Retrieving Spent Cathodes from Lithium-Ion Batteries through Flourishing Technologies
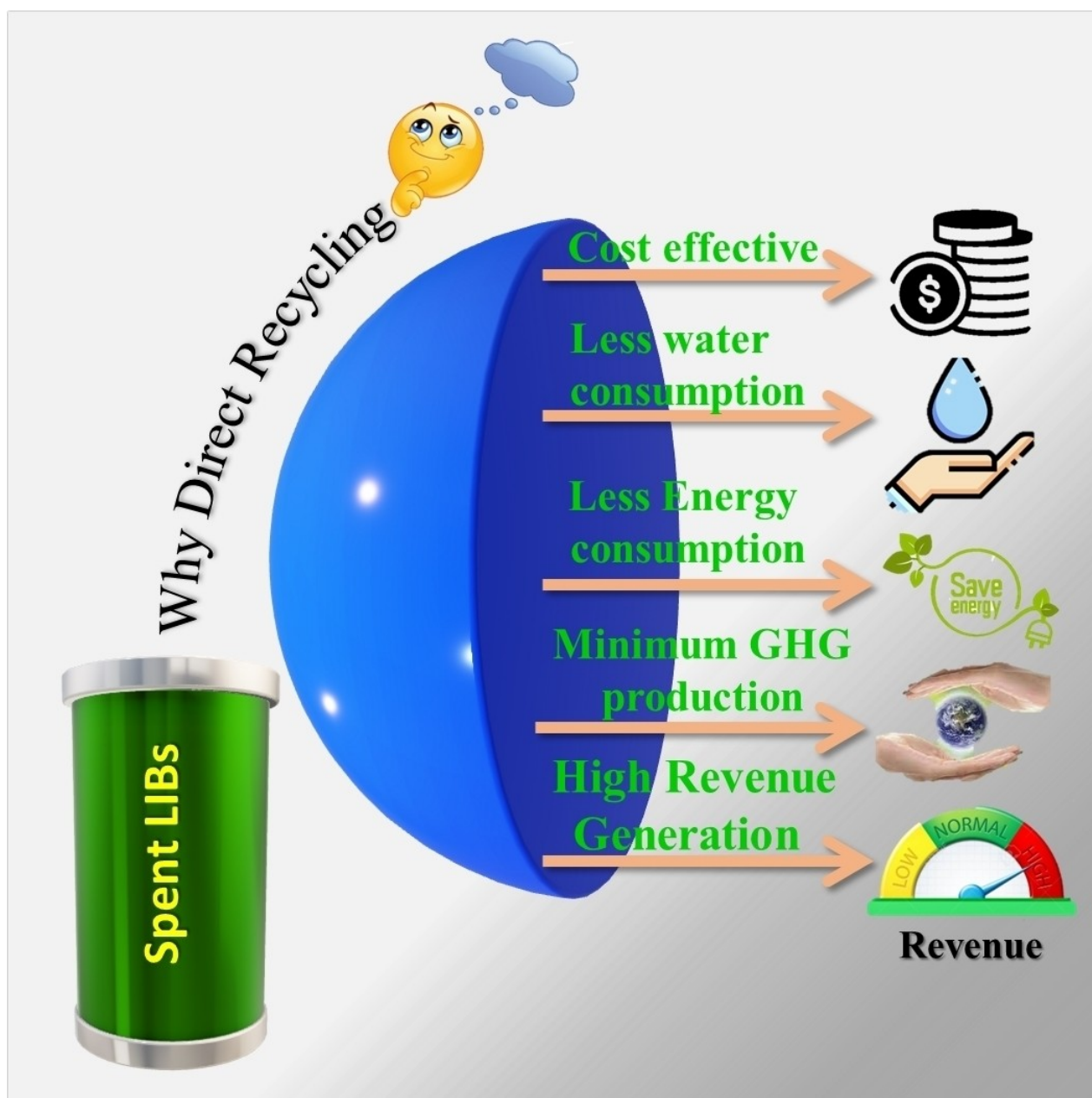
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The inherent advancement of lithium-ion batteries (LIBs) in electronic gadgets is expanding exponentially, and the ongoing surge of electric vehicles (EVS) in the near future will result in an unprecedented amount of lithium waste. Used cathode materials contain hazardous metal toxic, polymer binder, and electrolytes, posing a serious risk to the environment and public health. For socio-environmental reasons, it is required to recover all valuable metals or to immediately relithiate the used cathode materials by adding suitable salts in the stoichiometric ratio. As the consumption of batteries increases over time in daily life, recycling LIBs will become more and more crucial. Compared to the traditional hydrometallurgical and pyrometallurgical routes, direct recycling technologies can regenerate electrodes without using an intensive energy or chemicals, which saves money and reduces secondary waste. As a result, the authors emphasise direct relithiation methods for spent cathode relithiation, such as hydrothermal, ionothermal, electrochemical, and molten salts. In-depth analysis and discussion are also given to the aforementioned approaches. The deactivation, disintegration, and separation processes used in the physical processing of black mass and other constituents are discussed. We reviewed the obstacles, possible commercialization of technology, and recommendations to the reviewer for the developing ecologically friendly recycling technology in the near future toward the circular economy.

