



Queensland University of Technology
Brisbane Australia

This may be the author's version of a work that was submitted/accepted for publication in the following source:

Garole, Dipak, Hossain, Rumana, Garole, Vaman J., Sahajwalla, Veena, [Nerkar, Jawahar](#), & [Dubal, Deepak](#) (2020)

Recycle, recover and repurpose strategy of spent Li-ion batteries and catalysts: Current status and future opportunities.

ChemSusChem, 13(12), pp. 3079-3100.

This file was downloaded from: <https://eprints.qut.edu.au/200849/>

© 2020 Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim

This work is covered by copyright. Unless the document is being made available under a Creative Commons Licence, you must assume that re-use is limited to personal use and that permission from the copyright owner must be obtained for all other uses. If the document is available under a Creative Commons License (or other specified license) then refer to the Licence for details of permitted re-use. It is a condition of access that users recognise and abide by the legal requirements associated with these rights. If you believe that this work infringes copyright please provide details by email to qut.copyright@qut.edu.au

Notice: *Please note that this document may not be the Version of Record (i.e. published version) of the work. Author manuscript versions (as Submitted for peer review or as Accepted for publication after peer review) can be identified by an absence of publisher branding and/or typeset appearance. If there is any doubt, please refer to the published source.*

<https://doi.org/10.1002/cssc.201903213>



ChemSusChem

Chemistry–Sustainability–Energy–Materials

 **Chemistry
Europe**

European Chemical
Societies Publishing

Accepted Article

Title: Recycle, Recover and Repurpose Strategy of Spent Li-ion Batteries and Catalysts: Current Status and Future Opportunities

Authors: Dipak J. Garole, Rumana Hossain, Vaman J. Garole, Veena Sahajwalla, Jawahar Nerkar, and Deepak Dubal

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *ChemSusChem* 10.1002/cssc.201903213

Link to VoR: <https://doi.org/10.1002/cssc.201903213>

WILEY-VCH

Recycle, Recover and Repurpose Strategy of Spent Li-ion Batteries and Catalysts: Current Status and Future Opportunities

Dipak J. Garole^{1*}, Rumana Hossain², Vaman J. Garole³, Veena Sahajwalla², Jawahar Nerkar,^{4,5}
Deepak P. Dubal^{4,5**}

^{1*}Dipak J. Garole

Directorate of Geology and Mining,
Government of Maharashtra, Nagpur-440010, India.
Email: drdipakgarole@gmail.com

²Dr. Rumana Hossain and Prof. Veena Sahajwalla

Centre for Sustainable Materials Research and Technology (SMaRT@UNSW),
School of Materials Science and Engineering,
University of New South Wales (UNSW), Sydney, NSW 2052, Australia

³Vaman J. Garole

Department of Chemistry, K.E.S. S. P.Jain Jr. College, Nagothane, Dist.Raigad, M.S. India

^{4*}Dr. Deepak Dubal and Dr. Jawahar Nerkar

Centre for Materials Science, Queensland University of Technology (QUT), 2 George Street,
Brisbane, QLD 4001, Australia.

^{5*}Dr. Deepak Dubal and Dr. Jawahar Nerkar

School of Chemistry and Physics, Queensland University of Technology (QUT), 2 George Street,
Brisbane, QLD 4001, Australia
Email: deepak.dubal@qut.edu.au

Accepted Manuscript

Abstract

The disposal of hazardous waste of any form has become a great concern for the industrial sector due to improved environmental awareness. The increase in usage of hydroprocessing catalysts by petrochemical industries, and lithium-ion batteries (LIBs) in portable electronics and electric vehicles will soon generate a large amount of scrap and create significant environmental problems. Like general electronic wastes, spent catalysts and LIBs are currently discarded in municipal solid waste and disposed of in landfills in the absence of policy and feasible technology to drive alternatives enough policy and feasible technology. Such inactive catalyst materials and spent LIBs exhibit not only hazardous heavy metals but also toxic and carcinogenic chemicals. Besides polluting the environment, these systems (spent catalysts and LIBs) contain valuable metals such as Ni, Mo, Co, Li, Mn, Rh, Pt, and Pd. Therefore, the extraction and recovery of these valuable metals has significant importance. In this review, we have summarized the strategies used to recover valuable (expensive) as well as cheap metals from secondary resources – especially spent catalysts and LIBs. The first section contains the background and sources of LIBs and catalyst scraps with their current recycling status, followed by a brief explanation of metal recovery methods such as pyrometallurgy, hydrometallurgy and biometallurgy. The recent advancements in these methods are critically summarised. Thus, the review provides a guide for the selection of adequate methods for metal recovery and future opportunities for the repurposing of recovered materials.

Keywords: Metals recovery, Heavy metals, Spent catalysts and Li-ion batteries, Hydrometallurgy.

1. Introduction

The second half of the 20th century has witnessed enormous advancements in catalysis for the refining and petrochemical industries, as well as Li-ion batteries (LIBs) for portable devices (mobile phones, laptops, cameras, etc.) and large-scale energy storage systems (electric vehicles and renewable sources). In the former case, the main categories of catalysts belong to heterogeneous catalysis, and contain sulphur, metals, acid and bifunctional catalysts with lesser degree of oxide phases [1]. Catalysts are crucial in the production of gasoline, diesel fuel, jet fuel, heavy hydrocarbons, petrochemicals and plastics in the petroleum distillation and petrochemicals industry. Due to the lack of regeneration and reactivation technologies for deactivated catalysts, the spent catalysts are discarded as solid waste [2-4]. Although spent refinery catalysts correspond to about 4 wt.% of the overall refinery waste [5], they are classified as one of the most hazardous wastes generated in petroleum refineries. The main catalytic solid-waste contains various metals including V, Co, Ni, Mo, Al and Fe, and nonmetallic components such as sulphur, oil and carbon that are a threat to the environment [6].

Similarly, the usage of LIBs as power sources for devices ranging from mobile phones to electric vehicles (EV) is increasing at an alarming rate, which leads to a vast amount of waste at their end-of-life [7-9]. For instance, global sales of EVs were at 2 million units in 2018, and could reach 140 million by 2030 – once countries attain the Paris climate agreement to reduce greenhouse gas emissions [9]. As LIBs continue to electrify our world, it is estimated that over 11 million tonnes of spent LIBs will be discarded through to 2030, and less than 5% of them are being recycled so far [10]. In addition, the increased production of LIBs will impose an extra burden on crucial element resources (Li, Ni, and Co), which will result in increased prices of raw materials. Due to high prices of raw materials, the global LIBs recycling market was valued at about \$1.78 billion in 2017 and is expected to reach \$23.72 billion by 2030, suggesting a significant opportunity for the recovery of valuable metals from spent LIBs [11-12]. In addition to metals, LIBs contain poisonous electrolytes (lithium hexafluorophosphate, LiPF₆) and carbonaceous materials.

The disposal of inactive catalyst materials and spent LIBs containing hazardous heavy metals and toxic/carcinogenic chemicals has spurred an interest in recycling, and engenders acute effects on the environment [13-14]. The improper disposal of spent catalysts and LIBs prominently affects soil and underground water with the heavy metals like Co, Mn, and Ni [15-16]. Additionally, the accumulation of spent catalysts and LIBs need to be recycled to capitalize on resources for new LIBs – considering the shortage of raw materials (e.g. Co, Ni, Mn, Li, and Cu). Due to the infancy of spent catalysts and LIBs – unlike other solid waste – nearly all recovery or recycling technologies and processes persist up to the laboratory test. Few recent review articles have provided a summary of recycling or recovery technologies and processes for catalysts and spent batteries [17-18]. Most of

the reviews are focused on the recycling of portable batteries, involving collection, sorting, processing and associated recovery technologies. However, an independent review of the summary of recent advances in metal recovery technologies for spent catalysts and LIBs has not been presented.

Generally, physical, chemical, and combinations of physical and chemical processes are commonly used in recycling processes for spent catalysts and LIBs. Physical processes include mechanical separation, thermal treatment, mechanochemical processing, and dissolution processing. The present review begins with an introduction to different metal recovery methods such as pyrometallurgy, hydrometallurgy and biometallurgy with their merits and demerits. A brief summary of the recovery of nickel, cobalt, lithium, manganese and other metals from spent sources using leaching, extraction, precipitation, ion exchange, bio-adsorbent and solvent extraction methods is provided. This comprehensive summary will further guide researchers or industrialists in selecting of suitable methods for metals recovery from secondary resources. The reason spent catalysts and LIBs are grouped together in this review is their similar waste content as well as the utilisation of similar metal recovery methods. In addition to recycling, the present review provides new opportunities for the repurposing sector to recover materials for future applications such as LIB (back integrated), supercapacitors, oxygen evolution reaction (OER), adsorption and photocatalytic studies.

2. Background: Spent catalysts and LIBs

2.1 Spent catalysts

Spent catalysts are the most important solid wastes of the petrochemical, fertiliser and oil industries, and include a mixture of hazardous metal elements (such as Ni, Fe, Mo, Al and Co) and a few organic pollutants [19]. Due to the deposition of metal sulphides/oxides and metal-organic compounds during the reaction, the catalyst loses its activity as well as specificity [20, 21]. Conventionally, the spent catalysts were sent to landfill, however, due to severe environmental impacts, adequate methods need to be developed to recover precious metals from this waste [22, 23]. In order to protect the environment, spent catalysts are not subjected to metal extraction by different solubilisation processes or repurposed for diverse applications [24]. Processing of spent nickel catalyst technology, shown in the pre-treatment process Figure 1, involves crushing, screening and incineration depending on the nature of spent materials [25]. In addition, metal recovery can be achieved using different techniques – including pyrometallurgy, hydrometallurgy and bio-metallurgy methods – which are described in the following sections. Further, the metals are concentrated and purified using precipitation, cementation, extraction and ion exchange procedures, and recovered using electrolysis and precipitation methods [26].

2.2 Spent LIBs

The growing potential usage of Li-ion technology in automobiles and end-user electronics could continue their dominance in the future, and augments the demand for battery materials and resources. Energy demand in the battery sector was 102 Gigawatt hours (GWh) in 2017, and expected to reach 709 GWh until 2026 [27]. Additionally, the global sales of EVs were 2 million units in 2018 and could reach 10.79 million units by 2025 as nations reduce their greenhouse gas emissions [28-29]. This initiative will further boost the demand for resources including cobalt and lithium; and on the other hand, will increase the volume of spent LIBs (Figure 2) [30]. In order to develop recycling strategies, it is important to understand the structure, charge-storage mechanisms and components of LIBs. In contrast to conventional batteries, lithium ions transport from one electrode to the other, and electrodes are maintained at different potentials, generating electricity. In general, a LIB consists of an anode, cathode, electrolyte, separator, outer casing and sealing parts, and occurs in cylindrical, coin, prismatic and thin/flat pouch cell designs as shown in Figure 3. The anode is normally a graphite material while various Li-based oxides/phosphides such as LiCoO_2 , LiMn_2O_4 , LiFePO_4 , $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ (NCM) are used as cathode materials. However, the major market is still occupied by LiCoO_2 and $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ based cathode materials, which contain cobalt as a hazardous heavy metal [21]. Li and Co are also more costly relative to other metals. In addition, Co and Li content in LIBs is in the range of 2-7 wt. % and 5-15 wt. %, respectively, which are higher than those in natural ores [26, 31]. Such diverse chemistries (cathode materials) and different cell designs pose additional difficulties in LIB recycling.

A variety of research has been performed for the development of recycling of LIBs to recover battery components. However, to recover materials effectively, physical pre-treatment is typically applied – where special streams of waste materials ensure that efficient separation for further processing is obtained [31]. So far, researchers have proposed recycling and recovery of metals from spent LIBs, however, we have proposed 3-R approach, Recycling, Recovery and Re-use. Figure 4 shows 3-R, a closed-loop approach for the recycling of spent LIBs. At pre-treatment stage, hazardous materials are removed, and the LIBs' components are separated. The secondary treatment stage is concentrated on improving the dissolving the composition of spent LIBs and separation of the components. Finally, a deep recovery stage is utilised to recover expensive and low-cost metal products such as Mn, Li, Al, Co, and Fe, as well as plastics. Common metal products such as Al, Cu and Fe are removed in the elemental state, while the rest of the metals are retrieved in a combined state. The re-purposing of recovered metals (or wastes) from spent LIBs and catalysts is rarely reported, however, some recent reports are summarised in the next section.

3. Roadmap to the recovery of valuable metals from spent sources

Based on the literature, research into the recycling and recovery of metals from spent LIBs and catalysts is becoming a hotspot and global concern. To date, three main methods have been developed for the recovery of valuable metals from spent catalysts and LIBs – pyrometallurgy, hydrometallurgy, and biometallurgy. Thermal treatment (pyrometallurgy) is a commonly used method for the removal of carbon and organic moieties from the current collectors at certain temperature conditions. Nevertheless, this method consumes a large amount of energy for heating, as well as requiring a special set-up for the purification of toxic gases emitted by the combustion [32]. In addition, pyrometallurgy accounts for the lowest recovery rate of all the treatment approaches. In contrast, hydrometallurgical and biometallurgy are the most commonly preferred routes for the recycling of spent catalysts and LIBs – due to advantages such as low energy consumption, minimization of waste water, and a high percentage recovery of metals (57.25%) with high purity [33-35]. This section provides a brief description of the different metal recovery methods and summarizes their progress.

3.1 Pyrometallurgy

Pyrometallurgy is a conventional metal recovery method, which refers to the high-temperature treatment of various wastes and recycling them via high-temperature chemical reactions. This process contains several different steps, which include calcining, roasting, smelting and refining to recover the metals. Recovery involves heat treatment of metal and ores comprising wastes to perform the transformation of their physical and chemical states, which enables the extraction of valuable metals [36].

3.1.1 Pyrometallurgy for the spend catalysts

To recover metals from spent catalysts, a variety of processing approaches have been proposed [37], including pyrometallurgy followed by a hydrometallurgy process. To recover metals from spent hydro-processing catalysts, techniques such as direct smelting, calcination and smelting, chlorination and salt roasting have been applied [38]. Reagents such as NaOH, H₂SO₄, NH₃, (NH₄)₂SO₄ and oxalic acid have also been utilised for metal recovery [39-41]. Busnardo et al [42] reported on the spent catalyst leaching efficiency of Mo, Co, Ni, V and Al using oxalic acid solution with H₂O₂ addition; potassium bisulfate fusion between 350 and 600 °C; followed by water leaching. The effects of oxalic acid concentration and H₂O₂ on the rate of metal leaching were investigated, and it was found that high metal recovery was achieved at 3M conc. of H₂O₂ oxalic acid [43]. Typically, pyrometallurgy recovery processing can be classified in three different categories such as high-temperature incineration, vacuum carbon-thermal reduction and chlorination volatilization methods.

3.1.2 Pyrometallurgy for spent LIBs

Pyrometallurgy can quickly remove organic compounds such as carbon powder, PVDF, and plastics from spent LIBs. In brief, the method begins by dismantling full-size battery packs into individual cells. After that, the battery cells are fed into a shaft furnace. In the shaft furnace, the battery cells are heat treated in several temperature zones, namely, 1) pre-heating, 2) plastics pyrolysing and 3) smelting and reduction zone. In the pre-heated zone (or cold zone) of the furnace, the spent LIBs are heated up to a temperature less than 300 °C, to release electrolyte vapour without explosion. In the plastic pyrolysing zone, plastics from the spent batteries are destroyed and reduced. For this, the temperature is maintained at ~700 °C. Due to the reduction of plastics, the energy consumption in the next steps can be significantly reduced. In the last zone, the materials are smelted and form an alloy with copper, cobalt, nickel, and iron, there is also formation of a slag containing lithium, aluminum, silicon, calcium, and a part of iron.

3.1.3 High-temperature incineration

This process deals with the burning of wastes in an incinerator. In the incineration process, calorific values are generated by charging the flammable non-metallic compounds, and metals can be collected from the disposed residues. The purification of the metal extracted by the incineration process is carried out in other refining processes [44]. Currently, this method is mainly employed for the recovery of rare and precious metals – such as Au, Pt, Pd, and In – as well as Co from e-waste and spent catalytic converters from automobiles. The high-temperature ignition method can separate metals from non-metals, and rare earth metals are enriched in the residues – which can be further extracted by electrolytic or fire refining. The Umicore (battery recycling industry) integrated smelter and refinery is a good example of a high-temperature incineration process focused on the recovery of rare and precious metals from waste electrical and electronic equipment (WEEE). Metals recovered include Ag, Au, Pt, Pd, Rh, Ru, Ir, In, Se, and Te [45]. Initially, WEEE undergoes pre-treatment (such as dismantling, shredding and physical processing) followed by smelting in the Isa Smelt furnace. After smelting, nearly all the rare and precious metals are concentrated in the slag, which is further refined to gain high-purity rare and precious metals, step by step.

