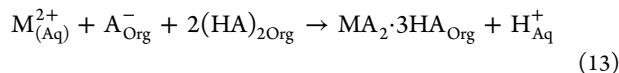
Zhao et al.<sup>147</sup> used a mixture of bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272, HA) and 2-ethylhexyl phosphinic acid mono-2-ethylhexyl ester (PC-88A, HL) in *n*-heptane to extract and separate cobalt(II), manganese(II), and lithium(I)



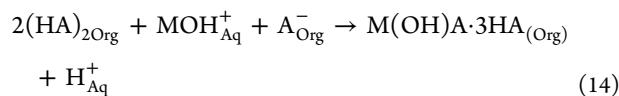
**Figure 10.** Effect of suitable pH on the solvent extraction of different extraction reagents (Lv et al., reproduced with permission).<sup>15</sup>

from a sulfuric acid leaching solution. Extraction of Co<sup>2+</sup>, Mn<sup>2+</sup>, and Li<sup>+</sup> follows the order as Mn > Co > Li, which is also independent of taking the single Cyanex272 or PC-88A or their mixtures as extractants. The possible extracted species MA<sub>2</sub>·3HA or M(OH)A·3HA for a single extractant (PC-88A and Cyanex272 are same) and MH<sub>3</sub>A<sub>2</sub>L<sub>3</sub> for the mixed extractant (M<sup>2+</sup> is Co<sup>2+</sup> or Mn<sup>2+</sup>) and synergistic effect of Cyanex272 + PC-88A were reported.

Granata et al.<sup>142</sup> and Zhao et al.<sup>147</sup> presented extraction mechanism as follows



or



Where,  $\text{A}^-_{\text{Org}}$   $2(\text{HA})_{2\text{Org}}$  represents the saponification reaction as



At the same time, the solvent extraction process has some limitations due to the high cost of the extractants, which can increase the treatment cost when it is scaled up in industry. Therefore, choosing appropriate and cheap solvent extractants is a major challenge that R&D has to overcome to decrease the recycling cost.

**3.3.3. Chemical Precipitation.** Chemical precipitation is a simple and effective process to recover metals from spent LIBs rather than the solvent extraction method. This gives a high purity product with low recycling cost if appropriate chemical precipitation agents are selected. This is based on the different solubilities of metal compounds at certain solution pH. Metal ion impurities and transition metals precipitate at low and high pH, respectively. Contestabile et al.<sup>148</sup> reported the recycling of cathode-active materials from spent LIBs using manual separation, acid leaching, and cobalt hydroxide precipitation processes. The dissolution process of cathode-active materials (LiCoO<sub>2</sub>) was conducted by using 4 M HCl at 80 °C for 1 h. Precipitation agents such as NaOH were used to precipitate

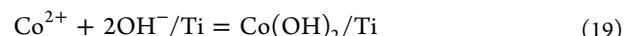
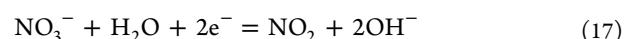
precious cobalt metal to cobalt(II) hydroxide ( $\text{Co(OH)}_2$ ). In this work,  $\text{Co(OH)}_2$  was recovered from an acid leaching solution by addition of 4 M NaOH solution. The authors also observed that precipitation of cobalt hydroxide started at pH 6 and completed at pH 8 (slightly alkaline), and  $\text{Co(OH)}_2$  precipitate can be easily separated from the solution by filtration. Dai et al.<sup>149</sup> found the precipitation rate of Co is over 97% by adding some dispersant and flocculants. They confirmed that ammonium bicarbonate is the best precipitator except for oxalic acid through a series of systematic experiments. Shuva and co-worker<sup>86</sup> reported a leaching and chemical precipitation process to recover Co and Li from LIBs. The optimum condition to recover Co and Li from spent LIBs was found to be HCl (3 M),  $\text{H}_2\text{O}_2$  (3.5 vol %), solid–liquid (S/L) ratio = 1/20 g/mL, 80°, and 60 min. It was reported that around 89% Li and Co were recovered. They also found that  $\text{LiCoO}_2$  dissolution increases with increasing temperatures, HCl concentration, leaching time, and S/L ratio. They suggested that this method can be used in a large scale due to high recovery rates of metal from the spent LIBs.