1. Introduction

The pressing demand for uninterrupted power supply mitigates the use of fossil fuels and minimizes the CO_2 emissions forcing the considerable research interest for the scientific community to develop renewable sources of an energy storage system.[1–4] The use of petroleum products negatively impacts over the environment, causing severe global warming issues by polluting the air and water.[5–7] In 2020, global CO_2 emissions from fossil fuels combustion were around 30.6 Gt CO_2, which is almost 8% lower than in 2019.[8] It is expected that the earth will run into a petroleum catastrophe in the coming decade due to the excessive depletion of fossils. To mitigate the use of the above-mentioned fossils, lithium-ion batteries (LIBs) play a vital role as an alternative energy source for small portable devices to large-scale electric vehicles (from an electric vehicle to a microchip).[9–12] Generally spent LIBs contain 5–20% cobalt (Co), 5–10% nickel (Ni), 5–7% lithium (Li), 5–10% other metals (copper (Cu), aluminum (Al), iron (Fe), etc.), 15% organic compounds, and 7% plastics.[13–15] There is a substantial increase in the production of LIBs due to the increasing demand for portable electrotonic devices.[16] The inevitable production reduced up-gradation and application of LIBs leads to the enormous amounts of spent LIBs due to their limited life expectancy (about 3 to 10 years) and charging-discharging of 1000 cycles.[17,18] It was reported that the weight of spent LIBs in the year 2020 produced around 25 million tons around the world.[19,20] Similarly, in the electric vehicle sector, it is expected that approximately 1 million of the battery will reach their end-of-life (EOL) by 2025. Thus, Research and Development (R&D) sectors and the scientific community started thinking about minimizing the amounts of spent LIBs by developing advanced materials and technology to decrease environmental issues with increasing the life span of LIBs.[21,22] Thus, it is a significant challenge for the scientific community and R&D sector to recover all the critical metals, such as Li, Co, Ni etc. to address the supply chain issue. Among all the valuable metals Li and Co are in greater demand due to the low reserves and high-cost.[1] Basically, three techniques are cataloged to extract the valuable component from the spent battery, i.e., pyrometallurgy, hydrometallurgy, and direct recycling of LIBs.[23–29] In the first two methods, lithium recovery is very sceptical, although tedious experimental conditions with high temperature and pressure were followed. Again, the surface morphology and structure are deformed and degraded into the elemental constituents and recycled as secondary raw materials. The direct recycling process can be treated as an alternative way for the treatment of spent LIBS. Direct recycling of spent lithium batteries can be processed via either of two different ways like, electrochemical and chemical direct-relithiation, without destroying the original structures and any tedious experimental conditions.[30] The direct recycling process retains the structure morphology and purity of the cathode materials leading to the resaleable product for the battery manufacturers. During the degradation mechanism, the loss of lithium on the cathode material is mainly happened due to the solvent reduction and formation of solid electrolyte interface (SEI) leading to the major cause of the capacity fade.[31] Quest for efficient relithiation/regeneration methods have been endured, which can permits cost-effective recycling along with the proper disposal of waste of spent LIBs.[32–34] The hydrothermal process has been directly employed for the regeneration of suitable cathode material like $LiCoO_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$, and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ etc. without using high pressure.[35–37] However, the direct-relithiation can restore their original electrochemical properties only if lithium-ion loss is the primary aging mechanism. Again, it is a big challenge to sort spent cathode materials which are suitable for direct relithiation. Numerous researchers are still working on a different process of recycling rather than that of the conventional method, but the main obstacle for the commercialisation of this methods is to scale up in pilot scale. In this review, we focussed on the recent development of relevant literature by setting the criteria, extracting useful

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information for the researchers from the current scientific journals, employing in the field of direct recycling and relithiation of spent battery by the insertion of Li$^+$.