3.1.4 Vacuum carbon-thermal reduction

In the vacuum reduction metal recovery method, metal oxides in the wastes are transformed into metals using reducing agents via thermal routes. Typically, some wastes – such as LiCoO_2 in spent LIBs, indium oxides in LCD screens, and germanium oxide in fly ash – are in the form of single oxides at high concentrations, and can be easily extracted by this process. Li [46] and co-workers have developed an eco-friendly, oxygen-free roasting and wet magnetic separation technology for the direct recovery of Co, lithium carbonate and graphite from mixed electrode materials [46]. The reaction was performed at below 1000°C for 30 min with excellent recovery rates of 95.72%, 98.93%

and 91.05% for Co, Li, and graphite, respectively. Thus, the oxygen-free roasting and wet magnetic separation processes involved in vacuum thermal reduction are promising for the recovery of the individual products of cobalt, lithium carbonate and graphite from the mixture of LiCoO_2 and graphite powders. In addition, it is essential to note that no toxic chemicals are utilized in the process, signifying a green approach.

3.2.5 Chlorination volatilization method

This process deals with the heating of waste resources in the presence of chlorination agents to generate the volatile chlorides trapped in soot and lotion. This is pursued by the metal recovery process of hydrometallurgy. This technique was first implemented to recover Au from mines, and is currently employed to extract metals from e-waste. Ma et al [47] utilized an efficient vacuum-chlorination separation process. In this case, NH_4Cl was used as chlorinated agent for the recovery of In from spent LCD panels. The results recommended that the rough vacuum atmosphere concurrently enhanced the recovery rate of In and decreased the effect of tin. Also, under different condensing temperatures, indium chloride and ammonium chloride can be selectively recovered. Experimental environments such as temperature, time, vacuum level and concentration of chlorinating agent (NH_4Cl) were optimised to improve the yield and purity of indium chloride. Thus, this method successfully recovered highly pure indium chloride from the waste LCD panels with In recovery rates of 98.02% and 99.50% purity of indium chloride.

In summary, pyrometallurgy is a promising metal recovery process for various waste materials, which is pursued by additional refining methods. The method is relatively easy and has a great capacity and broad range of applications, which additionally permits the calorific value of the non-metallic parts of urban mines to be recycled. Therefore, this technology has been in exercise for years, to recover valuable metals from waste. Nevertheless, the method is responsible to create a sequence of environmental issues including emission of hazardous organic volatile compounds and deadly smoke caused by the existence of halogenated flame retardants. Furthermore, it does not have a wide variety and has less selectivity, consumes huge amount of energy and accounts for low metal recovery. More significantly, the equipment is not cost-efficient, demanding large investment. Hence, the process is not suitable for small and medium-sized enterprises.

3.2 Hydrometallurgy

Hydrometallurgy is the most common and industrially adopted method, which consists of two important processes. These are dissolution and leaching of metals from waste; and their isolation, extraction and purification. Initially, the metal compounds (oxides) are selectively dissolved using an appropriate leaching agent, subsequently separated and purified using several different methods – such as precipitation, ion adsorption, solvent extraction, ion exchange, electrochemical reduction and other processes [48]. Various studies on metals recovery from spent catalysts and LIBs have been

performed globally [49, 50] using hydrometallurgy methods. These are shown in Table 1 (with different inorganic and organic acids). The following sections briefly describe the use of leaching to recover metals from spent LIBs and catalysts using separation and purification methods.

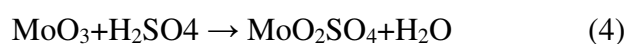
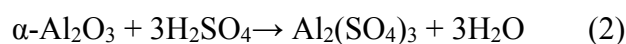
3.2.1 Metal recovery using Sulfuric Acid (H₂SO₄)

3.2.1.1 Sulfuric acid leaching from spent catalysts

In the hydrometallurgy process, inorganic acids are commonly used as leaching agents for the recovery of metals from spent catalysts. Sulfuric acid (H₂SO₄)-based leaching methods are the most popular to isolate nickel (Ni) from the roasting-dissolving residue of a waste catalyst. It has been reported that 93.5% of Ni in residue can be isolated by enabling the leaching conditions. Conditions included: particle sizes 0.074–0.100 mm, H₂SO₄ acid concentration 30% (mass fraction), temperature 80 °C, extraction time 180 min, mass ratio of liquid to solid 10, and stirring speed 800 r/min [51]. Al-Mansi et al [52] recovered around 99% of Ni from a spent catalyst, using 50% H₂SO₄ acid with a solid-liquid ratio of 1/12 for more than 5 h of leaching time at 100 °C. Some investigations suggest that a low concentration of H₂SO₄ is sufficient for the efficient recovery of Ni-metal [53]. For instance, 99.6% Ni was recovered using dilute H₂SO₄ (3%) and a persulfate-based additive (0.5%) in the very short time of 1 h. The utilization of a low concentration acid for efficient recovery is crucial to reduce environmental pollution. Nickel and vanadium are major components of catalytic waste, and can be recovered by leaching with diluted H₂SO₄, then precipitated into metal compounds such as nickel and vanadium oxides using NaOH [54, 55]. Similarly, nickel was extracted using 1-3 M H₂SO₄ from spent Ni/Al₂O₃ catalyst with a particle size of 200 nm for petroleum refining. Nickel was recovered electrochemically from the sulfate solution with 90% yield [56]. Spent silica-based catalyst containing Ni was treated with a mixture of air and steam in ratios from 1:4-1:8 at 325-425°C, with a steam partial pressure of 4-8 bars. The extracted Ni with 2N H₂SO₄ was saturated with SO₂ at 50°C for 10 h, where the recovery of Ni was 95%. The effect of solid-state impurities such as Li₂O and Cr₂O₃ on the dissolution of NiO in H₂SO₄ solution at 60 °C was further investigated. It was observed that the dissolution rate was decreased with the addition of Cr up to 1 M % Cr₂O₃, however, the addition of 1 M % Li₂O dramatically increased the dissolution rate. This might be attributed to the modification of the defect structure of NiO by the Li⁺ doping, which increases the surface concentration of Ni²⁺ - SO₄²⁻, and their interaction enhances NiO dissolution. Various studies have been performed to recover Co, Ni, Mo and Al₂O₃ from spent (HDS) catalysts [57-59]. The spent catalyst is leached with concentrated H₂SO₄ in an autoclave at 473-573K and 1-35 atm H₂S. After separating Al₂(SO₄)₃ products in an aqueous solution, the mixed sulphide was precipitated in residual aqueous slurry and then oxidized in the autoclave at 293-473K and 1-35 atm O₂. The slurry was processed to form MoO₃.H₂O from the residual solution containing sulphates of nickel and /or cobalt that was separated conventionally by electrolysis or ion exchange. The solid spent catalyst was

crushed to the size range of 0.3-0.4 μm and ground into powder. The obtained material was then dried at 100-110°C. Among which, 50 gm of dried catalyst powder was placed into a flask and 250 ml of 80% H_2SO_4 acid was added slowly to the flask with boric acid and nickel chloride, for 50 min at 70 °C [60].

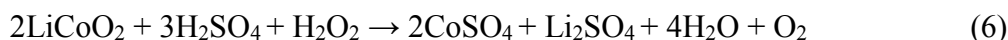
Alex et al. have developed a method for the recovery of nickel-bearing spent catalyst from hydrogenation plants. The process involved reduction and roasting of the catalyst, followed by H_2SO_4 leaching for the dissolution of nickel, and its subsequent recovery as NiO [61]. By optimizing the various process parameters, around 99% of pure NiO was extracted with an overall recovery of 83%. Likewise, Parton et al. implemented H_2SO_4 leaching and selective precipitation for recovery of Ni, V, Fe, and Mg hydroxide, with the carbonaceous material coming from fly ash [62]. In a similar study, aqueous H_2SO_4 was used under atmospheric and O_2 pressure to produce a leach liquor of sulfates of both Ni and V [63]. Abdel and Rashad have studied the kinetic leaching of spent nickel oxide catalyst [64] and extracted 94% of nickel, using a spent catalyst with particle size of 200-270 mesh. The concentration of H_2SO_4 was maintained at 50%, at a temperature of 85°C for 150 min, with a constant solid-liquid ratio of 1:20 g/ml. Leaching kinetics indicates that the chemical reaction at the surface of the particles is the rate-controlling process. Leaching of spent commercial NiMo/ Al_2O_3 and CoMo/ Al_2O_3 - SiO_2 catalysts was performed in an aqueous substance containing fluoride ions under mild experimental conditions for the recovery of Ni [65], which can be expressed as follows.



3.2.1.2 Sulfuric acid leaching from spent LIBs

The extraction of metals from spent LIBs using H_2SO_4 and sodium metabisulphite have been assessed and improved via several experiments, outlined by a techno-economic approach. The optimum conditions for this process were obtained with an acid concentration of 2.5 M and a liquid-solid ratio of 5 L/kg, at 40 °C for 2 hr [66]. The cathode material of LIBs was refined to extract Co- and Li-based materials through the assessment of the chemical behaviors of these metals in various oxidation states. The active substances were separated from the cathode, dissolved in H_2SO_4 and H_2O_2 solution, and then precipitated in the form of $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ [67]. The selective dissolution of metals from the active material of cathode is a two-step process. In the first step, cathode powder (baked at 300 °C) is subjected to leaching using aqueous H_2SO_4 solution. This results in extraction of 78.6% Li, 80.4% Co in 60 min at 75 °C and 25% pulp; recovery of Ni and Mn was low ($\leq 15\%$) in this step. In the second step, reductive leaching with an acid mixture of H_2SO_4 and HNO_3 with glucose is

solubilised 67% Ni, 64.8% Mn in 45 min. After this two-step process, the overall recovery achieved as follows: 93.2% Li, 90.52% Co, 82.8% Ni, and 77.7% Mn [68]. The leaching efficiency could be improved with an ultrasonic-assisted acid leaching method using chemical reagents. This would reduce reagent consumption, and consequently cause less environmental pollution. This strategy was applied in a study to improve the effectiveness of acid leaching of Co from LiCoO₂ using H₂SO₄ with mechanical stirring. The effect of ultrasound was significant when the concentration of H₂SO₄ is low (<1.0 mol l⁻¹) [69]. In the acid-leaching step, the effectiveness of H₂SO₄ and H₂O₂ concentration in the solution, leaching time, liquid-solid mass ratio, and reaction temperature on the leaching percentage were examined – where leaching of the cathode material was performed with 2M H₂SO₄ and 10 vol.% H₂O₂ at 70 °C and 300 rpm. The liquid-solid mass was kept 30 ml/g. The leaching efficiency achieved for Co 98.5%, Li 99.8%, Ni 98.6% and Mg 98.6% under optimum conditions [70]. A sustainable method for recovering valuable metal from LIBs using ammonium chloride (NH₄Cl) has been proposed. The NH₄Cl used in this process is reusable and has minor environmental impacts. The effectiveness of different parameters – for example, H₂SO₄ concentration, NH₄Cl concentration, temperature, leaching time, and solid-to-liquid mass ratio – on the leaching performance of Li, Ni, Co, and Mn was thoroughly investigated in this study [71]. Some similar examples are given, as follows: Cyanex 272 (bis-(2,4,4-tri-methyl-pentyl) phosphinic acid) was selected for Co recovery [72]. Selective separation of Al (III), Fe (III), Li (I), Mn (II), Co (II), Ni (II) and Cu (II) via acid leaching of spent LiNi_{0.46}Co_{0.2}Mn_{0.34}O₂ battery [73]. Recovery of Li and Co from spent LIBs using H₂SO₄ and H₂O₂ with varying the process parameter [74]. The process parameters were optimised by adjusting the concentration of leachant, density of the pulp, volume of reductant, and reaction temperature. The optimum conditions were 2 M H₂SO₄ with 5% H₂O₂ (v/v) at a pulp density of 100 g/l and 75 °C temperature – leading to the extraction of 99.1% Li and 70.0% Co in 60 min [75].



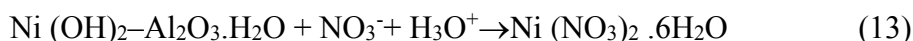
3.2.2 Metal recovery using nitric acid (HNO₃)

3.2.2.1 Nitric acid leaching from spent catalysts

The leaching of spent catalysts using mineral acids such as nitric acid (HNO₃) has been investigated by several researchers. For instance, Sheik et al. studied the kinetics of HNO₃ acid leaching on a spent NiO–Al₂O₃ catalyst. The influence of process parameters on leaching – i.e. reaction temperature in the range of 60-90°C, concentration of nitric acid in the range of 1.5-5M, and average particle size in the range of 5-601 μm – was investigated. It was revealed that up to 90% of

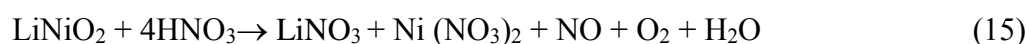
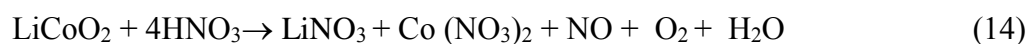
nickel was recovered. On the other hand, 90-98% Ni and NiO were recovered via the process of carbonylation – where leaching was performed using HNO₃ and HNO₃-HCl mixture, and 65-99% of the metal and oxide were extracted, based on the type of catalyst. Inefficient extraction via acid treatment in certain situations was ascribed to the greater amount of NiAl₂O₄ and NiSiO₃ –and the resulting higher resistance to acid leaching [76]. Sheik et al. used HNO₃ acid for extraction of Ni from spent reforming catalysts. The recovery of Ni was completed using 2.1-6.3 M HNO₃ at a 90°C temperature. The extraction was dependent on temperature, activation energies (2.8-6.7 Kcal/mol), and was also dependent on the weight of the solid to be processed [77]. A dissolution rate of NiO in HNO₃ acid solution as a function of prior annealing temperature in air was investigated by Jones and his coworkers. They observed that the dissolution rate decreased remarkably with annealing temperatures from 500 to 1450 °C. Oxide annealed at temperatures below 700°C had a higher dissolution rate, which was attributed to an excess concentration of point defects over thermodynamic equilibrium concentration [78]. The three-stage counter current extraction of nickel from spent nickel catalysts was performed using 1-3M HNO₃ for 1-3 h at 100 °C, with various proportions of spent catalyst-to-acid ratios (from 1:3-1:7 (w/v)). The recovery of nickel was found to be 95.2%[79, 80].

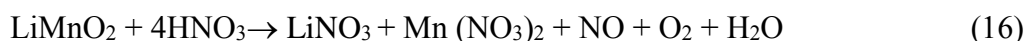
The reaction mechanism with nitric acid leaching can be expressed as follows:



3.2.2.2 Nitric acid leaching from spent LIBs

The cathode materials in spent LIBs can also be leached using nitric acid. For example, cobalt was recovered from LiCoO₂ based cathode materials using nitric acid as a leaching agent and hydrogen peroxide as a reducing agent. The rate and efficiency of recovery was assessed by varying the concentration of nitric acid and the reaction temperature. The results revealed that the most favorable leaching conditions were 30 min of leaching reaction, 3 M HNO₃ and leaching temperature of 90°C – resulting in 98% cobalt recovery [81]. The recovery of cobalt metal reached 95% using acid with a concentration of 1M HNO₃ and 1.7 vol % H₂O₂. However, in the past few years, HNO₃ leaching techniques have rarely been used to extract valuable metals from electrical and electronic waste [82]. An effective method for selective extraction of lithium to produce battery-grade Li₂CO₃ includes nitration, selective roasting, water leaching and preparation of Li₂CO₃ [83].