Guzolu et al.<sup>87</sup> reported that nickel, copper, iron, aluminum, cobalt, and manganese were precipitated from a leaching solution using NaOH, while lithium carbonate was precipitated by addition of a saturated sodium carbonate solution. Saturated diammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  was used to precipitate  $\text{Co}^{2+}$  in the solution and was reported by Hu et al.<sup>150</sup> In this work, the authors calculated the recovery rate of Co and found it to be 96.3% when the pH value is 2, temperature 60 °C, and volume ratio of  $\text{Co}^{2+}$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  is 1:1.5. Zhu et al.<sup>104</sup> reported both an acid leaching and chemical precipitation method which gives recovery rates of 96.3% for Co and 87.5% for Li. They also used diammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  in the leaching solution to get precipitated cobalt(II) oxalate dihydrate ( $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) microparticles, and separated  $\text{Li}_2\text{CO}_3$  precipitates by addition of  $\text{Na}_2\text{CO}_3$ .

**3.3.4. Electrochemical Process.** Nowadays, alternative purification processes such as electrolytic methods are also investigated as boosters in the hydrometallurgical recycling processes. Zhang et al.<sup>151</sup> reported a paired electrolysis approach for recycling spent lithium iron phosphate batteries in molten salts.  $\text{LiFePO}_4$  acts as both anode and cathode, and molten carbonate is the electrolyte in the paired electrolysis approach. The paired electrolysis converts  $\text{LiFePO}_4$  to Fe at the cathode and to  $\text{Fe}_3\text{O}_4$  at the anode while releasing  $\text{Li}^+$  and  $\text{PO}_4^{3-}$  into the molten salt. In another reported work, Zhang et al.<sup>152</sup> used a green electrochemical process to recover Co and Li from spent  $\text{LiCoO}_2$  batteries in molten salts. Lupi et al.<sup>153</sup> has adopted the electrolytic method to recycle Co and Ni from Li-ion and Li–polymer batteries. The cathode-active materials were leached with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  in an appropriate ratio to obtain cobalt and nickel solutions. They applied 250 A/m<sup>2</sup>, pH 3–3.2, and 50 °C, with 87% current efficiency and 2.96 kWh/kg specific energy to recover Ni. They observed that poor Ni powder was produced in 1 h with changing current efficiency (from 70% to 45%) by potentiostatic electrolysis. A current efficiency of 96% and specific energy consumption of 2.8 kWh/kg were obtained for Co at 250 A/m<sup>2</sup>, pH 4–4.2, and 50 °C using a solution containing manganese and  $(\text{NH}_4)_2\text{SO}_4$ . Co recycling as a cobaltite took place at the following conditions: potentiostatic conditions, −0.9 V vs SCE, pH 4, and room temperature. Compared with other technologies, Co produced by the electrolytic method has higher purity and minimal

impurities, but too much electric energy is needed in this recycling method.

Myoung et al.<sup>154</sup> used leaching, an electrolytic method, and a dehydration procedure to extract Co from waste  $\text{LiCoO}_2$ . They used inorganic acid and nitric acid as a leaching agent to recover cobalt ions, and then, the cobalt ion potentiostatically transformed into cobalt hydroxide on a titanium electrode. Finally, a dehydration procedure was used to collect cobalt oxide. Hydroxide ion formation near the electrode via the electroreduction of dissolved oxygen and increase in the local surface pH of the titanium due to nitrate ions was confirmed by the observation of distinct cathodic current peaks in linear sweep voltammetry (voltammetry is the study of current as a function of applied potential). Under appropriate 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. The detailed electrochemical reactions of the electrolytic method are as follows



The reduction of dissolved  $\text{O}_2$  and nitrate ion, i.e., reactions 16 and 17, could increase the local pH of the electrode. Thus, the precipitation of hydroxide films of  $\text{Co(OH)}_2$  (eq 19) under an appropriate pH condition is possible. Therefore, this process provides a good way for recovering cobalt oxide from  $\text{LiCoO}_2$ .

**3.4. Direct Recycling Process.** In this recycling process, active materials of LIBs are recovered directly after a pretreatment process without disturbing the original compound structure. Initially, LIB elements are separated, by using physical separation methods, magnetic separation, and thermal processing to avoid chemical breakdown of the active materials. In the second step, recovered purified active material surface and bulk defects are repaired by relithiation or hydrothermal processes. Recycling of NMC batteries by a direct recycling process is still challenging due to the mixture of more than one active material. However, a direct recycling approach has many advantages compared to pyrometallurgy and hydrometallurgy because of the following: (a) It is a simple recycling process. (b) Cathode materials can be reused directly after regeneration. (c) It is associated with lower emissions and less secondary pollution.<sup>155</sup> This relatively short, green, and simple recycling process shows great potential for commercial recycling of spent Li-ion batteries. The advantages and disadvantages of direct recycling process are summarized in Table 2.