2. Challenges

Inspite of all beneficiaries with an endless application of LIBs in daily life, it has much negative impact, directly/indirectly to the human being and environmentally benign. Nowadays, the spent LIBs are concerned as one of the global environmental issues for being an essential source of water, air, and land pollution. Moreover, ample of recycling processes are carried out for spent LIBs, resulting in reducing the environmental footprint. Over the past decade, the government of the entire world focussing on the recycling or relithiation of the spent cathode to mitigate environmental challenges. However, recycling or relithiation faces enormous challenges, limiting its scalability and fast development. The major challenges are discussed as one face during the recycling/relithiation of the spent cathode is as below.

- One of the major challenges in the relithiation process is to collect the spent batteries of the same grade.
- The collection of spent batteries is costly as it requires the involvement of every section of the consumption chain, including the producers, sellers/distributors, governments, waste managers, and consumers.
- After collection, the shipment of large lithium-ion battery pack is challenging, which has been discussed several times in many reputed journals of scientists in the national/internal conferences as well.
- The diversity of battery grade material is also one of the significant challenges because the chemical composition is slightly different from one another like Lithium cobalt (LCO), Lithium Nickel Manganese Cobalt oxide (NMC), Lithium Nickel-Cobalt-Aluminium oxide (NCA), Lithium-ion Manganese Oxide (LMO), etc.
- There is a big gap between the recyclers and battery producers as it is not economically viable.
- To make it cost-effective, by reducing the consumption of energy, labour and also develop favourable close loop system to protect the human health and environmental concern.

Dr. Benjamin Raj received his PhD degree (2020) in Chemistry, Central University of Jharkhand. Currently he is working as senior project associate in the CSIR-Institute of Minerals and Materials Technology Bhubaneswar. He is the recipient of BRICS Young Scientist Forum Conclave 2022. His research focuses on the development of materials for the energy conversion (supercapacitor and batteries) and aslo to develop a technology for the recycling of waste materials (slag and spent LIBs).

Manoj Kumar Sahoo received his B. Tech degree in Metallurgical & Materials engineering from the Biju Patnaik University of Technology, Rourkela, Odisha, in 2020. He is currently working as project associate in CSIR-Institute of Minerals and Materials Technology. He is working on the recycling of spent lithium-ion batteries through utilizing hydro and electrometallurgy routes.

Prof. Nikoloski is an expert in the development of technology for the extraction and recovery of metals and minerals. His main area of expertise is the application of electrochemical techniques to the study of leaching and reduction processes used in the hydrometallurgical treatment of primary and secondary resources. He has 25 years of experience spanning industry and academia. Prof. Nikoloski is the head of the Hydrometallurgy Research Group at Murdoch University and leads the FBICRC flagship projects on Beneficiation and Processing of Lithium Minerals and on the Production of Vanadium Electrolytes for application in redox flow batteries.

Prof. Pritam Singh has been a Senior University Academic and Researcher spanning a period of over forty years. He taught Chemistry at several International Universities. His research expertise includes development of zinc-bromine and lithium batteries, hydrometallurgy, arsenic remediation of ground drinking water and applied aspects of ion-solvent interactions. Currently he is an Emeritus Professor at Murdoch University, Western Australia.

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- To avoid expenses in the field of high energy consumption, cost of reagents is also a big challenge among the researchers and scientific community to provide suitable pathways or techniques to overcome these issues.
- The cycling stability, capacity, and life span of relithiated cathode materials are also principal challenges in the path of relithiation.
- The academic and scientific community needs to give more attention towards the development of new technology to tackle the vast amounts of spent LIBs in the coming decades.

3. Pretreatment

The LIBs exhibit a complex structure containing the cathode, anode, electrolyte, and separator.[38,39] The cathode, anode, separator, binder, and non-aqueous electrolyte are packed into the external casing cell. The direct opening of external cells poses health issues and also environmental concerns around the surrounding.[6,40,41] The most precious cathode electrode comprises active cathode materials, aluminium current collectors, conductive agents, and a polymeric binder. During the pre-treatment process, the spent battery cells are dismantled manually and then discharged through different means of approaches.