3.2.3 Metal recovery using hydrochloric acid (HCl)

3.2.3.1 Hydrochloric acid leaching from spent catalysts

Hydrochloric (HCl) is another mineral-leaching acid broadly used in the recovery of metals from spent catalysts. Ganguli et al. have studied the recovery of Ni from spent catalysts using 32% HCl at 70 °C. The leached liquor was treated with an oxidising agent to convert Ni²⁺ to Ni⁴⁺ and pH was adjusted to 8-8.5 to precipitate NiO. Later, NiO was leached using concentrated H₂SO₄ to obtain aqueous Ni sulphate, from which Ni was recovered with a 96% yield [57]. Welsh et al. have studied the recovery of Mo, V, Al, Co and Ni from spent catalysts. The residues were chlorinated with a gaseous mixture of Cl₂, HCl and 15 vol % water vapors, where Mo and V volatilised as oxychlorides and Al as chlorides. Chlorination was performed at 200-400°C and absorption at 20-70°C. The Co and Ni were recovered from the residue by water leaching in chloride form [84]. Chaudhary et al., developed two processes based on HCl leaching for Ni recovery, where the first method demonstrated Ni-precipitation as solid NiCl₂ using HCl gas saturation of the solution. Repetitive leaching precipitation cycles were investigated to understand its effects. It was observed that an increasing number of cycles decrease the purity of the NiCl₂. Anion exchange treatment was adopted for further purification. In the second method, impurities such as Cu solution were removed from purified NiCl₂ using a cementation process. The recovery of NiO in both methods was carried out by precipitating Ni (OH)₂ followed by calcination – to achieve a compatible purity of NiO for a feasible smelting process. This study reported 99% extraction of Ni from spent catalysts using HCl [85]:



3.2.3.2 Hydrochloric acid leaching from spent LIBs

Researchers have shown the engineering repercussions of the recovery of value-added material from industrially-collected spent LIBs. They have used HCl-assisted hydrometallurgical processes followed by a mechanical process. Lithium, which is usually lost in the slag fraction, was extracted via direct leaching [86]. The battery powder was leached in a 500 mL, three-necked, round-bottomed flask using concentrated HCl, and the overall concentrations of all metal ions (Ni²⁺, Co²⁺, and Al³⁺) were identified. To maintain an appropriate temperature for the process, a water bath was used. The leaching parameters were selected very carefully, with a solid-liquid ratio of 100 g/l, 4 M acid concentration, and 60 min reaction time, and a temperature of 80 °C was maintained. During the leaching process, an overhead stirrer was used to enable the agitation, while filter bag paper was used to filter the leachate residue. Using Atomic Absorption Spectroscopy (AAS), the concentration of Ni²⁺, Co²⁺, and Al³⁺ was used to determine the leaching efficiency [87]. A solution of 1.5 M HCl, 2.0% H₂O₂ (volume fraction), with a solid-liquid ratio of 20 g/L was used to dissolve 93% of Co. The

most effective recovery was achieved when the reaction time was 60 min and temperature was 90°C, when compared with the other acids used in this study [88]. Likewise, researchers have investigated the effects of process parameters on LiCoO₂ leaching with HCl. The dissolution of LiCoO₂ was increased when process parameters such as temperature, time, HCl concentration, and solid-liquid ratio increased. The study revealed that around 89% Li and Co were recovered from LiCoO₂ by using 3.5 % of H₂O₂ as a reducing agent [89]:

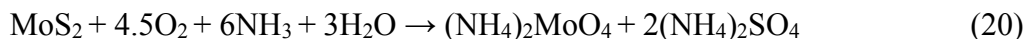


3.2.4 Metal recovery using ammonia solution (NH₄OH)

3.3.4.1 Ammonia solution leaching from spent catalysts

Several researchers have proposed the use of ammonia solution (NH₄OH) and its salt solutions to extract metals including Ni, Mo, V and Co from spent catalysts. For example, Mo, V and Ni metals were leached by (NH₄)₂CO₃ solution from spent catalysts with an excellent recovery efficiencies of ~90% and 60-70%, respectively, at 150°C. Likewise, Millsap and Reisler reported the extraction of metals using Ni–Mo/Al₂O₃ spent catalysts, which was performed by first roasting Mo and Ni, and then leaching with a NH₄OH and (NH₄)₂CO₃ solution to leave Al₂O₃ as waste. Finally, nickel carbonate was recovered by draining excess NH₃ from the leaching solution while the Mo and Calcium molybdate were recovered by a solvent extraction and precipitation method [90]. The use of NH₄OH solution to extract metals from waste catalysts is also discussed in some patents from Chevron Research Company [91, 92]. For instance, Hubred et al. extracted around 85% Mo, 45% Co, 75-85% V and 75–80% Ni from decoked hydroprocessing catalysts – by using aqueous solutions of (NH₄)₂CO₃ or (NH₄)₂SO₄ as leachants. The pH of NH₄OH solution was in the range of 9.5-11 at 85-95 °C extraction temperature. The extraction of Ni and Co was strongly affected by temperature and time for decoking and leaching. The Co recovery was strongly influenced by leaching time – with maximum recovery in 5-10 min, which subsequently decreased. The extraction of aluminum was unsatisfactory (<0.1%) during the whole process. The separation of individual metals from leaching solutions such as mixed metals was attained using extracting solvents. Using a separation method with quaternary amine at a pH of 10.4, V and Mo were extracted from Ni and Co solution, and then LIX₆₄N and LIX₅₁ were used for the extraction of Ni and Co [83]. In connected research, Marcantonio et al. recovered Ni, V, Mo and Co from end-of-life hydroprocessing catalysts using ammonia solution, (NH₄)₂CO₃, (NH₄)₂SO₄ salts and H₂O₂. The extent of metal extraction was significantly affected by the concentration and pH of the reagents, where V and Co recovery was considerably enhanced by the use of H₂O₂, while that of Ni and Mo was not affected by H₂O₂. Remarkably, Mo, Ni, V and Co of 93%, 80%, 88% and 78% were extracted using a leaching solution of 2M NH₄OH, 0.5M ammonium salt and 0.14M H₂O₂ with pH of 10.4, respectively [94]. In a recent study, Marcantonio used an ammonia pressure leaching technique with oxygen to generate ammonium molybdate,

ammonium metavanadate (AMV), and nickel ammonium sulphate from end-of-life hydroprocessing catalysts containing sulphides of Mo, V and Ni. The reactions which occurred in the process are as follows:



In this case, ammonium molybdate and nickel ammonium sulphate were left in the leaching solution, while ammonium metavanadate was separated out as a solid from the leaching slurry that was collected using filtration, and finally calcined to obtain V_2O_5 . Moreover, the solution underwent further extraction to separate Ni and Mo. Thus, the resultant products included V_2O_5 , nickel sulphate, and ammonium molybdate [95]. In a recent study, ammonium sulfate solution was used to leach Ni from used hydrodisulphurised catalysts. Interestingly, by using leaching with a 2.6M $(\text{NH}_4)_2\text{SO}_4$ solution, approximately 94% of Ni was recovered from the catalyst [96].

3.3.4.2 Ammonia leaching from spent LIBs

Comprehensive hydrometallurgical development has been established to achieve selective recovery of Li, Co and Ni from the cathode scrap of spent LIBs. The selective recovery of Ni, Co and Li in the first step is more than 98.6%. With a leaching solution of ammonia-ammonium sulphate and sodium sulphite, around 1.36% Mn can be recovered. Such selective leaching of metals can be achieved by optimising the effect of different parameters – including the composition of leaching solution, time for leaching (0-480min), pulp density (10-50g/L), speed of agitation (200-700rpm), and operating temperature (323-353K). In the leaching solution, primarily, Mn is reduced from Mn^{4+} to Mn^{2+} , followed by precipitation to form $(\text{NH}_4)_2\text{Mn}(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$ residue – while Li, Co and Ni are left as metal-ions or amine complex forms [97]. A ternary leaching solution of ammonium bicarbonate, ammonium sulphate and ammonia was utilised to investigate the leaching performance of Al, Ni, Li, Co and Cu obtained from cathode materials. In this case, ammonium sulphate acts as a reductant, which improves the leaching efficiency of Co, Ni and Li, while ammonium bicarbonate serves as a buffer in ammonia. To understand the leaching process, several parameters were optimised viz. composition of leaching solution, time of leaching (from 0 to 300 min), speed of agitation (from 300 to 700 rpm), leaching temperature (from 40 to 90 °C), and finally ratio of solid-to-liquid (from 10 to 50 g/L). The complete recovery of Cu and Ni was achieved. However, Al was hardly separated, and only 60.5% of Li and 80.9% of Co were recovered at the optimum solid-liquid ratio of 20 g/L leaching ratio with high temperature and prolonged reaction time [98]. Similarly, Ku et al. [99, 100] have developed a strategy to recover valuable metals from spent LIB cathode materials collected from hybrid electric vehicles, using ammonia-based leaching solutions. Ammonium sulphite improves the leaching kinetics of Co and Ni by acting as reductant, while ammonium carbonate acts as a pH buffer.

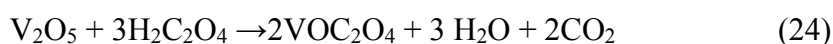
In this process, complete recovery of Cu and Co was obtained, while very little separation of Al and Mn was observed [99].

3.2.5 Metal recovery using organic acid leaching

3.2.5.1 Organic acid leaching from spent catalysts

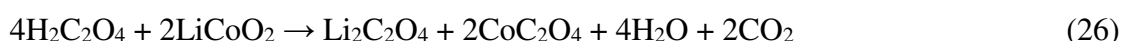
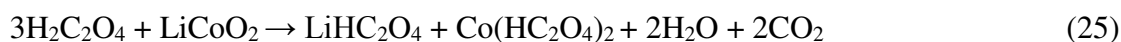
Many researchers have studied organic acid leaching of spent hydroprocessing catalysts. Beuther and Flinn compared the efficiencies of leaching metals including Co, V, Ni and Mo from used hydrotreating catalysts using a range of organic acids, viz. malonic, tartaric acid, oxalic, citric, salicylic, glycolic, succinic, phthalic and lactic. In this study, one percent of aqueous acid solution was utilised at room temperature and atmospheric pressure. The highest efficiency for leaching was observed for oxalic acid, where V, Mo, Co and Ni were recovered with 47%, 59%, 60% and 56%, respectively, using 1 wt. % oxalic acid. Other conditions, such as the effect of reagent concentration, were not investigated [101]. Marafi et al. implemented organic acids – including tartaric, citric and oxalic acids – to selectively leach V, Ni and other metal contaminants present in spent residue hydroprocessing catalysts. Both coked (sulphide) and decoked (oxidic) leaching were carried out using spent catalysts. The leaching of catalysts before decoking exhibited a greater selectivity for the separation of metal (V) foulant; however, in this case, it is necessary to add oxidising agents – viz. H_2O_2 , $\text{Al}(\text{NO}_3)_3$ or $\text{Fe}(\text{NO}_3)_3$ – to increase the efficiency of organic acids [102,103]. Marafiet al. compared the leaching efficiency of an aldehyde, four organic acids and water on the recovery of metals from used hydrodemetallisation catalysts. Prior to leaching, the deposited coke on the catalyst surface was removed at a temperature of 350-450 °C, using a combustion method in the presence of 4% O_2 in N_2 . The decoked solution exhibited 2.5 wt. % Fe, 4.4 wt %Mo, 5.9 wt % Ni, 11.6wt % V, and the rest was Al_2O_3 . An ultrasonic bath with agitation was used to conduct the leaching experiments at 50 °C. The leaching efficiency for the six reagents was found to be in the following order: tartaric = citric >glyoxylic >lactic>glycolic acid > water >glyoxal [104-106].

Present research is focused on the optimisation of different parameters for the separation of Al, Mo, V and Ni from hydrodisulphurised waste catalysts. For example, Mulak et al. studied the effects of concentrations of oxalic acid and H_2O_2 , as well as speed of stirring, on the rate of nickel leaching. The findings suggested that the addition of up to 3M H_2O_2 to oxalic acid improved the leaching efficiency of Al, Mo, V and Ni, and thereafter remained largely constant. The steady increase in the efficiency of the recovery of Al, Ni, Mo and V was observed with increases in the concentration of oxalic acid up to 0.5M, and slightly reduced with further increases. The maximum extraction of metals from the used catalyst was estimated to be 90%, 94%, 65% and 33% of Mo, V, Ni and Al respectively, using a 0.5M $\text{H}_2\text{C}_2\text{O}_4$ and 3 M H_2O_2 solution for 4 h [107]:



3.2.5.2 Organic acid leaching from spent LIBs

Organic acid leaching is an effective hydrometallurgy method for the leaching of cathode materials in spent LIBs. For example, Li and Co can be selectively leached using formic acid and H₂O₂ with the efficiency of 99.9 % and 99.9%, respectively by optimising the different parameters including leaching time, stoichiometric ratio, H₂O₂ concentration, temperature and the solid-to-liquid ratio [108]. Citric, malic and aspartic acid were utilized as leachants in with H₂O₂ where around 90% of Co and Li can be extracted using citric and malic acids while in aspartic acid, it is considerably less [109]. In this study, different acids (citric, oxalic, sulphuric, hydrochloric and nitric acid) as well as reducing agents (H₂O₂, glucose and ascorbic acid) were implemented for recovery of metals from spent LIBs [110]. The response surface methodology (RSM) was used to optimize the leaching parameters [111]. In addition, the effect of different reducing agents e.g. H₂O₂ [112], sodium thiosulfate [113], sodium bisulphite [114], some carbohydrates viz. D-glucose [115] and ascorbic acid [116] were investigated. Various organic acids were investigated as leachants such as succinic, citric, ascorbic and DL-malic acid where their leaching efficiencies are comparable or even higher than strong acids, avowing the secondary pollution caused [117]. The cobalt recovery from spent LIBs was performed using H₂O₂ as reducing agent with citric acid as leaching agent where the concentration of citric acid was varied from 0 to 2 M, at reaction temperature of 50-80°C [118]. Naturally available organic acid as leaching agents were developed to recover Li and Co from spent LIBs-cathode materials. For example, succinic acid was utilized as leaching agent with H₂O₂, which is basically a green recovery method that involves pre-treatment, leaching with citric acid, precipitation and circulatory leaching [119].



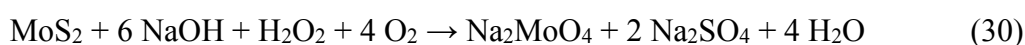
3.2.6 Metal recovery using alkaline leaching

3.2.6.1 Alkaline leaching from spent catalysts

A group of researchers utilized caustic soda solution for the leaching of spent catalyst and treated the residue with sulphuric acid solution for the extraction of Ni [120]. In another study, optimum leaching conditions were achieved for the recovery of nickel from Al₂O₃ support using (NH₄)₂CO₃ for 600 mm particle size at 80 °C [121]. Ni precipitation was carried out at alkaline pH using 1M Na₂CO₃ solution. However, there are certain limitations to the leaching procedure described in the literature [122]. An effort was made to extract Ni from the waste catalyst using an aqueous solution of 15–23% ammonia at 60–90 °C and a pH in the range of 7.5–9. Nickel was recovered as Ni (NO₃)₂ however the ammonia used in the process is a toxic gas [123]. In the similar work, Al as Na-aluminate was dissolved to leaching of the spent nickel catalyst with 50% caustic soda solution

in autoclave at 150-175 °C [124]. The residue was treated with Nitric acid (1:1) at 60 °C to dissolve the remaining nickel in the solution [125].

A few other studies have reported the leaching of the spent catalyst with aqueous alkaline solution using NaOH or Na₂CO₃ [126]. One study reported a process for the recovery of Mo and V selectively from unroasted waste hydroprocessing catalysts by using the mixture of aqueous alkaline solution of Na₂CO₃ and H₂O₂ where H₂O₂ acts as an oxidizing agent. Mo and V recovery in this process was about 99% and 85% respectively while the extraction of Ni, Co and Al₂O₃ were relatively much lower. Recently, this research was enhanced by Park et al. for selective isolation of highly pure MoO₃ from spent HDS catalyst utilizing the mixture of H₂O₂ and Na₂CO₃. According to the results obtained, the recovery of Mo was mostly conditional on the Na₂CO₃ and H₂O₂ concentrations in the reaction medium. These concentrations control the pH of the leach solution and carryover of impurities such as Al, Ni, P/Si and V. The method was exothermic and Mo leaching efficiency increased with a decrease in solid to liquid ratio. For the leaching of the spent catalyst at large scale and under the optimum conditions (20% pulp density, 85 g/L Na₂CO₃, 10 vol. % H₂O₂ and 1 h reaction time); the recovery of Mo was attained 84%. The leach solution thus obtained was found to contain (g/L): Mo 22.0, Ni 0.015 and Al 0.82, P 1.1, Si 0.094 and minor quantities of V 8 mg/L, As and Co <1 mg/L. Purification of the leach liquor using the carbon adsorption at a pH of around 0.75 followed by the desorption of the adsorbed molybdate with 15% NH₄OH produced a high purity ammonium molybdate from which MoO₃ with 99.4% purity was obtained via calcinations [127]. Villarreal et al. compared two solutions with different concentrations of caustic soda; one containing 10% and the other containing 40%. The solution containing 10% recovered Mo and V 92% and 89%, respectively by using leaching, whereas for the concentrated solution, the extraction was much lower at 79 and 72%, respectively [128].