Shi et al.<sup>155</sup> used a hydrothermal treatment and a short annealing process to reuse cathode materials. This process is very simple, environmentally friendly, and effective compared to the conventional chemical leaching or solid-state synthesis approach. The morphology and structure of  $\text{LiCoO}_2$  particles along with high specific capacity and cycling stability were maintained after the recycling process. The authors also proposed a greener, simpler, and more energy-efficient strategy to recycle and regenerate  $\text{LiCoO}_2$  cathode materials with high electrochemical performance. Shi et al.<sup>156</sup> reported a non-

**Table 6.** Direct Recycling Process to Recover Cathode Materials and Their Performances

Direct recycling process	Performance	Literature
Hydrothermal: 220 °C 4 h	LiCoO <sub>2</sub> : 91.2% capacity retention after 100 cycles at 1C (3–4.3 V); 141.9 mAh/g at 2C and 130.3 mAh/g at 5C	Shi et al. <sup>155</sup>
Short annealing: 800 °C 4h		
Hydrothermal: 220 °C 4 h	NMC 111: first discharge capacity of 158.4 mAh/g at 1C and 122.6 mAh/g after 100 cycles	Shi et al. <sup>156</sup>
Short annealing: 850 °C 4h in O <sub>2</sub>	NMC 532: 128.3 mAh/g after 100 cycles	
Solid phase sintering: 700 °C 8 h; doping ratio between spent LFP with new LFP: 3:7	LiFePO <sub>4</sub> : 144 mAh/g at 0.1C (2.5–4.1 V); 135 mAh/g after 100 cycles	Song et al. <sup>157</sup>
Solid phase heat treatment: 650 °C 1 h under Ar/H <sub>2</sub> flow; Li <sub>2</sub> CO <sub>3</sub> as lithium source	LiFePO <sub>4</sub> : first discharge capacity of 147.3 mAh/g (2.5–4.2 V); 140.4 mAh/g after 100 cycles at 0.2C and capacity retention 95.32%	Li et al. <sup>158</sup>
Solid phase sintering: 850 °C; Li <sub>2</sub> CO <sub>3</sub> as lithium source	LiCoO <sub>2</sub> : first discharge capacity of 150.3 mAh/g (3.0–4.3 V) at 0.1C; 140.1 mAh/g after 100 cycles	Chen et al. <sup>159</sup>
Hydrothermal: 80 °C 6 h; ultrasonic power: 600 W	LiCoO <sub>2</sub> : first discharge capacity of 133.5 mAh/g; 99.5% capacity retention after 40 cycles	Zhang et al. <sup>160</sup>

destructive process to directly reuse degraded NCM cathode particles to obtain new active particles. Directly regenerated high performance NCM cathodes showed high specific capacity, good cycling stability, and high rate capability when compared to the traditional hydrometallurgical methods. Song et al.<sup>157</sup> reported direct regeneration of cathode materials from spent LiFePO<sub>4</sub> batteries using a solid phase sintering method. The battery capacities of regenerated LiFePO<sub>4</sub> can reach over 120 mA h g<sup>-1</sup> at 0.1C discharge conditions, especially with the highest value of 144 mA h g<sup>-1</sup> with a doping ratio of 3:7 at 700 °C. Li et al.<sup>158</sup> reported a green recycling process (direct regeneration process) of a cathode mixture material from scrapped LiFePO<sub>4</sub> batteries. The high purity cathode material mixture, anode material mixture, and other byproducts are recycled at high yields. Chen et al.<sup>159</sup> reported a simple and green recycling process to recycle spent 18650-type LiCoO<sub>2</sub> batteries. Solid phase sintering at 850 °C and Li<sub>2</sub>CO<sub>3</sub> as the lithium source were used for renovation of the LiCoO<sub>2</sub> with outstanding cycling stability. Table 6 shows the direct recycling process to recover the cathode materials and the expected performance of the new produced LIBs.

**3.5. Challenges and Life Cycle Assessment of LIBs.** Li-ion batteries (LIBs) have been used in cell phones and laptops for about two decades, and technology is considered relatively mature based on the current battery chemistry. Nowadays, LIBs have been commercialized and play a major role in electric vehicles. One of the major challenges of LIBs is their ability to be used as competitive energy storage technology to store sustainable energy generated from renewable sources, which requires development of next-generation LIBs at low cost. The increasing demand for energy storage requires further improvements in the existing Li-ion batteries. However, it is still considerably challenging to develop new battery chemistry to replace the existing Li-ion battery technology.<sup>29</sup> In order to improve the performance of batteries, researchers have discussed large numbers of anode candidates which could dramatically increase the specific energy capacities. Si- and Sn-based anodes are highly attractive and are of great interest to researchers<sup>161</sup> and industry to develop high performance batteries, but preparing Si nanomaterials on a large scale with low cost seems to be a little challenging for this technology. Additionally, Sn-based anodes show poor cycling performance due to pulverization. The existing cathode material LiCoO<sub>2</sub> is expensive and highly toxic, which partly played a role in increasing the demand of LiFePO<sub>4</sub> and other cheaper cathode chemistries. The NMC-based cathodes developed by Argonne National Laboratory are highly attractive and are used