To avoid short-circuiting, the cells are dipped into the mild brine or salt solution.[42] Moreover some other means of approaches like electrical discharging, cryogenic processing, and thermal processing are also used. However, the industrial application for dismantling is still a big challenge for the R&D sector because of its extremely high-cost, labour, and more time-consuming procedure. Before the direct relithiation process spent LIBs must be often pre-treated to reduce the scrap volume during the separation and to concentrate over the valuable components. The major advantages of the pre-treatment process are to enhance the recovery efficiently and lead to a decrease in energy consumption. With all beneficiary components, safety issues should also be stressed with environmental concerns as it contains flammable organic solvents which release toxic gasses.[40] The pretreatment process and the recycling of spent cathode from LIBs are shown in Figure 1.
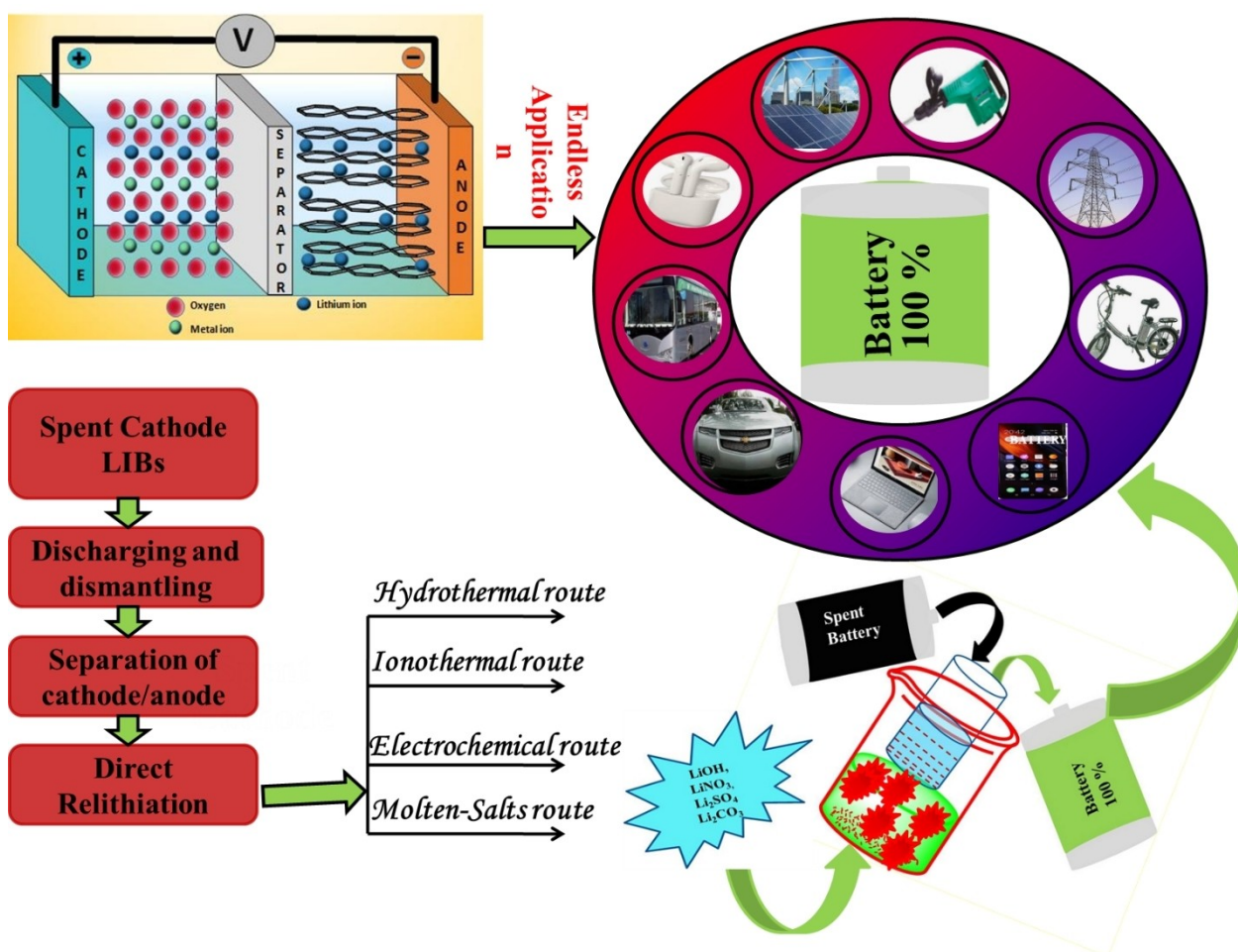

Figure 1. Schematic representation for the process of pretreatment methods of recycling and end-uses of spent cathode materials.

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4. Electrochemical Process of Relithiation