3.2.6.2 Alkaline leaching of spent LIBs

The research focused on optimising the hydrometallurgical pre-treatment process for Li-ion battery cathode materials by changing the parameters such caustic soda concentration, the ratio of solvent volume to the mass of the test sample (liquid-solid ratio (L/S)) and reaction time. The cathode material retrieved from the used batteries collected from a local market was dried in an oven at 50°C for 24 hours, subjected to alkaline leaching with 2, 3 or 4M NaOH solution, followed by filtration at room temperature [129]. For a mixture of different types of spent Li-ion mobile batteries acid leaching was performed using sulphuric acid and H₂O₂ after alkali decomposition using NH₄OH. In the alkali decomposition step aimed at removing Al, Cu, Mn, Ni, Co, and Li, the effects of reaction time, Ammonium hydroxide concentration, liquid/solid mass ratio and reaction temperature on the

decomposition process are investigated. After alkaline treatment, the remaining metals are recovered by leaching treatment of the alkali paste using H_2SO_4 and H_2O_2 [130]. The recovery processes are usually performed by utilizing the ammoniacal and/or acidic leaching processes, precipitation, and thermal processes [131-135].

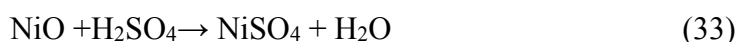
3.2.7 Two-stage leaching of spent catalysts

Many researchers argued that a two-stage leaching process is effective for the recovery of valuable metals from the spent catalysts. Jong et al. reported a method where two-stage processes were adopted. Firstly, the spent Ni-Mo/ Al_2O_3 catalyst leaching was carried out using caustic soda solution to isolate Mo and portion of Al, however, the rest of the Al and Ni persisted in the solid. Mo was then isolated by precipitation method using CaCl_2 from the alkali leach solution. The residue obtained in the first stage was leached in the subsequent step with sulphuric acid to isolate Ni. After obtaining the leachate by utilizing this step further treated with NH_4OH and $(\text{NH}_4)_2\text{SO}_4$ to have the precipitation of Al and other metal impurities. At a pH value of ~10, Ni was recovered via solvent extraction. 81 to 91 wt. % recovery of Mo was achieved in NaOH leaching step. 92 to 98 wt. % of Ni recovery was in the same step. In the second step of recovery, more than 84 wt. % of Mo and 99 wt. % of Ni could be isolated and extracted [136]. In many other studies, two-stage processes involving first-stage leaching with an alkali and second stage leaching with an acid or ammonia or the other way around have also been identified. Typically, spent catalyst comprises valuable metals such as Mo, Co, Ni. These metals are layered on other materials like $\gamma\text{-Al}_2\text{O}_3$. Current research proposes a two-stage alkali/acid leaching process for the targeted separation and isolation of Mo and Co/Ni to enable the downstream processing. Calcination of the spent catalyst was carried out at 500 °C prior to the leaching process to eliminate C and S which also converted the sulphides of the metals to the oxides. This process effectively recovered around 98% Mo, 93% Co and 90% Ni. An alkali-treated solution when leached with sulphuric acid, isolate Mo, generated a solution rich in Ni, Co and Al. To isolate Co and Ni, it is important to remove Al impurity [137]. A simple hydrometallurgical route is suggested for the effective recovery of Ni from spent NiO/ Al_2O_3 catalyst. The sulphuric acid leaching achieved a Ni recovery of 99.5%. The leached solution was partially neutralized and the adding of ammonia forms precipitation of nickel ammonium sulphate. The Ni in the supernatant was concentrated by the extraction of the solvent utilizing D2EHPA and then disrobed back into H_2SO_4 solution to return to the stage of precipitation [138]. In the primary stage of alkali leaching, insignificant amount of Co/Ni dissolution was observed (<0.1%). Likewise, Mo leaching was insignificant (<0.3%) in the acid leaching of the second stage. Nonetheless, a major amount of Al was leached in both stages. During the first stage, 12–14% and in the second stage, 55–65% Al was leached [139, 140]. A pre-calcination process between the temperature of 400 and 500 °C followed by leaching with H_2SO_4 was carried out on the spent catalyst [141]. Spent hydrodesulfurization (Co-

Mo/ γ -Al₂O₃) catalyst generally comprises of valuable metals like Mo, Co, Al on a supporting material, such as γ -Al₂O₃. In this research, a two stages alkali/acid process was performed to investigate the leaching of Co, Mo and Al from Co-Mo/ γ Al₂O₃ catalyst. The acid leaching of spent catalyst, formerly treated by alkali solution to obtain Mo, yielded a solution that was rich in Co and Al [142]. The aim of the research was to develop an environmental-friendly method for the extraction of Ni, Mo, and V from the spent hydroprocessing catalyst from the processing plant waste. The two stages leaching process recommended, where the initial stage is to separate Al₂O₃ and next stage involves the isolation of other compounds of metal. The efficiency of leaching agents has been reported to be dependent on the reagent concentration, leaching time and temperature during the isolation of Mo, V, Ni, and Al from the refinery spent catalyst. The leaching agents investigated in this study were NH₄OH, (NH₄)CO₃ and (NH₄)₂CO₃ and (NH₄)₂S₂O₈. The optimal leaching conditions with the maximum possible recovery of Mo, Ni, and V metals were achieved [143]. Caustic leaching of Ni-Mo-Al can be expressed as follows



Acid leaching of AL-Ni from caustic residue,



3.2.8 Deep Eutectic Solvents (DES) leaching for spent LIBs

The widespread and rapid progress in the fabrication and usage LIBs and the advancements in the end-user electronics, hybrid and electric vehicles has boosted the amount of the scrap battery production [144, 145]. While spent LIBs are usually not categorized as harmful waste, owing to the existence/production of poisonous elements from the combustible and toxic substances/compounds, their improper disposal can lead to environmental hazards. Consequently, recycling of spent LIBs by extracting expensive metals present in the active material of cathode has become progressively more significant to maintain the economic production and comply with the environmental regulations and legislations. Several processes are involved in the method for the recovery of important metals from spent LIBs which are primarily mechanical processing, thermal treatment, and chemical processing. In the chemical processing, basically the steps involved are acid or alkaline leaching, precipitation, separation and electrochemical recovery [146-150]. The purity of the metal extracted from the spent LIBs is a concern, so that, more attention has been paid in case of the solvent extraction to generate highly pure metals that could meet the economic aspects and quality requirements to replace the conventional separation processes, predominantly the methods of precipitation. Several hydrometallurgical methods have been reported in the literature, which has employed as solvent extraction for the isolation and recovery of value-added metals from the spent LIBs [151-152]. These

processes largely aimed at optimizing the circumstances for the extraction of Co due to its high value when compared with other components. Deep eutectic solvent (DES) is a fluid which usually consists of 2 or 3 low cost as well as safe elements efficient of self-association, usually via hydrogen bond interactions, to produce a eutectic mixture, which has a lower melting point than that of each particular component on its own. Even at temperatures lower than 100°C, DESs are generally in liquid form, which display comparable physio-chemical properties to the conventionally used ionic liquids while being relatively cost-effective and eco-friendly. Because of these extraordinary benefits, DESs are now getting an increased attraction in a variety of research areas [153].

An environmentally friendly deep eutectic solvent was reported by Mai K. Tran et al. to extract valuable metals from lithium-ion battery cathodes. The primary goal of the work was to reduce the utilization of complex procedures to recycle the batteries to cease the landfills. The solvent prepared from choline chloride and ethylene glycol was able to recover more than 90% of Co from grounded compounds. This process can recover a lesser but still substantial amount of value-added material from spent batteries [154]. Another work reported the advancement of the sustainable industrial process for the recycling of spent batteries using a deep eutectic solvent [155] where the effect of lactate anions on the metal extraction from chloride media by extraction of a lipophilic chloride ionic liquid was studied utilizing the solvent extraction experiments with a special emphasis on Co and Ni behavior.

A mixed extract was also developed by the researchers for the isolation and refinement of Co and Li from spent lithium-ion battery leach solutions. The Acorga M5640 was added to the organic solution of Ionquest 801 to produce a substantial shift in the pH isotherm for Cu with a ΔpH_{50} value of around 3.45. Therefore, the separation of Fe (III), Cu and Al from Co, Ni and Li could easily be achieved with the mixed extractant system [156].

DESs ptsa: choline chloride, ptsa: tetrabutylammonium chloride and ptsa: tetrabutylammonium chloride was prepared at three different molar ratios [157]. Wherein those work, physicochemical characteristics (density, viscosity, thermal decomposition, melting point, and spectroscopic studies) were examined to define the H-bonding interactions. The ptsa-based DESs exhibited lower viscosity and broader operational windows compared to other commonly used DESs. The solubility of the various metal oxides in the DES ptsa: choline chloride at 3 different molar ratios of 2:1, 1:1 and 1:2 was measured. The solubility of the metal oxides was found to increase with the increase in the acidity of the HBD. The effect of the DES molar ratio on the solubility of the metal oxides was also studied. The solubility and the selectivity of the DESs towards different metals can be changed by modifying the molar ratio of the DES. Certain forms of sulfonic acid based DESs could also be expected to result in high solubility of metal oxides, which is important due to the

possibility of using cheaper HBDs, such as methane sulfonic acid. This is one of the potential interests for the valorization of residues from low-grade ores or metal processing.

3.3 Bio-metallurgy

Bio-metallurgy is one of the most exciting and innovative biotechnologies for the recovery of heavy metal ions via microbiological processes. The idea of microbiological leaching has played an important role in the last few decades to retrieve valuable metals from a variety of sulfide minerals or low-grade ores [158]. The microbiological leaching procedure has been further developed for its implication to extract high-value metals from various manufacturing waste. There are several microorganisms that could play crucial role in extraction of heavy metals from industrial wastes [159]. Bio-hydrometallurgical methods seem to present excellent prospects for recovering important metals from used petroleum catalyst [160]. Briand et al. utilized *Acidithiobacillus thiooxidans* to treat a spent vanadium phosphorus catalyst [161]. *Acidithiobacillus thiooxidans* was also used by Bosio et al. for the treatment of the spent Ni catalyst generated during the vegetable oil hydrogenation [162]. A few reports discussed bioleaching processes employed for the recovery of valuable metals from spent refinery catalysts using Fe/S oxidizing bacteria [163]. Beolchini and Gholami et al. reported the toxicity of the environmentally hazardous metals in waste catalyst to bacteria. Additionally, they optimized pH, temperature, particle size, pulp density, and speed of the rotation for the recovery of the metals [164,165]. Several works in the literature are also reported on the use of *Aspergillus Niger* for the bioleaching of spent refinery processing catalysts [166,167]. This fungus (*Aspergillus Niger*) possesses the capability to generate organic acids such as citric, oxalic, malic and gluconic acids. The principal mechanism in bioleaching of metals by *Aspergillus Niger* is the acid hydrolysis [168]. The present review reports the use of different techniques for the extraction and isolation of Ni, Co, Mn, Li, etc. from secondary resources with selectivity, efficiency, economic viability, and environmental friendliness.

3.3.1 Bioleaching

Bioleaching is a new method for the metal recovery from a variety of solids. This depends on the capability of certain microorganisms to convert solid elements into recoverable metals [169]. In this study, the microorganisms can produce also organic or inorganic acids to participate in the dissolutions of metals.

3.3.1.1 Bioleaching from spent catalysts

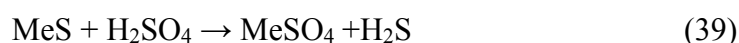
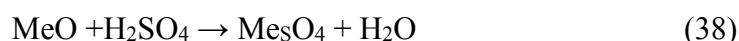
Bioleaching was employed at an industrial scale for the extraction of a range of metals from low-quality mineral resources [170]. Furthermore, the work reported by Santhiya and Ting lists the waste materials such as sewage sludge, fly ash, electronic scrap materials, spent batteries, as well as the face-centred cubic and hydroprocessing catalysts as potential solid materials that could be processed using bioleaching [171]. The bacteria such as *Thiobacillus ferrooxidans* and *T. thiooxidans*,

as well as the fungi such as *Aspergillus* and *Penicillium* genera are the most common types of microorganisms which are capable of solubilizing the metals [128]. Furimskyre viewed some of the trailer studies on possible applications of bioleaching for the recovery of metals from spent refinery catalysts [24]. It was in early 1990s when the initial stage to use the bioleaching process to used refinery catalysts was prepared. For instance, Blaustein et al. attempted to recover Mo from a coal liquefaction catalyst using *T. Ferrooxidans* and *L. ferrooxidans*. Bioleaching experiments were performed in an autoclave with shaking at 170–200 rpm at a temperature close to 30°C for about 6 weeks. The extent of Mo solubilisation increased with a decrease in the size of the catalyst particles. A series of research studies were done on another coal liquefaction catalyst ($\text{NiMo}/\text{Al}_2\text{O}_3$) for the United States Department of Environmental where *T. ferrooxidans*, *sulfolobus* and thermophilic cultures were examined for their bioleaching potential [172].

Santhiya and Ting described two steps processes for the metal bioleaching from used Face Centre Cubic and $\text{NiMoP}/\text{Al}_2\text{O}_3$ catalyst [173]. The waste catalyst and the fungus were incubated together with the sucrose medium at pH 5.5 in the one-step method. Herein, the system was agitated in an incubator at 120 rpm and 30°C. The samples were withdrawn, filtered and analyzed to determine the recovery efficiency at regular time intervals. In the case of the spent $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst, the difference in the bioleaching efficiency between two-step methods was insignificant. However, for smaller particles (e.g., 100–150 μ and <37 μ), the dissolution of Al was lower than Ni and Mo. The lower fungal biomass generation and secretion of the organic resulted in the lower metal extraction for 2.97 μ average particle diameter. In the case of the 70 days bioleaching for the <37 μ m diameter particles, the rate of leaching was $\text{Mo} > \text{Al} > \text{Ni}$. The concentration profiles matched with the variation in the concentration of citrate, oxalate and gluconate ions that were secreted during the growth of the *A. niger* fungus.



Ferric ion and sulphuric acid acts as lixiviant that solubilize MeS and MeO during the bioleaching. Where Me represents Ni, Al, Mo and V and their solubilization can be explained as follows:

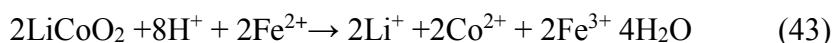
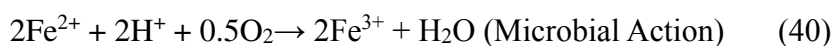


3.3.1.2 Bioleaching for spent LIBs

In the current study, Li and Co recovery from used lithium-ion batteries (27.5% LiCoO_2) by bioleaching were explored. The experiments were performed using the consortia of acidophilic bacteria of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans*. Two different media were used for the bioleaching of Li and Co [174]. The current work involved the use of

chemolithotrophic and acidophilic bacteria, *Acidithiobacillus ferrooxidans*, to utilize elemental sulfur and ferrous ion as the source of energy. This further generates metabolites like ferric ion and sulfuric acids in the leaching medium [175]. A bio-hydrometallurgical path based on fungal activity of *Aspergillus Niger* was also assessed for the detoxification and extraction of Cu, Li, Mn, Al, Co and Ni metals from used lithium-ion batteries under different method parameters. The highest extraction efficiency was found to be 100% for Cu, 95% for Li, 70% for Mn, 65% for Al, 45% for Co, and 38% for Ni at a pulp density of 1% in spent medium bioleaching [176].

Recovery processes via bioleaching use microorganisms as the leaching agents and therefore offer many attractive benefits. For instance, bioleaching has good extraction efficiency, low operating cost and very effective for the extraction of low concentration of Li from the spent batteries. This work aims to isolate local bacteria strains capable to recover Li from used LIB and to establish optimum conditions for the bioleaching [177]. In contrast with spent face-centred cubic catalyst, a minor difference in leaching efficiency was observed between bioleaching and leaching with the individual organic acids formed in the process of fungus growth [178] Bioleaching mechanism for the spent lithium-ion battery for the extraction of Li and Co by the mixed culture of acidophilic sulfur-oxidizing and iron-oxidizing bacteria can also be investigated [179].



3.3.2 Biosorption

The biosorption process is considered one of the promising and potential methods for the selective separation and recovery of metals as well as precious metals. In general, the biosorption is the properties of certain types of biomass materials which interact with metals ions so as to bind and concentrate them from aqueous solutions [180] Most of these biomasses or biomaterials are abundant in nature and thus make them inexpensive for application purpose. Further, the biosorption involves the utilization of dead microbial or plant biomass which can be directly brought to contact with high toxicity solution [181]. A major advantage of the biosorption process is its in-situ application without the proper need for process design or any industrial process operations, and also it can be incorporated into the industrial systems [182]. Several living and dead biomasses of fungi, bacteria, and microalgae have been used for heavy metal biosorption [183].