extensively in the industry.<sup>29</sup> However, the valuable metals used in NMC such as Co and Ni are expensive and toxic and also give a cathode with moderate specific capacity. Therefore, intensive research is required to gain better understanding of the cathode chemistry and charging/discharging mechanisms to develop low-cost cathode materials based on Mn and/or Fe. Environmental perspectives and safety concerns suggest that Co and Ni can be replaced with nontoxic and low-cost cathode materials. Developing nonflammable Li-ion batteries by using aqueous electrolytes or ceramic electrolytes and all-solid-state batteries are other solutions toward a more sustainable future of LIBs. Developing green batteries with low carbon footprints is another challenge for LIBs.<sup>162</sup> Therefore, the future LIBs should focus more on using biologically derived organic or inorganic electrodes, biomass-based carbon and silicon, and aqueous electrolytes.

Life cycle assessment (LCA) is an important tool for the development of the next-generation Li-ion batteries, which can contribute to a sustainable economy in the future. LCA studies always help researchers develop models to evaluate the next-generation Li-ion batteries with the goal of achieving optimized social, environmental, and economic impacts. LCA of a battery provides full information about production, use, end-of-life treatment, and final disposal and recycling. The existing cathode materials such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, and LiFePO<sub>4</sub>; anode materials such as graphite and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>; electrolytes/salts such as ethylene carbonate, diethyl carbonate, LiPF<sub>6</sub>, LiBF<sub>4</sub>, and LiClO<sub>4</sub>; and separators such as polypropylene and polyethylene still require further analyses from the LCA perspectives.<sup>163</sup> The environmental impact of battery production is the primary concern for researchers. Three major issues need to be addressed during battery production:<sup>28</sup> (1) environmental burden during the production of raw materials or battery manufacture, (2) battery component impact on the environment, and (3) environmental impact during development of alternative cathode materials and anode materials. The use of suitable cathode and anode materials might reduce the environmental burden. Yu et al.<sup>164</sup> studied the environmental impact of LiFe<sub>0.98</sub>Mn<sub>0.02</sub>PO<sub>4</sub>/C, LiMn<sub>2</sub>O<sub>4</sub>/C, C/LiFePO<sub>4</sub>, and FeF<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>/C batteries production processes by using a footprint family of indexes. LiFe<sub>0.98</sub>Mn<sub>0.02</sub>PO<sub>4</sub>/C batteries showed a higher environmental burden than that of C/LiFePO<sub>4</sub> batteries. The environmental burden of FeF<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>/C batteries is extremely smaller than the other batteries. This could be due to the simple and environmentally friendly synthesis technology and low amounts of raw materials. They concluded that the environmental effects of Li are greater than

those of Fe. Wu and Kong<sup>165</sup> compared the cradle-to-gate LCA of three batteries: Li metal anode (NCM-Li), silicon nanowire anode (NCM-SiNWs), and graphite anode (NCM-C). They found that a high specific energy anode produces less pollution during battery production. They also found that a NCM-Li battery has a lower environmental burden than the other two types of LIBs they considered in this study.

#### 4. CONCLUSIONS

In this electrified world, a significant and state-of-the-art role has been played by LIBs due to their abilities to store and release energy in short times, to reduce energy use via higher roundtrip charge–discharge cycles, to reduce environmental pollution in stationary, portable, and transport systems. The increasing interest on using LIBs in portable electric devices and electric vehicles (EVs) have introduced large amounts of spent batteries in some countries (e.g., China and some European countries), which results in a major environmental issue; therefore, recycling of LIBs has become an urgent need to save the environment and simultaneously reduce the dependency on mined, high cost materials such as cobalt and lithium. In this review, battery chemistry, degradation mechanism, pretreatment processes, and pyrometallurgical and hydrometallurgical methods are well explained. In the leaching of cathode-active materials,  $\text{LiCoO}_2$ , with inorganic acid produces  $\text{Cl}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_2$  gases, which have adverse impacts on the environment. These gases react with moisture in the air to produce  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  acid molecules that later form acid rain. To overcome these issues, many researchers implemented organic acid leaching agents such as citric acid, ascorbic acid, malic acid, succinic acid, maleic acid, and tartaric acid in the recycling process of Li-ion batteries and at the same time to avoid the consumption of high acid amounts. Other researchers have also used  $\text{H}_2\text{O}_2$  and organic reducing agents to increase the dissolution process and leaching efficiency within a short period of time. Many researchers concluded that the variable operating temperatures and concentrations of leaching agents may not significantly impact the leaching process, but with the presence of reducing agents, the recovery percentage could be improved to more than 90% for both Co and Li elements.