The Electrochemical method is relatively simple to extract the valuable metals from the spent battery without introducing any reagent. It can be employed for the selective extraction of elements like lithium with ultra-high purity.[43,44] It requires only charging-discharging within the room temperature.[45,46] In this method, the spent materials were dissolved in water, where the lithium-ion is converted to Lithium hydroxide (LiOH). In pursuit of this, Zhang and co-workers[47] proposed and investigated an electrochemical method for the regeneration of lithium in the form of $LiCoO_2$ using a waste Li_xCoO_2 electrode material from the spent LIBs is cathode material. During this electrochemical process, the waste Li_xCoO_2 from spent LIBs used as a working electrode for the insertion of Li^+. The insertion of Li^+ has been done by using the variable amount of lithium sulphate ($LiSO_4$) and by applying higher cathodic current density. The phase analysis of inserted sample has been done by using the X-ray diffraction (XRD) techniques and compared with the standard lithium cobalt oxide ($LiCoO_2$) of insertion of Li^+. At the higher concentration of $LiSO_4$, the relithiation process was controlled by the charge transfer process, whereas at low concentration, it led to the diffusion-controlled pattern. They have also compared the electrochemical charge capacity of regenerated material and commercially available $LiCoO_2$ with 136 and 140 $mAh\,g^{-1}$, respectively, within the potential window ranges from 0.2 to 0.8 V. The schematic illustration and mechanistic approaches have been shown in Figure 2i(a and b). Figure 2i(b) reveals the electrochemical mechanism of direct relithiation of $LiCoO_2$ by insertion of Li-ion into the waste Li_xCoO_2 electrode by electrochemical insertion of Li^+ and electrolyte diffusion. To move Li^+ toward the lithium vacancies in the Li_xCoO_2 structure, the electrons from a power source must first passes through the conductive material to a cathode with a negative charge. Free Li^+ can overcome the energy barrier of the electrochemical insertion reaction when the energy delivered by the electrode exceeds the activation energy (E_a) of the reaction, at which point it becomes enmeshed in the Li_xCoO_2 crystal's faulty lattice. The layered structure of waste Li_xCoO_2 interstices may contain some Li^+ ions that do not reach the lattice. The electrochemical insertion process could lead to the formation of hydrogen bonds, which would cause the $LiCoO_2$ particles to expand. The earlier research also mentioned this enlargement brought on by crystalline water.[48,49] Finally, to remove crystalline water and restore the lattice structure of $LiCoO_2$ the sample was annealed at 700 °C. The electrochemical relithiation process that has been proposed has the potential to be advantageous due to its straightforward operation and minimal chemical input. The electrochemical behaviour of the of the regenerated cathode are presented in Figure 2ii(a–d).

Yang et al.[31] demonstrated the recycling of degraded waste cathode material by electrochemical relithiation using an aqueous electrolyte. The recycling process has been applied in both harvested cathode powder as well as cathode sheet where the active material was bonded together and electrically connected to the aluminium current collector. The relithiation of degraded waste cathode materials was performed without any atmospheric protection. After the insertion process, the reliability/feasibility of relithiated material has been evaluated against the commercially available cathodic material using various physicochemical techniques (i.e., XRD, RAMAN, etc.). The obtained crystal structure and surface morphology of spent Li_xCoO_2 material was fully restored, and morphology was also well retained. They have also suggested that a very trace amount of Co_3O_4 was also present over the particle surface. They have also compared the electrochemical properties of both the treated sample and commercially available cathode material, revealing an almost similar voltage profile during charge-discharge. The charge-discharge capacities of treated samples and commercially available samples were well examined within the voltage window of 2 to 4.5 V. They have found around 150 $mAh\,g^{-1}$ and 140 $mAh\,g^{-1}$, for the treated sample and commercial sample, respectively, with a better retention capacity of 93 % than that of the commercially $LiCoO_2$ (87 %). Lehtinen and co-workers[50] demonstrated the reuse of spent battery material by adding stoichiometric amounts of $LiCoCo_2$ (LCO) employing electrochemical techniques. The materials were aged in LCO/graphite pouch cells within the voltage range of 3.0–4.4 V at a current density 0.4 $mA\,cm^{-2}$, and their properties were well documented. They have deeply investigated the cause of why the material performance/capacity losses in the case study, as shown in Figure 3(a–h). The capacity loss mainly happened due to the loss of lithium in solid electrolyte interphase layer formation on the graphite electrode. The positive electrode was recovered from pouch cells and assembled into half cells and their electrochemical properties were investigated. The observed results showed that after relithiation, the original structure LCO was restored, the capacity of an aged $LiCoO_2$ reverted close to the commercially available LCO. They found only a slight deviation in the rate capability properties with the fresh materials revealing the promising methods of cyclability in waste LCO by adding a stoichiometric amount of lithium salt for the half-cell.