3.3.2.1 Biosorption for spent catalysts

Choudhary et al. demonstrate the claim of a low cost and eco-friendly biosorbent, soluble tannins cross-linked and PEI modified *L. speciosa* leaves powder (TLS) for sorption and recovery of palladium (II) from the acid-leached solution of monolithic ceramic capacitors and simulated spent

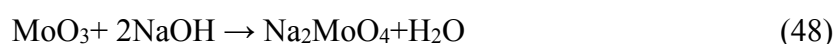
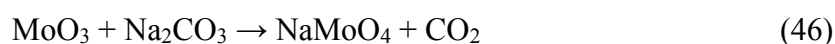
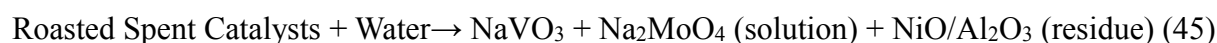
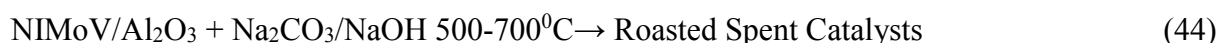
automobile catalyst and gold from various waste water samples.[184, 185]. Garole et al. reported the absorption and extraction of platinum from acid-leached spent catalyst solution using low-cost and eco-friendly PEI modified *L. speciosa* leaves powder (PEI-LS) [186]. Another biodegradable biosorbent was reported from the red marine alga *Gelidiummamsii* biomass. This is a promising, economic and environmentally friendly biosorbent to remove the 100% Pb^{2+} from aqueous solution where the solid/liquid concentration is 200 mg/L and the reaction time is 3 h. this method is adopted to treat the wastewater effluents [187]. The native and dried *Oscillatoria* sp. Cyanobacterium biomass is also investigated in another study as a biosorption in the batch mode to remove the Cd (II) ions from aqueous solutions [188].

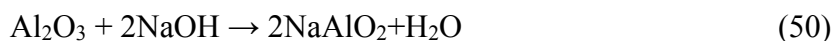
3.3.2.2 Biosorption for spent LIBs

Isolation and recovery of valuable metals, such as Co and Li from spent LIBs through leaching and cobalt through biosorption was applied simultaneously [189]. Pyrometallurgical and hydrometallurgical recycling techniques are commonly employed in industries to recover PMs. However, these techniques have certain disadvantages such as high cost and generate secondary hazardous waste. Thus, to have a green and sustainable method, the adsorption techniques like biosorption process making use of easily available biomass materials results in cost-effective and eco-friendly techniques.

3.4 Roasting with sodium salts for spent catalysts

Chen et al. reported metals recovery from a spent hydroprocessing catalyst containing V, Mo, Ni, Co, and Al_2O_3 using alkali (NaOH) fusion. The roasting of the catalyst with NaOH (mole ratio of $Na_2O:Al_2O_3 = 1:2$) was performed at $750^\circ C$ for 30 minutes. The water was used for the leaching of the roasted product. In the leaching process, V and Mo were dissolved in sodium aluminate solution while leaving Ni and Co in the residues. Recovery of the metals was 95.8% for V, 98.9% for Mo, 98.2% for Ni and 98.5% for Co [179]. The spent catalyst examined in the present work comprised of 60.4% Al_2O_3 , 21% MoO_3 , and 1.52% Co_3O_4 , and 0.85% NiO, and 4.67% SiO_2 . The effects of temperature, concentration of soda ash (Na_2CO_3) and roasting time on Mo recovery were studied and under selected experimental 92% Mo was recovered as sodium molybdate [190]. The pH of sodium molybdate solution was adjusted at 2 and then purified with ammonia by adsorption on activated charcoal. The solution thus obtained was heat-treated at $90^\circ C$ to generate ammonium poly molybdate which was followed by the calcination at $450^\circ C$ to produce MoO_3 with high purity (99.9%) [191].





4. Repurposing strategies for recycled materials

A hydrometallurgy and bio-metallurgy process help to achieve high purity of metals via the NH. However, what to be done with the recycled materials from spent LIBs and catalysts. There are no clear strategies and industries to address these issues therefore further research is urgently required to investigate the opportunities of utilization of recycled materials.

4.1 Recycled materials from spent catalysts

Recently, the researchers demonstrated that the recovery metals from spent catalysts can potentially support their re-use in the energy-storage applications similar to advanced batteries, supercapacitors as well as the energy conversion applications with water splitting [119]. Using Mn and Co from spent LIBs as metal precursors, a spherical spinel MnCo_2O_4 was developed for oxygen evolution reaction (OER) in 1 M KOH [192]. It was revealed that overpotential of 358 and 400 mV was achieved to generate current density of 5 and 10 mA/cm^2 with a relatively low catalyst loading ($1.025 \text{ mg}/\text{cm}^2$). This newly synthesized spinel MnCo_2O_4 spheres prepared from different recovered materials such as LiCoO_2 , LiMn_2O_4 displayed better electrocatalytic performances as compared to commercially available catalysts as presented in Figure 7.

4.2 Recycled materials from spent LIBs

In one of the recent efforts, Aravindan and co-workers [193] explored utilization of carbonaceous materials (GC) from used LIBs as a negative electrode in LIBs again as well as in Li-ion capacitors (LICs) with activated carbon positive electrode. Interestingly, LIB assembled with LiFePO_4 cathode delivered a remarkable energy density of 313 Wh/kg while LIC with commercial activated carbon displayed an energy density of 112 Wh/kg with decent cycling profiles as shown in Figure 5. Recently, the various researchers developed the innovative eco-friendly and cost-effective way to recycle anode material of spent LIBs for the simple preparation of graphene and also for other applications includes energy storage. For instance, Zhang and co-workers [194] converted retired Li-ion battery graphite anodes to graphene and graphene oxide and investigated their supercapacitive performances. It was further revealed that the graphene productivity enhanced by 4 times compared to the graphene from pristine graphite due to lithiation aided pre-expansion (see Figure 6). The graphite powders collected from spent LIBs exhibits irregular expansion because of the lithium-ion intercalation and de-intercalation in the graphite during charge/discharge processes. Likewise, Natrajan et al [195] developed reduced graphene oxide (rGO) using different parts of spent LIBs such as graphite, metallic cases (such as aluminum (Al) and stainless steel (SS)). The rGO prepared using graphite and Al-casing displayed superior specific capacitance of 112 F/g at a current density of 0.5 A/g, which was attributed to the high surface area and mesoporous nature. It was further interesting to note that the electrode showed excellent cycling stability over 20000 cycles as seen from Figure 6.

The same group [196] further demonstrated the synthesis of carbon hollow spheres (CHS) and reduced graphene oxide (rGO) from the spent LIBs-recovered separators and graphite, respectively and employed them for gas storage such as N₂, H₂, and CO₂. Both the materials (rGO and CHS) showed an affordable specific surface area of 374 and 402 m²/g. The studies revealed that both materials displayed good gas adsorption properties for all three gases.

As discussed earlier, the cathode is the most precious part of the battery and researchers have taken maximum efforts to recycle them due to the high value of metals. However, very few reports are available on the repurposing of recycled metals from spent LIBs. For example, researchers [197] have regenerated the Mn-Co carbonate from the mixed composition of cathodes of spent LIBs and implemented as positive electrode materials in asymmetric supercapacitors. The as-fabricated asymmetric cell with activated carbon negative electrode and Mn-Co carbonate positive electrode delivered a specific capacitance of 119 F/g with good cycling stability after 9000 cycles within 1.6 V. As a practical demonstration, flexible solid-state supercapacitor was assembled, which efficiently powered a greenlight-emitting-diode (LED).

5. Conclusions and future opportunities

The review provides a brief summary of methods used for the recycling of end-of-life LIBs and spent catalysts such as pyrometallurgy, hydrometallurgy, and bio-metallurgy (see Table 2). It was revealed that the hydrometallurgy and bio-metallurgy are the most efficient methods to recover the metals from repurposing point of view. The leaching of nickel, cobalt, manganese, lithium and other metals from different waste materials, particularly spent LIBs and catalysts could be performed using acidic and alkaline solutions. The studies have been carried out in different lixiviants, such as H₂SO₄, HNO₃ & HCl in the presence of oxidizing agent. On the other hand, the addition of an oxidizing reagent such as Fe (NO₃)₃, Al (NO₃), H₂O₂ was found essential to improve the leaching efficiency of leaching of nickel, cobalt, manganese, lithium and other associated metals. The process has been employed on the commercial scale for recovery of nickel, cobalt, manganese, lithium from spent materials. However, it suffers from an environmental viewpoint as it generates NO_x and chlorine and acid fumes due to the presence of HNO₃. A high concentration of HCl in the leaching solution also generates fumes and Cl₂ gas. To reduce the emission of HCl fumes during the leaching, H₂SO₄ has been employed without affecting the efficiency of nickel, cobalt, manganese, lithium leaching. An alternative approach to dissolving the substrate using H₂SO₄, ammonia, alkali or bioleaching has been proposed, which could be subsequently leached to recover nickel, cobalt, manganese, lithium. To replace the HNO₃ oxidizing agent, H₂O₂ also has potential to be used for the leaching of nickel, cobalt, manganese, lithium and other metals. Similarly, other leaching agents, such as tartaric, citric, glyoxylic, lactic, glycolic acid, glyoxal etc. are also effective as leaching agents for the dissolution of nickel, cobalt, manganese, lithium and other metals. Bio-metallurgical for industrial waste appears to

be an attractive method for heavy metals recovery. Approximately without exception, microbial extraction procedures are more environmentally friendly, while giving high extraction yields in excess of 90%. In recent years deep, eutectic solvent is employed for dissolution of metal oxide and good solvent to improve the metal recovery from solid waste.

Thus, it is imperative to recover the materials from spent LIBs in order to reuse them again as the next-generation energy conversion and storage systems. Hence, energy storage performance for the renovated materials from the waste is highly significant and will assuredly get inordinate industrial importance when the recycling of spent LIBs from electronic wastes are considered besides the resource conservation and environmental protection. However, much more research needs to be in the future to develop different opportunities for re-purposing of recycled waste from retired LIBs and spent catalysts.

Environmental restrictions and economic benefits have obliged countries to promote recycling processes from secondary resources like spent catalyst and spent lithium ion batteries (LIBs) instead of using primary ones. In spite of the developments have been made on industrial scale for the technologies involved in recycling processes, most of these technologies suffer from lack of efficiency and eco-friendliness. To reduce the footprints of the recycling processes, several efforts are made. A major development area is the use of green methods which are considered as promising agents for leaching of valuable metals from spent catalysts LIBs. For this purpose, necessity of green methods and advantage of leaching agent in recycling of spent catalysts LIBs.

Acknowledgments

D.P.D. acknowledges Queensland University of Technology (QUT) and Australian Research Council (ARC), Australia for the Future Fellowship (FT180100058).

References

1. C. Marcilly, J. Catal. 2003, 216, 47–62.
2. M. Marafi, A. Stanislaus, Resour. Conserv. Recycl. 2008, 52, 859–873.
3. M. Marafi, A. Stanislaus, Resour. Conserv. Recycl. 2008, 53, 1–26.
4. L.E. Macaskie, Mikheenko, I.P., Yong, P., Deplanche, K., Murray, A.J., Paterson-Beedle, M., Coker, V.S., Pearce, C.I., Cutting, R., Patrick, R.A.D., Vaughan, D., van der Laan, G., Lloyd, J.R., Hydrometallurgy, 2010, 104, 483–487.
5. Liu, C., Yu, Y., Zhao, H., Fuel Process. Technol. 2004, 86, 449–460.
6. D. J. Mishra, Kim, D.E. Ralph, J.G. Ahn, Y. Rhee, J. Hazard Mater. 2008, 152, 1082-1091.
7. W. Lv, Z. Wang, H. Cao, Y. Sun, Y. Zhang, Z. Sun, ACS Sustainable Chem. Eng. 2018, 6, 1504.
8. M. Vanitha, N. Balasubramanian, Environ. Technol. Rev. 2013, 2, 101.
9. X. Zeng, J. Li, J. Hazard. Mater. 2014, 271, 50.
10. M. Jacoby, C&EN, 2019, 97, 1-3.
11. X. Zhang, Li Li, E. Fan, Qing Xue, Yifan Bian, Feng Wu and Renjie Chen. Chem. Soc. Rev., 2018, 47, 7239-7302.
12. S. Natarajan, V. Aravindan, ACS Energy Lett. 2018, 3, 2101–2103.
13. N. J. Boxall, N. Adamek, K. Y. Cheng, N. Haque, W. Bruckard, A. H. Kaksonen, Waste Manage. 2018, 74, 435.
14. X. Chen, H. Ma, C. Luo, T. Zhou, J. Hazard. Mater. 2017, 326, 77.
15. X. Chen, C. Luo, J. Zhang, J. Kong, T. Zhou, ACS Sustainable Chem. Eng. 2015, 3, 3104.
16. <https://seekingalpha.com/article/4139266-look-lithium-ion-battery-recycling-industry-companies> (accessed: June 2018)
17. Xianlai Zeng, Jinhui Li, Narendra Singh, Critical Reviews in Environmental Science and Technology 2016, 10(44), 1129-1165.
18. A. Akcil, F. Vegliò, F. Ferrell, M. D. Okudan, A. Tuncuk, Waste Management, 2015, 45, 420-433.
19. Angelids T.N., Tourasanidis E., Marinaou E., Stalidis G.A., Resour. Conserv. Recycl. 1995, 13, 269-82.
20. Sperl G.T., Hitzman D.O, United States Patent 1993, 5, 250, 483.
21. Rapaport D., Hydrocarbon Process. 2000, 79, 49-53.
22. Lassner J.A., Lasher L.L., Koppel R.L., Hamilton J.N., Chem. Eng. Prog., 1994, 90, 95–97.
23. Marafi M., Stanislaus A., J. Hazard. Mater. B, 2003, 101, 123–132.
24. Furimsky E., Catal. Today 1996, 30, 223-286.
25. Abdel-latif M.A., Miner. Eng. 2002, 15, 953-961.
26. Hoque M., Philip O., Mat.Sci. Eng. C., 2011, 31, 57-66.

27. <http://rockstone-research.com/index.php/en/research-reports/716-92-Resources-on-the-case-for-Hard-Rock-Lithium> (accessed: June 2018)].
28. International Energy Agency (IEA) Global EV Outlook 2018 (IEA, 2018).
29. G. Harper, R. Sommerville, E. Kendrick, L. Driscoll, P. Slater, R. Stolkin, A. Walton, P. Christensen, O. Heidrich, S. Lambert, A. Abbott, K. Ryder, L. Gaines, P. Anderson, *Nature* 2019, 575, 75-86.
30. S. Natarajan, V. Aravindan, *Adv. Energy Mater.* 2018, 8, 1802303.
31. Weiguang Lv, Zhonghang Wang, Hongbin Cao, Yong Sun, Yi Zhang, Zhi Sun, *ACS Sustainable Chem. Eng.*, 2018, 6, 2.
32. J. Xu, H. R. Thomas, R. W. Francis, K. R. Lum, J. Wang, B. Liang, *J. Power Sources* 2008, 177, 512.
33. J. Li, G. Wang, Z. Xu, *J. Hazard. Mater.* 2016, 302, 97.
34. S. P. Barik, G. Prabakaran, L. Kumar, *J. Cleaner Prod.* 2017, 147, 37.
35. D. Dutta, A. Kumari, R. Panda, S. Jha, D. Gupta, S. Goel, M. Kumar Jha, *Sep. Purif. Technol.* 2018, 200, 327.
36. González J., Rivarola J., Ruiz M., *Metallurgical and Materials Transactions B* .2004, 35, 439, 448.
37. Yoo J.S., *Catalysis Today* 1998, 44, 27-46.
38. Gaballah I., Diona M., *Resources Conservation and Recycling*, 1994, 10, 87-96.
39. Marafi M., Stanislaus A., Absi-Halabi M, *Applied Catalysis B: Environmental*, 1994, 4, 19-27.
40. Marafi M., Stansilaus A., *Journal of Hazardous Materials*, 2003, 101, 123-132.
41. Rabah M.A., Hewaidy I.F., Farghaly F.E., *Powder Metallurgy* 1997, 40, 283-288.
42. Busnardo R.G., Busnardo N.G., Salvato G.N., Afonso J.C., *J. Hazard Mater* 2007,139, 391-398.
43. Mulak W., Szymczycha A., Lesniewicz A., Zyrnicki W., *Physicochemical Problems of Mineral Processing*, 2006,40, 69–76.
44. Zhang L, Xu Z. *Journal of Cleaner Production*, 2016,127,19–36.
45. Corti C W. *Gold Bulletin*, 2010, 43(3), 209–220.
46. Li J, Wang G, Xu Z. *Journal of Hazardous Materials*, 2016, 302, 97-104.
47. Ma E, Lu R, Xu Z. *Green Chemistry*, 2012,14(12), 3395.
48. Yoo J M, Jeong J, Yoo K, Lee J, Kim W. *Waste Management*, 2009, 29(3), 132–1137.
49. Oza R., Patel S, *Research Journal of Recent Sciences*, 2012, 1, 434-443.
50. D.Quintero-Almanza, Z. Gamiño-Arroyo, L. E. Sánchez- Cadena, F. I. Gómez-Castro, A. R. Uribe-Ramírez, A.F.Aguilera-Alvarado and L.M. Ocampo Carmona, *Batteries* 2019,5(2), 44.
51. Invascanu S., Roman O., I. Solvation process. *Buletinul Institutului Politehnic Iasi, Sect. II*