#### Future Perspectives.

- Many researchers have been working on different leaching (acid, bioleaching, and alkaline leaching) and separation processes to recover precious metals such as cobalt, lithium, and nickel from spent Li-ion batteries, but as per our knowledge, there is a lack of research on recycling of anode materials from spent LIBs. Very few studies such as the one by Natarajan and Aravindan<sup>166</sup> reported the present status of LIB recycling in industries or research progress of graphite reuse in lab scale and applications in energy. However, more research is needed in this area to recover graphite (anode) and electrolytes from Li-ion batteries and to develop high performance LIBs for EVs
- The chance of corrosion during the leaching process is highly possible. Instruments are used during the leaching and separation process, which indicates the need for R&D of the advanced leaching equipment and systems.
- Recent research in the bioleaching process supports its environmentally friendly aspects, yet the high cost may limit scaling of the process at industrial levels. In

addition, this process has lower recovery rates and requires long leaching times. Therefore, research may need to focus more on the recycling efficiency and application of this novel leaching process.

- Studies on the use of recovered cathode materials are limited, which implies the need for more work in this area to compare recycled vs virgin materials in making current and future generation Li-ion batteries.
- Potential to recycle and/or appropriately dispose of other materials such as polymers, electrolytes, current collector metals, and separators can lead to more economic advantages of the recycling process and can help reduce the environmental impacts from battery recycling.

#### ■ AUTHOR INFORMATION

##### Corresponding Author

Ahmad T. Mayyas – Department of Industrial and Systems Engineering, Khalifa University, 127788 Abu Dhabi, United Arab Emirates (UAE);  [orcid.org/0000-0002-0367-6503](https://orcid.org/0000-0002-0367-6503); Phone: +971-50-4381470; Email: [ahmad.mayyas@ku.ac.ae](mailto:ahmad.mayyas@ku.ac.ae)

##### Authors

Kishore K. Jena – Department of Industrial and Systems Engineering, Khalifa University, 127788 Abu Dhabi, United Arab Emirates (UAE);  [orcid.org/0000-0002-9941-1859](https://orcid.org/0000-0002-9941-1859)

Akram Alfantazi – Department of Chemical Engineering and Emirates Nuclear Technology Center, Khalifa University, 127788 Abu Dhabi, United Arab Emirates (UAE);  [orcid.org/0000-0002-4039-5110](https://orcid.org/0000-0002-4039-5110)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acs.energyfuels.1c02489>

##### Author Contributions

K.K. Jena selected the topic of this review and wrote the final draft. A.T. Mayyas supervised and did the final checking of the manuscript. A. Alfantazi did the final checking of the manuscript.

##### Notes

The authors declare no competing financial interest.

##### Biographies

Dr. Kishore K. Jena is currently working as a research scientist at Khalifa University, Abu Dhabi, UAE. Dr. Jena received his Ph.D. in 2012 from IICT-CSIR, Hyderabad, India, with a specialization in polymer chemistry. Then, he joined the University of Hawaii at Manoa, USA, as a postdoctoral fellow. His research interests focus on hybrid materials, polymers, coatings, functional materials for energy storage devices, and the recycling techniques for spent LIBs. He has published 40 research articles.

Dr. Akram Alfantazi is a professor in the Department of Chemical Engineering at Khalifa University, Abu Dhabi, UAE. He obtained his M.A.Sc. and Ph.D. in metallurgical engineering from Queen's University, Canada. Dr. Alfantazi has 200 refereed journal publications. He is a Fellow of the NACE International and Engineering Institute of Canada. He has received awards for his work including the Canadian Materials Chemistry Award. He was appointed a Chang Jiang Scholar at the China University of Mining and Technology.

Dr. Ahmad T. Mayyas is an assistant professor of Industrial and Systems Engineering in Khalifa University, Abu Dhabi, UAE. Before

joining Khalifa University, he worked as a clean energy systems analyst at the National Renewable Energy Laboratory in Golden, Colorado. He is currently involved in R&D activities of renewable energy systems, manufacturing of fuel cells, and Li-ion batteries. Dr. Mayyas worked as a research fellow at the University of California-Berkeley and Lawrence Berkeley National Laboratory between 2013–2015.

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