Park et al.[51] demonstrated a cost-effective and environmentally friendly scalable method for the direct relithiation of spent cathode materials using a redox-mediated process. For the recovery/relithiation they have taken 3,5-di-tert-butyl-o-benzoquinone (DTBQ), which shuttle charge very fast between Li metal and spent cathode. The reduction of DTBQ on lithium is evidenced by chemical changes of Li metal and successful relithiation of the spent cathode by subsequent oxidation of DTBQ and was verified by electrochemical analysis and structural evaluation. The phase changes before and after relithiation process were confirmed by using XRD, and restoration of surface morphology was examined by Field Emission Scanning Electron Microscopy (FESEM) analysis. After the successful insertion of Li over the spent cathode material was investigated by the electrochemical performances. For the electrochemical test, they have fabricated half-cell as well as full cell. Furthermore, for half-cells, they dispersed 90 wt % of the spent cathode, 5 wt % carbon black and 5 wt % PVDF and allowed it for blending; and for the full cell testing consists of 90 wt % $Li_4Ti_5O_{12}$, 5 wt % carbon black and 5 wt % polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidone (NMP).
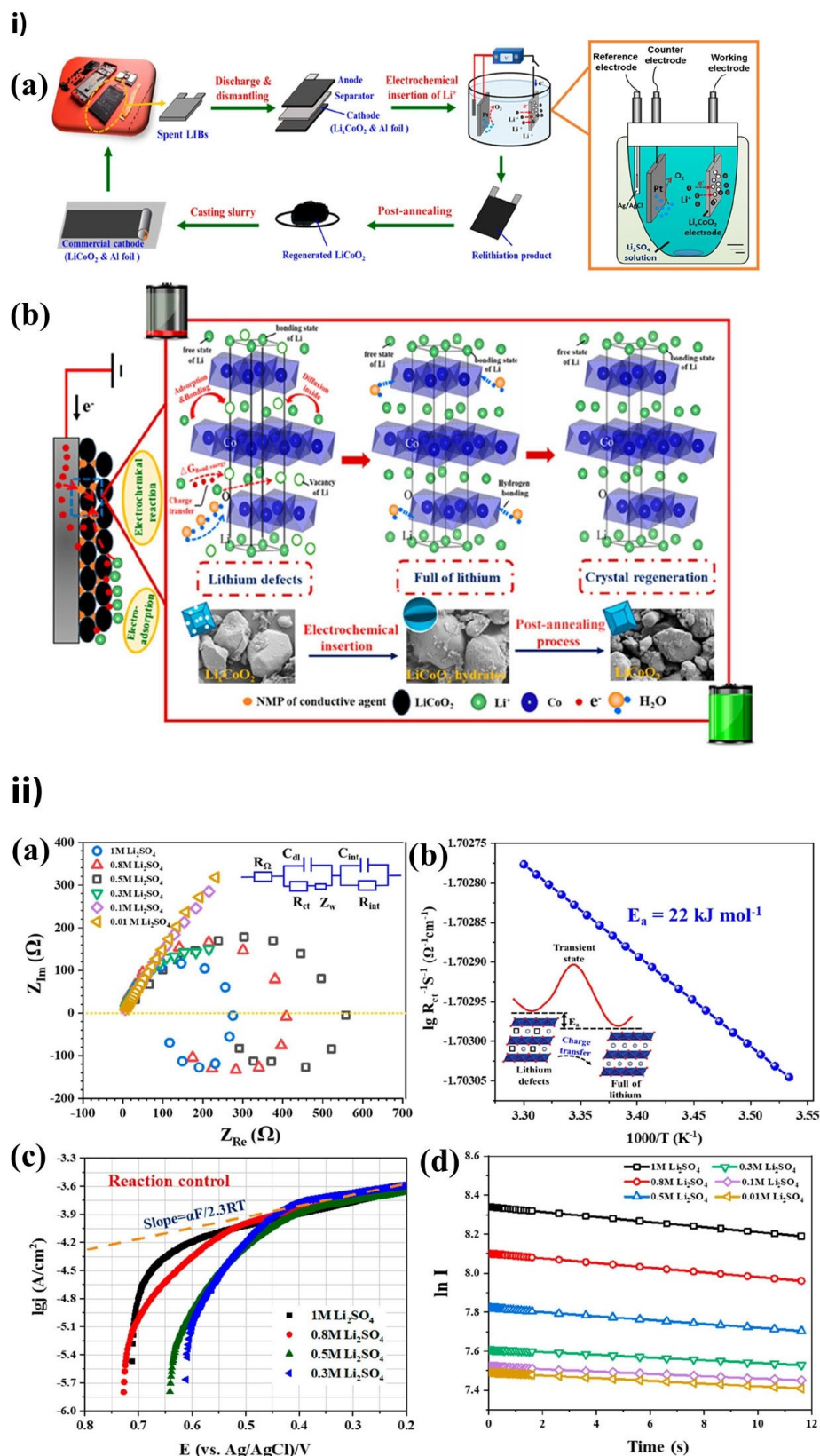
Figure 2. i. Schematic representation of a) insertion of Li$^+$ ions on spend Li$_x$CoO$_2$, b) proposed electrochemical mechanism of direct relithiation of LiCoO$_2$ by insertion of Li-ion into the waste Li$_x$CoO$_2$ electrode. Reproduced with permission from Ref. [47]. Copyright (2020) American Chemical Society. ii. a) Nyquist plots of the cathode electrode between frequencies 10 kHz and 10 mHz with different Li$^+$ concentrations. B) The activation energy of electrode reaction for electrochemical insertion. c) Tafel curve of the cathode with different Li$^+$ concentrations. d) ln I-t curve of cathode electrode with different Li$^+$ concentrations. Reproduced with permission from Ref. [47]. Copyright (2020) American Chemical Society.
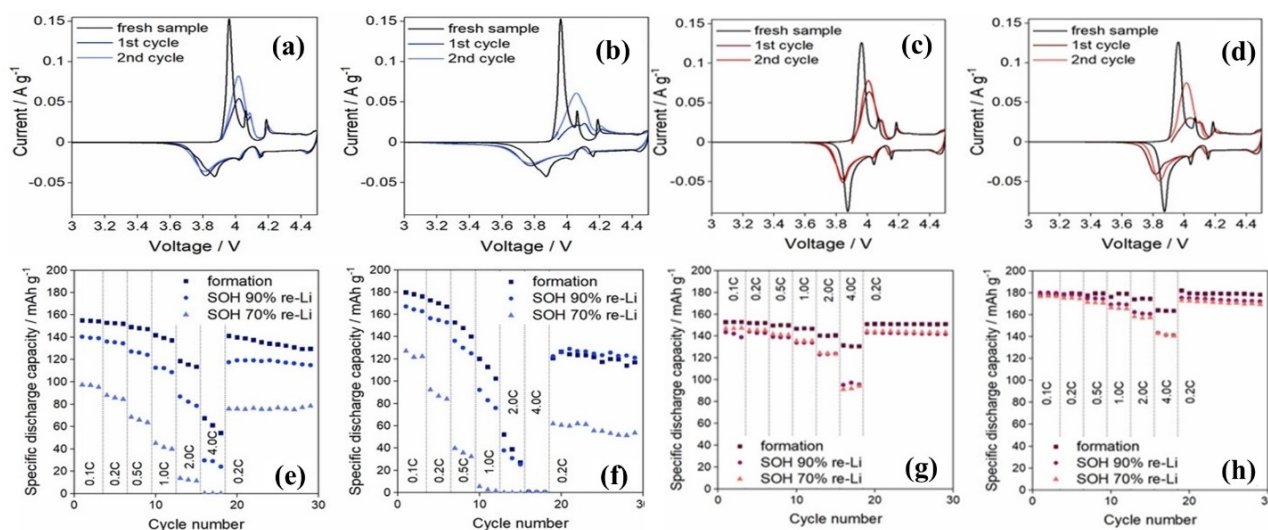
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Figure 3. CV plots of a) S- LCO at SOH 90%, b) S-LCO at SOH 70%, c) D-LCO at SOH 90% and d) D-LCO at SOH 70% in the voltage range of 3.0–4.5 V compared to the CV plots of the fresh samples. Rate capabilities of the LCO electrodes recovered from the aged pouch cells and re-lithiated. e) S-LCO in the voltage range of 3.0–4.3 V, f) S- LCO in the voltage range of 3.0–4.5 V, g) D-LCO in the voltage range of 3.0–4.3 V and h) S-LCO in the voltage range of 3.0– 4.5 V. Reproduced with permission from Ref. [50]. Copyright (2021) Wiley-VCH. (SOH = state of health, S-LCO = stoichiometric lithium cobalt oxide and D-LCO = Mg−Ti dopped LCO)