- 1975, 2, 47-51.
52. Al-Mansi N.M., Abdel Monem, *Waste Management*, 2002, 22, 1, 85-90.
53. Sahu K.K., Pandey B.D., Chand P., 2005, US Patent No. 6733564 B1
54. Ganguli P., Bhat A. N., Ghuge K. D., *Indian IN*, 1988 163, 871.
55. Nazemi M.K., Rashchi F., Mostoufi N., *International Journal of Mineral Processing*, 2011, 100, 21–26.
56. Sinka G., Vigvari M., Kovacs G., Legat T., Gyulasi I., Gabor G., Pusztai M., Hung. Teljes, 1988. HU, 46, 566.
57. Stork, Wellem Harman Jurriaan, 1978, DE 2,812,597.
58. Lussiez P., Osseo-asare K., Simkovich G., *Metallurgical Transactions B*, 1981, 12, 4, 651-657.
59. Hyatt D.E., 1987, US Patent 4, 657, 745.
60. Prajapati R.P., Sharma A., Tiwari D.R., *Orient. J. Chem.*, 2010, 26, 2, 721-723.
61. Alex, Mukherjee T.K., Sundaresan M., *Metals Materials and Processes*, 1991, 381-392.
62. Parton G., Moretti G., Zingales A., *Rivistadei Combustibili*, 1993, 47, 169–175.
63. Amer, Al-mansi, *Waste Manag.* 2002, 22, 515-520.
64. Abdel-Aal E.A., Rashad M.M., *Hydrometallurgy*, 2004, 74(3-4) 189-194.
65. De Lima T.S., Campos P.S., Afonso, J.C., *Hydrometallurgy*, 2005, 80, 211–219.
66. Vieceli N, Nogueira C.A, Pereira MFC, Durão F.O, Guimarães C, Margarido F., *J Environ Manage.* 2018, 15, 228, 140-148.
67. Zhu Shu-guang, He Wen-zhi, Li Guang-ming, Zhou Xu, Zhang Xiao-jun, Huang Ju-wen, *Trans. Nonferrous Met. Soc. China*, 2012, 22, 2274–2281.
68. Pratima Meshram, Abhilasha, Banshi Dhar Pandeya, Tilak Raj Mankhand, Haci Deveci, *Journal of Industrial and Engineering Chemistry*, 2016, 43, 117–126.
69. Jin, YJ, Mei, GJ, Li, SY. *Hydrometallurgy of China*, 2006a 25, 97–99.
70. W. S. Chen and H. J. Ho, *Key Engineering Materials*, 2018, 775, 419-426
71. Weiguang Lv, Zhonghang Wang, Hongbin Cao, Xiaohong Zheng, Yi Zhang, *Waste Management*, 2018, 79, 545-553.
72. Daniel Quintero-Almanza, Zeferino Gamiño-Arroyo, Lorena Eugenia Sánchez-Cadena, Fernando Israel Gómez-Castro, Agustín Ramón Uribe-Ramírez, *Batteries*, 2019, 5, 44.
73. Jing Gao, Yunren Qiu, Maolin Li, Huishang Le, *Hydrometallurgy*, 2019, 189, 105127.
74. S.M. Shin, NakHyoungh Kim, JeongSooSohn, Dong HyoYang, Young HanKim, *Hydrometallurgy*, 2005, 79, 3–4, 172-181.
75. M. K. Jha, A. Kumari, A. K. Jha, V. Kumar, Jhumki Hait, B. D. Pandey, *Waste Management* 2013, 33, 9, 1890-1897.
76. Sheik A. R., Ghose M.K., Sanjay K., Subbaiah T., Mishra B.K., *Journal of the Taiwan Institute of*

- Chemical Engineers, 2013, 44,(1), 34-39.
77. Girgis B.S., Youssef A.M., Fertilizer Technology, 1976, 13, 265.
78. Jones C.F., Segall R.L., Smart R.S.C., Turner P.S., J. Chem. Soc., Faraday Trans. 1977, 1, 73(10) 1710
79. Singh S., Ind. J. Chem. Techn., 1993, 31, 577-580.
80. Loboiko A.Y., Atroshchenko V.I., Grin G.I., Kutovoi V.V., Otkrytiâ, Izobreteniâ, PromyshlennyeObrazcy, TovarnyeZnaki, 1983, 14, 33.
81. Yuliusman, Radifan Fajaryanto, Annisaa Nurqomariah, and Silvia, E3S Web of Conferences 2018, 67, 03025.
82. Bas, A. D., Deveci, H., & Yazici, E. Y., Sep. Purif. Technol., 2014, 130, 151-159.
83. Chao Peng, Fupeng Liua, Zulin Wang, Benjamin P. Wilson, Mari Lundström., Journal of Power Sources, 2019, 415, 179-188.
84. Welsh J.Y., Picquet P.C., Schyns P.D., Eur. Pat. 1980, 172, 85.
85. A. J. Chaudhary, J.D. Donaldson, S.C. Boddington, S.M. Grimes. Hydrometallurgy, 1993, 34, 137-150.
86. Antti Porvali, Miamari Aaltonen, Severi Ojanen, Omar Velazquez-Martinez, Emmi Eronen, Benjamin P. Wilson, Rodrigo Serna-Guerrero, Mari Lundström., Resources, Conservation and Recycling, 2019, 142, 257-266.
87. Soraya Ulfa Muzayanha, Cornelius Satria Yudha, Adrian Nur, Hendri Widiyandari, Hery Haerudin, Hanida Nilasary, Ferry Fathoni and Agus Purwanto, Metal, 2019, 9, 615.
88. Md. Rashid Al-Mamun Related information, Md. Faridul Islam, Mala Khan Sumiya Aktar, S. Akther, K. Fatema., International Journal of Environment and Waste Management, 2016, 17, 3-4.
89. Md. Al Hossaini Shuva, ASW Kurny, American Journal of Materials Engineering and Technology, 2013, 1(1), 8-12.
90. Millsap W.A., Reisler N., Eng. and Min. J., 1978, 179, 105-107.
91. Hubred G.L. US Patent 1984, 4,514,368.
92. Hubred L.G., Van D.A., Leirsburg P. US Patent 1984, 4,432,949.
93. Hubred G.L. & Van Leisburg, D.A., 1985, US No. 4514369.
94. Marcantonio J. P., 1991 US Patent No. 5, 66, 469.
95. Paul J. Marcantonio., 2009, US Patent No. 7, 485,267 B2.
96. Yoo J.M., Lee J.C., Kim B.S., Lee H.S., Jeong J.K., Journal of Chemical Engineering of Japan 2004, 37, 1129-34.
97. Zheng X, Gao W, Zhang X, He M, Lin X, Cao H, Zhang Y, Sun Z., Waste Management 2017, 60, 680-688.

98. Caibin Wu ,Bensheng Li , Cheng fang Yuan , Waste Management, 2019, 93, 153-161.
99. Ku Heesuk, Jung, Yeojin, Jo, Minsang, Park, Sanghyuk, Kim, Sookyung, Yang, Donghyo, Rhee, Kangin, An, Eung-Mo, Sohn, Jeongsoo, Kwon, Kyungjung, Journal of hazardous materials, 2016, 313, 138-146.
100. Ku Heesuk, Yeojin Jung, Kyungjung Kwon, Journal of the Korean Institute of Resources Recycling, 2015, 24, 3, 44-50.
101. Beuther H., Flinn R.A., Industrial and Engineering Chemistry Product Research and Development, 1963, 2, 53.
102. Marafi M, Stanislaus A. Applied Catalysis, 1989, 47, 85–96.
103. Marafi M., Kam E.K.T., Stanislaus A., Absi-Halabi M., Applied Catalysis A: General, 1996, 147, 35–46.
104. Stanislaus A., Marafi M., Absi-Halabi M., Applied Catalysis A: General, 1993, 105, 195-203.
105. Marafi A., Fukase S., Al-Marri., Stanislaus A., Energy and Fuels, 2003, 17, 661–668.
106. Marafi M., Furimsky E. Erdol, ErdgasKohle, 2005, 121,93–96.
107. Mulak W., Miazga B., Szymczycha A., 2005. Int. J. Miner. Process, 2005,77, 231-236.
108. Zheng, Y., Long, H. L., Zhou, L., Wu, Z. S., Zhou, X., You, L., Yang, Y., & Liu, J. W., International Journal of Environmental Research, 2016, 10 (1), 159–168
109. Li Li, Jennifer B.Dunn, Xiao XiaoZhang, LindaGaines, Ren JieChen, FengWu, KhalilAmine, Journal of Power Sources, 2013, 233,180-189.
110. MiamariAaltonen, Chao Peng, Benjamin P. Wilson and Mari Lundström, Recycling , 2017, 2(4), 20 .
111. Golmohammadzadeh R, Rashchi F, Vahidi E., Waste Manag. , 2017, 64,244-254.
112. Wang, F.; Sun, R.; Xu, J.; Chen, Z.; Kang, M., RSC Adv. 2016, 6, 85303–85311.
113. Wang, J.; Chen, M.; Chen, H.; Luo, T.; Xu, Z, Procedia Environ. Sci. 2012, 16, 443–450.
114. Meshram, P.; Pandey, B.D.; Mankhand, T.R.; Deveci H., JOM, 2016, 68, 2613–2623.
115. Pagnanelli, F.; Moscardini, E.; Granata, G.; Cerbelli, S.; Agosta, L.; Fieramosca, A.; Toro, L. J. Ind. Eng. Chem. 2014, 20, 3201–3207.
116. Nayaka, G.P.; Manjanna, J.; Pai, K.V.; Vadavi, R.; Keny, S.J.; Tripathi, V.S., Hydrometallurgy, 2015, 151, 73–77.
117. Xue Q, Zhang X, Li L, Wu F, Chen R., Environmental Mining. Montreal (Canada): FLOGEN Star Outreach. 2016, 152-153.
118. Yuliusman, AnnisaaNurqomariah, RadifanFajaryanto, Silvia, E3S Web of Conferences 2018, 67, 03036.
119. Li, Li., Qu, W., Zhang, X., Lu, J., Chen, R., Wu, F., & Amine, K., Journal of Power Sources, 2015, 282, 544–551.

120. Shinohara Y., Mitsuhasli M., Japan kokai, 1976, 76, 82–86.
121. Floarea O., Mihai M., Morarus M., Kohn D., Sora M., *Revista de Chimie (Bucharest)* 1991, 42, 553.
122. Veal J.T., Anderson K.A., Kowaleski R.M., US Patent 2001, 6, 180, 72.
123. Vicol M., Heves A., Potoroaca M., *ombinatuldeIngrasaminteChimice Piatra Neamt*, 1986,112, 832.
124. Garole D.J., 2005. Novel methods of recovery of industrial important and environmentally hazardous metals from spent catalysts, Ph.D. Thesis University of Mumbai, Mumbai, India.
125. Manoliu C., Olara I., Zugravescu P., Serdaru M., Popescu E., *Rom. Ro.*, 1985, 87, 980.
126. Rokukawa N., US Patent 1983, 4, 382, 68.
127. Park K.H., Mohapatra D., Reddy B.R., Nam C.W., *International Journal of Mineral Processing*, 2006, 80, 261–265.
128. Villarreal S.M., Kharisov B.I., Torres Martinez L.M., Elizondo V.N, *Industrial Engineering Chemistry Research*, 1999, 38, 4624-4628.
129. NangoGaye, RokhayaSyllaGueye , Jérôme Ledauphin, Mamadou Balde, MatarSeck , Alassane Wele and MahyDiaw, *Asian Journal of Applied Chemistry Research*, 2019,3, 2, 1-7.
130. Nayl A.A., R.A. Elkhashab, Sayed M. Badawy, M.A. El-Khateeb, *Arabian Journal of Chemistry*, 2017, 10, S3632-639.
131. Senanayake, G., Shin S.M., Senaputra, A., Winn, A., Pugaev, D., Avraamides, J., Sohn,J.S., Kim,D.J., *Hydrometallurgy*,2010, 105 (1-2), 36–41.
132. Sayilgan, E., Kukrer, T., Yigit,N.O., Civelekoglu, G., Kitis, M., *J. Hazard. Mater.*, 2010, 173 (1-3), 137–143.
133. Xiao, L., Zhou, T., Meng, J., *Particuology*, 2009, 7(6), 491–495.
134. Peng, C., Bai, B., Chen, Y., *Waste Manage.*, 2008, 28 (2), 326– 332.
135. Freitas, M. B. J. G., Pegoretti,V.C., Pietre, M.K., *J. Power Sources*,2007, 164(2), 947–952.
136. Jong B.B., Rhoads S.C., Stubbs A.M., Stoelting T.R., 1989. U.S. Bureau of Mines, Report No. 9252.
137. Park KH, Mohapatra D, Nam CW, *J Hazard Mater*. 2007, 148, (1-2):287-95.
138. MK Nazemiand F Rashchi, *Waste Management & Res*, 2012, 30, 492-497.
139. Sun D.D., Chang L., Tay J.H., Navratil J.D., Easton C., *Journal of Environmental Engineering* 2001a, 127, 916-21.
140. Sun D.D., Tay J.H., Cheong H.K., Leung D.L.K., Qian G., *Journal of Hazardous Materials*, 2001b, 87, 213-23.
141. Valverde Jr., I.M., Paulino J.F., Afonso J.C., *Journal of Hazardous Materials*, 2008, 160, 2–3, 310–317.

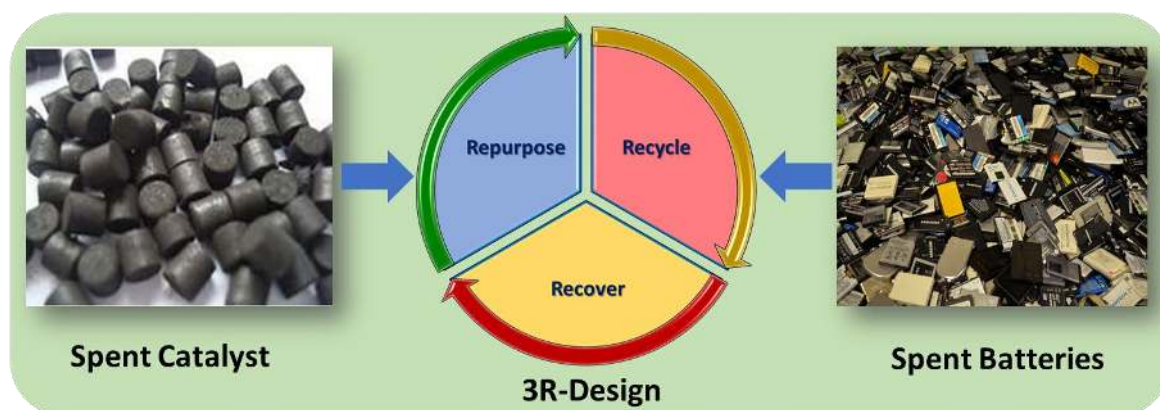
142. Wadood T. Mohammed, Nada S. Ahmedzeki, Mariam F. AbdulNabi, Iraqi Journal of Chemical and Petroleum Engineering, 2011, 12 (4), 21-35.
143. Meena Marafi and Mohan Rana, Journal of Environmental Science and Health, Part A , 2018, 53, 11, 951-959.
144. Chagnes, A. and Pospiech, B., J. Chem. Technol. Biotechnol, 2013, 88, 1191-1199.
145. Georgi-Maschler, T., Friedrich, B., Weyhe, R., Heegn, H. and Rutz, M., J. Power Sources, 2012, 207, 173-182.
146. Ferreira, D. A., Prados, L. M. Z., Majuste, D., Mansur, M. B, J. Power Sources, 2009, 187(1), 238-246.
147. Harvianto, G. R., Jeong, S. G. and Ju, C. S., Korean J. Chem. Eng., 2014, 31(5), 828-833.
148. Lee, J. K., Jeong, S. G., Koo, S. J., Kim, S. Y. and Ju, C. S., Korean Chem. Eng. Res., 2013, 51(1), 53-57.
149. Sakultung, S., Pruksathorn, K., & Hunsom, M., Korean Journal of Chemical Engineering, 2007, 24(2), 272-277.
150. Xu, J., Thomas, H. R., Francis, R. W., Lum, K. R., Wang, J. and Liang, B, J. Power Sources, 2008, 177, 512-527.
151. Kang, J., Senanayake, G., Sohn, J. S. and Shin, S. M., Hydrometallurgy, 2010, 100, 168-171.
152. Swain, B., Jeong, J., Lee J.-C., Lee, G. H. and Sohn, J. S., J. Power Sources, 2007, 167, 536-544.
153. Zhang, P., Yokoyama, T., Itabashi, O., Suzuki, T., Inoue, K., Hydrometallurgy, 1998, 47, 259-271.
154. Qinghua Zhang, Karine De Oliveira Vigier, Sébastien Royer and François Jerome, Chemical Society Review, 2012, 7, 41(21), 7108-46.
155. Mai K. Tran, Marco Rodrigues, Keiko Kato, Ganguli Babu, Pulickel M. Ajayan, Nature Energy, 2019, 4, 339-345.
156. Albler, Franziska-Jane, Bica, Katharina, Foreman, Mark R. StJ., Holgersson, Stellan, Tyumentsev, Mikhail S, Journal of Cleaner Production, 2017, 167, 806-814.
157. Pranolo Y., Wensheng Zhang, C. Y. Cheng, Hydrometallurgy, 2010, 102(1):37-42.
158. Nerea Rodriguez, Lieven Machiels & Koen Binnemans, ACS Sustainable chemistry and engineering, 2019, 7, 3940-3948.
159. Havlik T., Orac D., Petranikova M., Miskufova A., Kukurugya F., Takacova Z., Journal of Hazardous Materials, 2010, 183, 866-873.
160. Jadhav U.U., Hocheng H., Journal of Achievements in Materials and Manufacturing Engineering, 2012, 54, 159-165.
161. Mishra D., Kim D.J., Ralph D.E., Ahn J.G., Rhee Y.H., Hydrometallurgy, 2007, 88, 202-209.