They fabricated cells using 2032-type coin cells in the Ar-filled glove box. The battery testing was carried out on a Maccor series 4000 battery tester, and the temperature was controlled at 30 °C within the voltage range of 3.0–4.3 V. Fan and co-workers[52] developed an electrochemical procedure for the successful regeneration of degraded $LiFePO_4$ by employing the functionalised prelithiation separator (FPS). For the regeneration they have used lithium oxalate as a source of Li^+ ion, due its cost-effectiveness, air-stability, and excellent irreversible capacity of over 500 mAh g^{-1}. The separator was formulated by mixing 90% of $Li_2C_2O_4$/CMK-3 and 10% of PVDF in NMP as binder and casted on PP separator Celgard 2500 using a line coater. The surface morphology and purity of phases was analysed by the FESEM and XRD techniques. The electrochemical performance of regenerated cathode was carried out using a coin cell where commercially graphite was taken as anode and FPS as a separator within the voltage range of 2.5 to 4.0 V. The electrochemical reproducibility, storage capacity, and stability were confirmed with various electrochemical techniques. They have also compared with various existing methodologies with this new developed one and revealed that this modified new technique shows a great advantage over the cost-effectiveness and easy to formulate the same for the whole electrode. The cited literature reveals that the extraction of lithium ranges between 90–100% at laboratory scale. For the commercialisation of this method, the extraction efficiency and speed should be scaled up. By creating a cell structure with a sizable surface of solid electrolyte and a stacking method, extensive research has been done. However, unlike the hydrometallurgy approach, the commercialization of this method is not economically viable.[44]