162. Briand L., Thomas H., Donati E., *Biotechnology Letters*, 1996, 18, 505-508.
163. Bosio V., Viera M., Donati E., *J. Hazard. Mater.* 2008, 154, 804-810.
164. Zeng L., Cheng C.Y., Part: I. Metallurgical Processes, *Hydrometallurgy*, 2009, 98, 1-9.
165. Beolchini F., Fonti V., Ferella F., Vegliò F., *J. Hazard. Mater.* 2010, 178, 529- 534.
166. Gholami R., Borghei S., Mousavi S., *Hydro-metallurgy*, 2011, 106, 26-31.
167. Anjum F., Bhatti H., Asgher M., Shahid M., *Appl. Clay Sci.* 2010, 47, 356-361.
168. Aung K. M. M., Ting Y. P., *Bio-technology*, 2005, 116, 159-170.
169. Johnson D.B., *Hydrometallurgy*, 2006, 83, 153-166.
170. Brandl H., Bosshard R., Wegmann M., 2001. *Hydrometallurgy*, 201, 59(2-3), 319-326.
171. Bombarcher C., Bachofen R., Brandl H., *Applied and Environmental Microbiology*, 1998, 64:1237–41.
172. Santhiya D., Ting Y.P., *J. Biotechnol.* 2005, 116, 171–184.
173. Blaustein B, Hauck J.T., Olson G.J., Baltrus J.P., *Fuel.* 1993, 72, 1612–8.
174. Santhiya D., Ting Y.P., *Journal of Biotechnology*, 2005, 116,171–84.
175. Marcincakova, Jana kadukova, Anna Mrazikova, Oksana Velgosova, Alena Luptakova, Stefano Ubaldini, *Journal of the Polish Mineral Engineering Society*,2016, 117-120.
176. Debaraj Mishra, Dong-JinKim, D.E.Ralph, Jong-GwanAhn,Young-HaRhee, *Waste Management*, 2008, 28, 2, 333-338.
177. N. BahalooHoreh , S.M. , Mousavi, S.A.Shojaosadati, *Journal of Power Sources*, 2016, 320, 257-266.
178. M. Hartono, M. A. Astrayudha, H. T. B. M. Petrus, W. Budhijanto and H. Sulisty Lithium. *Rasayan J. Chem.*, 2017,10(3), 897-903.
179. Strasser H., Burgstaller W., Schinner F., *S. Microbiological Letters*, 1994, 119, 365-70.
180. Xin B, Zhang D, Zhang X, Xia Y, Wu F, Chen S, Li L. *Bioresour Technol.* 2009, 2, 100(24), 6163-9.
181. R. S. Dobson and J. E. Burgess, *Bio;ogical treatment of precious metals refinery wastewater : a review. Miner. Eng.*, 2007, 20, 519–532.
182. B. Volesky and Z. R. Holan, *Biotechnol. Prog.*,1995, 11, 235–250.
- 183 .N. Tewari, P. Vasudevan and B. K. Guha, *Biochem. Eng. J.*, 2005, 23, 185–192.
184. Wang, J., Chen, N., *Biotechnol. Adv.*2009, 27(2), 195-226.
185. B.C Chaudhary, D. Paul, A. U.Borse, Dipak J Garole, *Journal of Chemical Technology and Biotechnology*, 2017, 92,1667-1677.
186. B.C Chaudhary, D. Paul, A. U. Borse, D. J Garole, *Separation and Purification Technology*, 2018, 195,260-270.

- 187.D. J. Garole, B.C Chaudhary, D. Paul, A. U. Borse, *Environmental Science and Pollution Research*, 2018, 25, 10911-10925.
188. Noura El-Ahmady El-Naggar, Ragaa A. Hamouda, Ibrahim E. Mousa, Marwa S. Abdel-Hamid & Nashwa H. Rabei , *Scientific Reports*,2018, 8, 13456.
189. A.N.Aziz, A.S.Colagar, S.M. Hafeziyan, *The Scientific World Journal*, 2012,1-7
191. Dolker T, Pant D. J.,*Environ Manage.*2019, 248:109270.
191. Chen Y., Feng Q., Shao Y., Zhang G., Qu L., Lu Y., *Mineral Engineering*, 2006,19, 94-97.
192. Sebenik R.F., Ference R.A., In: *Symposium Stork Willen Hartman Jurrian, GerOffen*, 1982, 2, 812, 597.
- 193 S. Natarajan, S. Anantharaj, R. J. Tayade, H. C. Bajaj, S. Kundu, *Dalton Trans.*,2017, 46,
194. V. Aravindan, S. Jayaraman, F. Tedjar, S. Madhavi, *ChemElectroChem*,2019, 6, 1407-1412.
195. Y. Zhang ,N. Song, J. He, R. Chen, X. Li., *Nano Lett.*, 2019, 19, 512-519.
196. S. Natarajan,S. Rao Ede, H. C. Bajaj, S. Kundu, *Colloids and Surfaces A: Physicochemical andEngineering Aspects.*, 2018, 543, 98-108.
197. S. Natarajan, H. C. Bajaj, V. Aravindan, *J. Mater. Chem. A*, 2019, 7, 3244-3252.
198. S. Natarajan, M. Ulaganathan, H. C. Bajaj, V. Aravindan, *ChemElectroChem*, 2019, 6, 5283-5292.

TOC:

Recycle, recover and repurpose (3R) strategy to wipe out spent catalyst and spent battery waste.



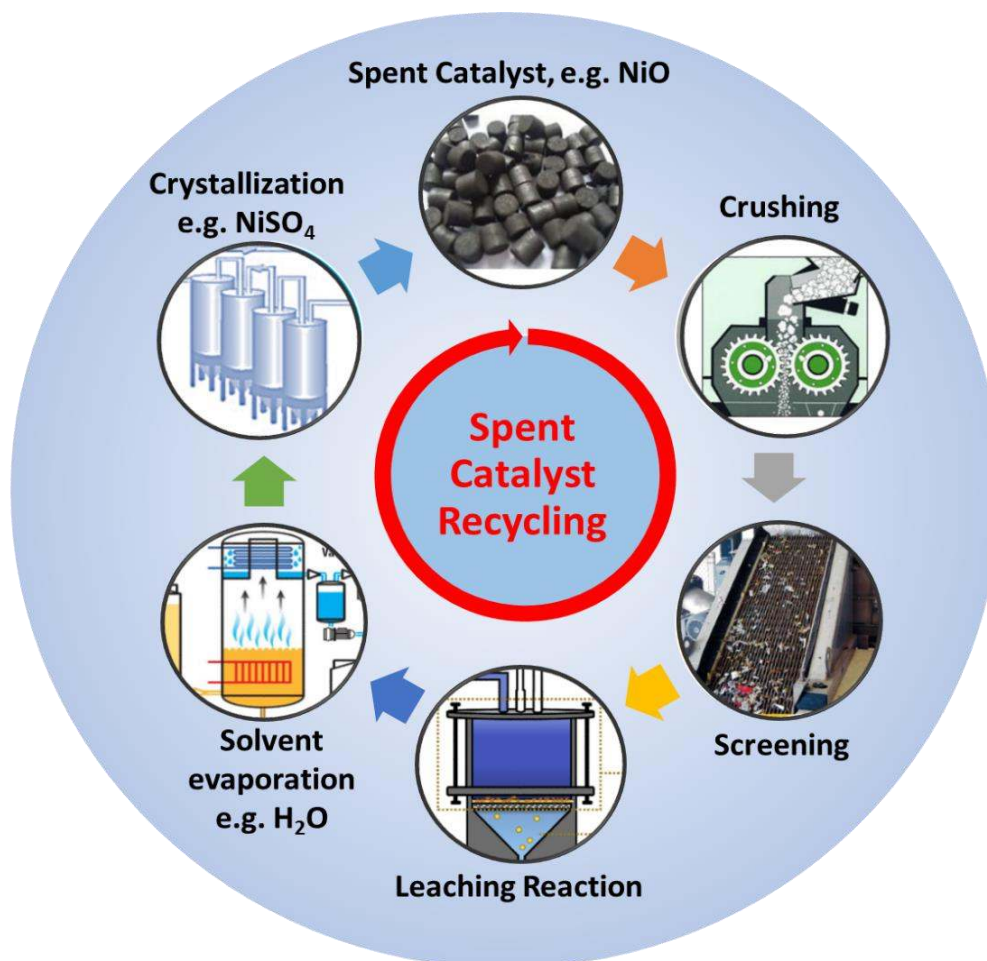


Figure 1. Flow diagram of the processes involved in the recycling for spent catalyst

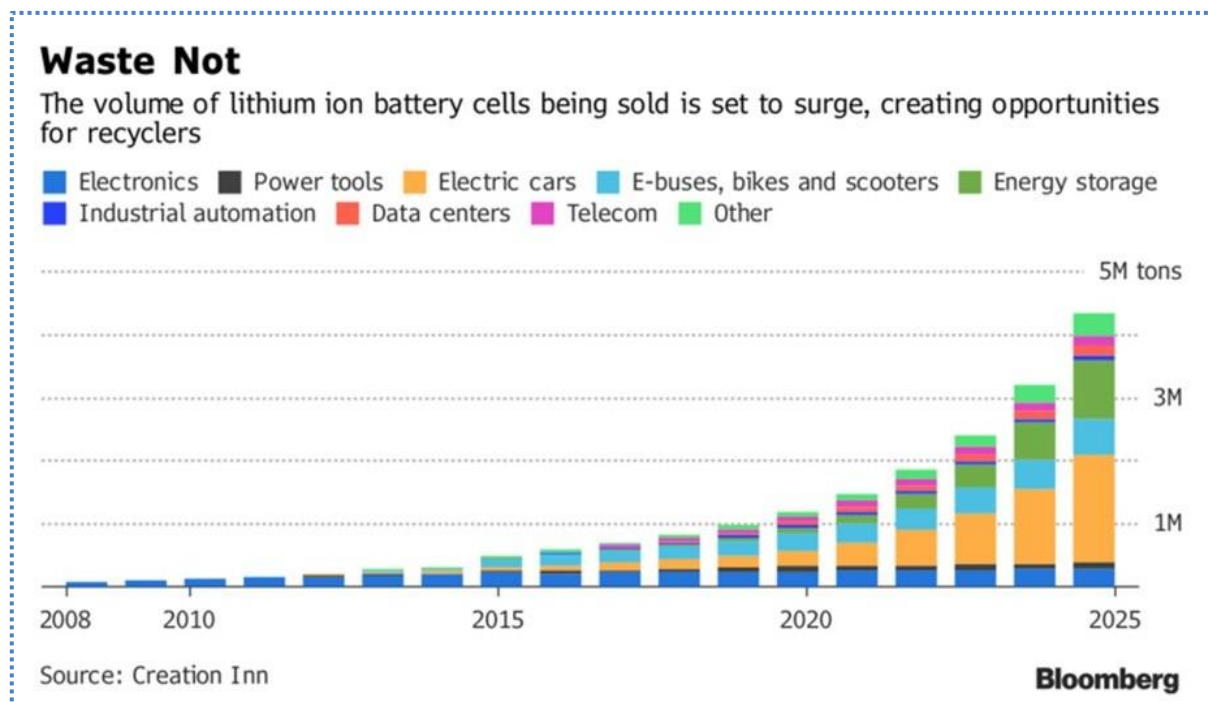


Figure 2 The forecast of LIBs going to be retired and amount of generated waste in near future.

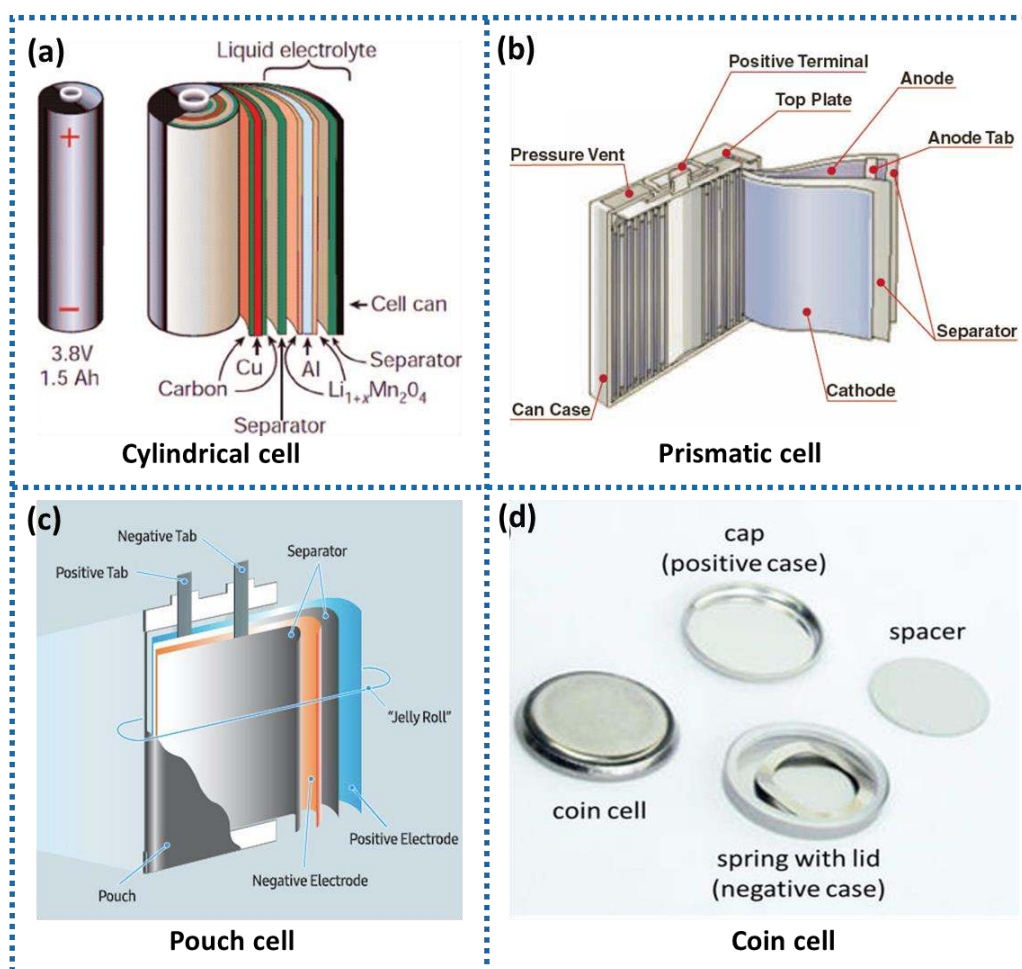


Figure 3 Different cell designs of LIBs (a) Cylindrical cell, (b) Prismatic cell, (c) Pouch cell and (d) Coin cell.

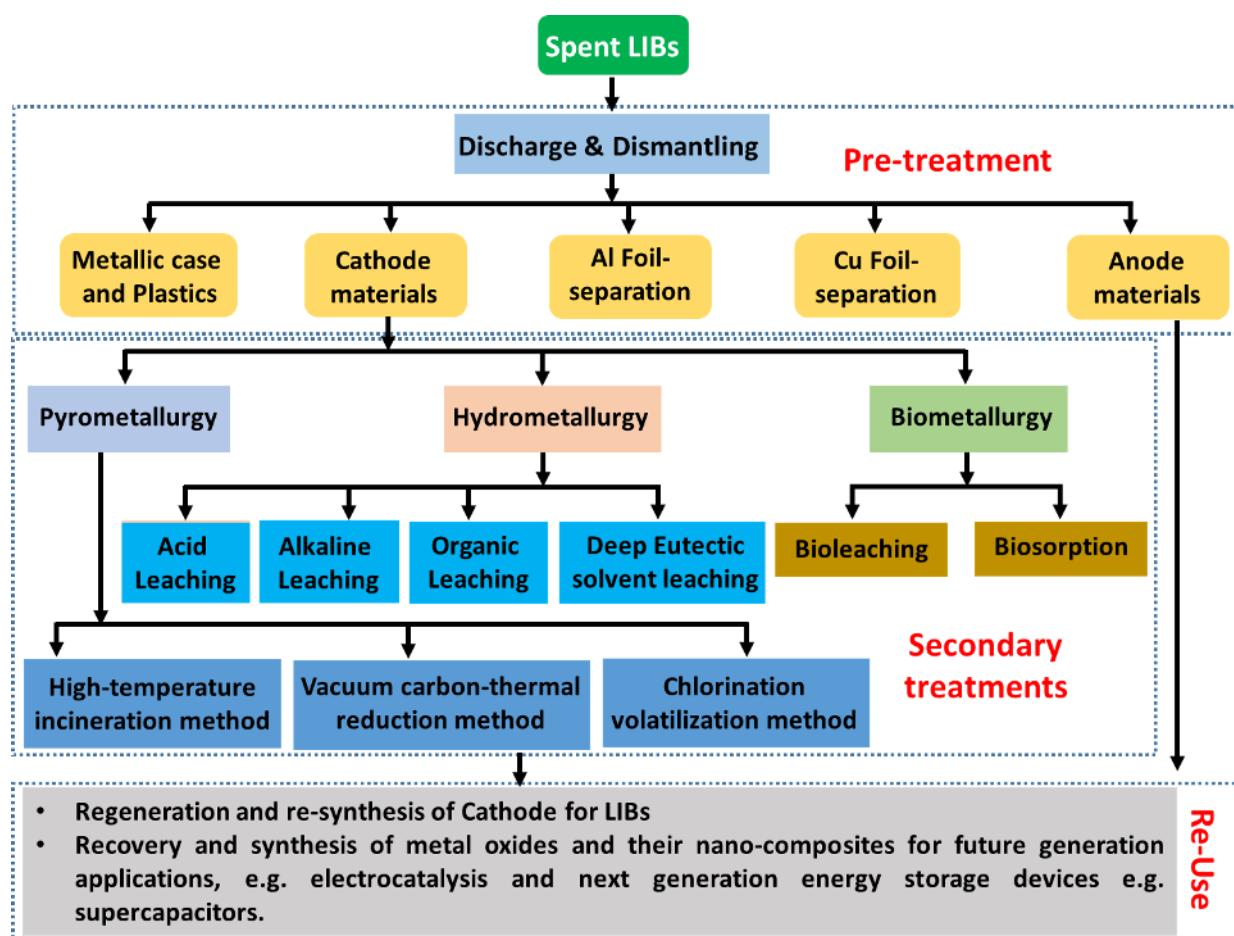


Figure 4 Recover, Regenerate and Re-use (3R): A closed-loop-approach for recycling of spent lithium ion batteries (LIBs)

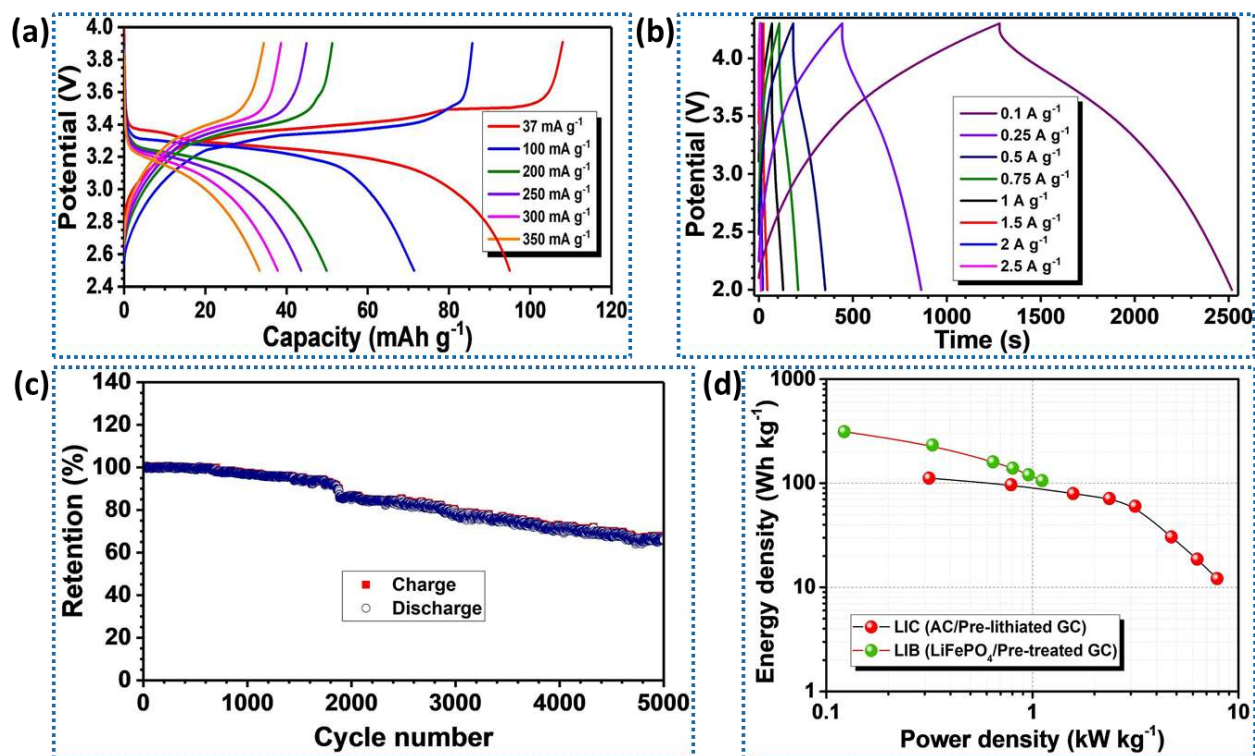


Figure 5 (a and b) Galvanostatic charge/discharge curves for LiFePO₄/pre-treated GC full LIB and activated carbon/pre-lithiated GC based Li-ion capacitor (LIC) at various current densities, respectively. (c) Cycling stability of activated carbon/pre-lithiated GC based LIC. (d) Ragone plot with the values of energy and power densities of LIC and LIBs. Reprinted with permission from ref. 171, Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

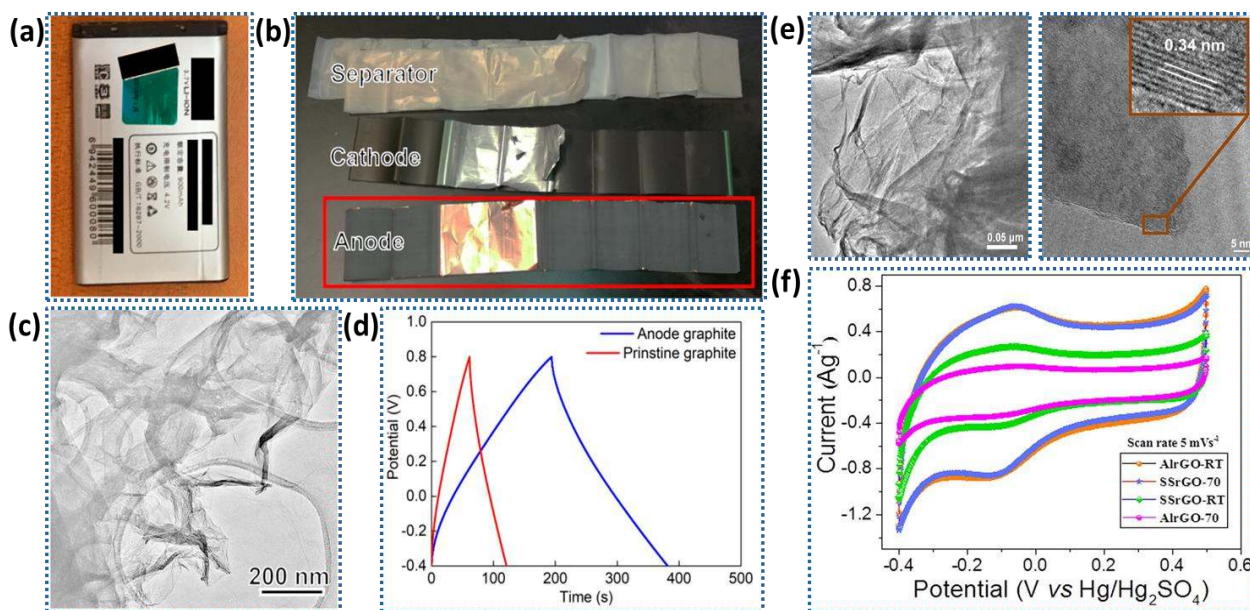


Figure 6 (a) End-of-life LIBs recovered from electronic devices (b) Different components of LIBs after physical dismantling. (c) Scanning electron micrograph of graphene prepared by shear mixing method. (d) Galvostatic charge/discharge curves for graphene prepared from fresh and used graphite. Reproduced with permission from ref. 172, Copyright 2019 American Chemical Society. (e) SEM images of reduced graphene oxide (rGO) prepared by Hummers method using Al as reducing agent. (f) Cyclic voltammetry curves of rGO prepared using Al and stainless steel casings as reducing agents. Reprinted with permission from ref. 173, Copyright 2018 Elsevier.

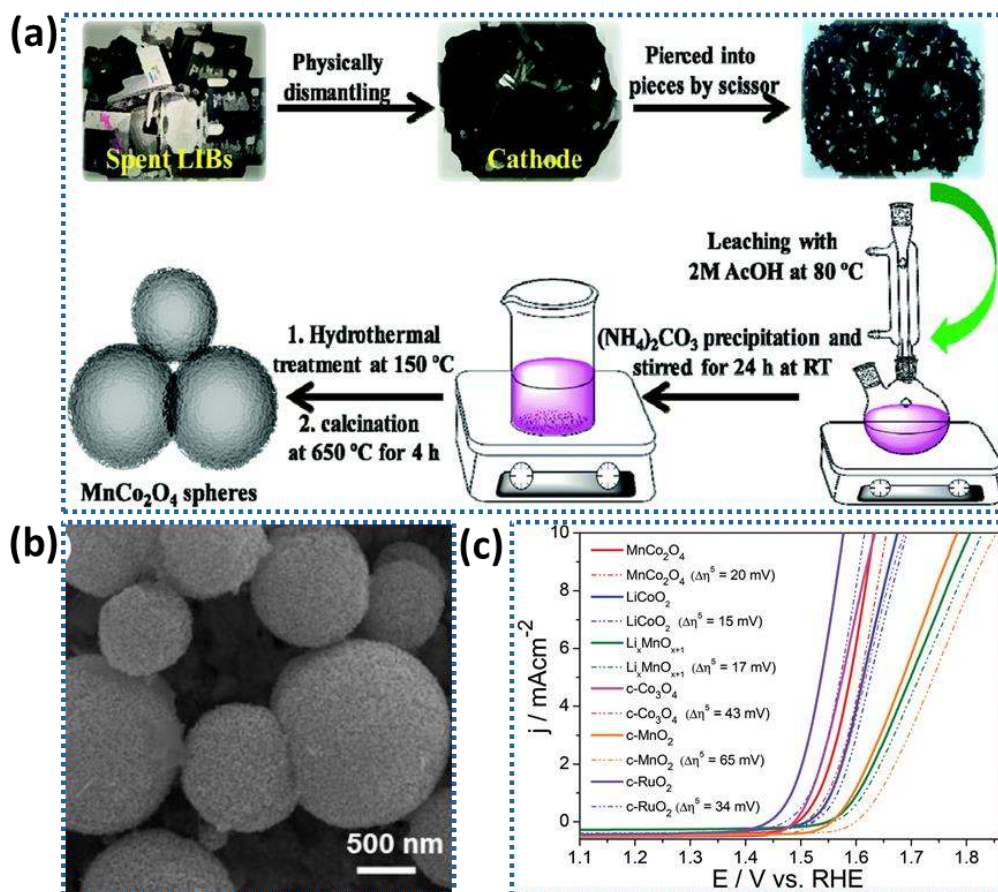


Figure 7 (a) Schematic illustration of overall recovery and synthesis spinel MnCo₂O₄ microspheres from the spent LIBs. (b) SEM image of spinel MnCo₂O₄ microspheres. (c) Linear sweep voltammetry (LSV) curves for re-synthesized spinel MnCo₂O₄ microspheres, recovered LiCoO₂, Li_xMnO_{x+1}, c-Co₃O₄, c-MnO₂ and c-RuO₂ measured at scan rate of 5 mV/s in 1 M KOH. Reproduced with permission from ref. 176, Copyright 2017, The Royal Society of Chemistry.

Table 1 List of leaching agents used for spent catalyst and spent lithium ion batteries materials

Reagents	Type of Spent Material	References
Sulphuric acid (50 %)	Spent catalyst (NiO/Al ₂ O ₃)	44
Sulphuric acid (18 %)	Spent catalyst (NiO/Al ₂ O ₃) from fertilizer process from steam reforming process	25
Sulphuric acid (8 %)	(NiO/Al ₂ O ₃ /Fe ₂ O ₃) from urea production unit	33
Sulphuric acid (50 %)	Spent catalyst (NiO/Al ₂ O ₃)	32
Sulphuric acid 60 g/L under atm. and oxygen pressure	Egyptian boiler ash	43
Hydrochloric acid	Low grade spent catalyst	65
(NH ₄) ₂ CO ₃	Spent catalyst (NiO/Al ₂ O ₃)	100
H ₂ SO ₄ (80%)	Spent catalyst (NiO/Al ₂ O ₃) in an ammonia plant	31
60–70%	Spent NiO catalyst	60
Nitric acid	spent NiO–Al ₂ O ₃ catalyst	56
H ₂ SO ₄ + H ₂ S	Spent Catalyst	39
Tartaric acid	Spent catalysts	86
HCl	Fatty nickel catalysts	103
Na ₂ CO ₃ + H ₂ O ₂	Spent catalyst	106
NaOH 10% pH 8.8	Spent catalyst	107
NaOH atm pressure leaching two step	Spent catalyst	101
NaOH (1 st stage) & H ₂ SO ₄ (2 nd stage)	Spent catalyst	115
NaOH (1 st stage) & H ₂ SO ₄ (2 nd stage)	Spent catalyst	10
Na ₂ CO ₃ (roasting + Leaching with H ₂ O)	Spent catalyst	161
KHSO ₄ Fusion + water Extraction	Spent catalyst	24
Aqueous NH ₃ + NH ₄ CO ₃ + H ₂ O ₂	Spent catalyst	74
Glycine + ascorbic acid	Lithium ion batteries	95
Citric Acid + H ₂ O ₂	Lithium ion batteries	9

HCl	Lithium ion batteries	128
HCl + H ₂ O ₂	Lithium ion batteries	69
H ₂ SO ₄ + H ₂ O ₂	Lithium ion batteries	109
H ₂ SO ₄ + H ₂ O ₂	Lithium ion batteries	27

Table 2 Comparison chart in terms of efficiency and recovery process

Recovery Process	Advantages	Disadvantage	Environmental Hazards
Pyrometallurgy	High Capacity Simple Operation	High Temperature High Energy Consumption Low Metal recovery ration	Waste Gas Dusts
Hydrometallurgy	Low Energy Required High Metal recovery ratio High Purity Product	Recovery process take time Chemical Consumption is very high	Generate of waste water effluent
Biometallurgy	Low Energy Consumption Mild operation conditions High metal recovery ratio	Long Reaction Period Bacterial are difficult to cultivate	Waste water effluent