5. Hydrothermal Process of Relithiation

Hydrothermal relithiation is a promising technique in future for the recycling of spent LIBs. It is a non-destructive approach towards recycling spent LIBs by optimizing the parameters without sacrifing the material properties. This method demonstrates cleaner, greener, simpler and more energy-efficient to regenerate the spent materials with high electrochemical performances than conventional methods (i.e., hydrometallurgy, pyrometallurgy, solid-state etc.).[53] This process is adapted for the regeneration of $LiCoO_2$ and $LiNi_xCo_yMn_zO_2$ cathode materials. In this method, the recycled cathode material and source of Li solution is used to keep in a reactor. The solution is heated at a low temperature, around 120–220 °C.[38] Gao and co-workers[54] demonstrated an efficient method for the direct recycling of spent LIBs in the form of lithium manganese oxide (LMO) cathode to restore their high capacity, long durability, cycling stability and high performance. They have reported that one-step hydrothermal treatment in dilute Li-containing solution enables the reconstruction of desired stoichiometry and the purity of phase. After treatment, the validation of the sample has been evaluated and compared with the commercially available pristine cathode material on the market. After hydrothermal treatment, the electrochemical properties were fully recovered with a discharge capacity of 109, 111, and 105 mAh g^{-1} after 100 cycles at the current density of 0.5 C. Additionally, the cycling stability of regenerated LMO was fully recovered with 88% capacity retention after 100 cycles which was slightly better than that of the original material. The plausible mechanism for the relithiation of spent cathode material by using this technique is also explained by them. Figure 4 demonstrated the movement of lithiation inside the spinel structure along the (110) direction
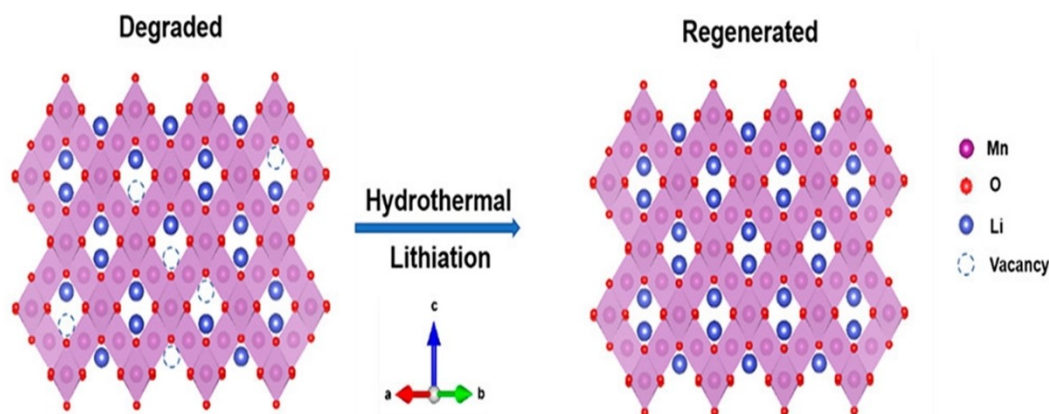
Figure 4. Proposed mechanism of direct regeneration by hydrothermal route of insertion of Li$^+$ ion into the spent cathode materials. Reproduced with permission from Ref. [54]. Copyright (2020) American Chemical Society.

throughout the hydrothermal process to show the relithiation process. Investigations into the causes of capacity fading over the past ten years have mostly focused on Li loss, Mn migration, and John-Tell distortion.[55,56] By adjusting the operating parameters, several physicochemical characterizations were used to comprehensively examine the composition and structure evolution of LMO during the regeneration process. The lithium loss and lattice distortion may be entirely restored to the pre-damaged materials' natural levels, according to the investigation on the kinetic mechanism and neutron diffraction. This research offers a fresh approach to battery recycling that is both affordable and environmentally responsible, with the potential to overcome the sustainability difficulties with LIBs.

Xu et al.[57] demonstrated the direct regeneration of Li-ion batteries by applying the hydrothermal process of relithiation of cathode materials as potential next-generation recycling technology. However, the feasibility of this approach at a large scale was systematically designed and optimized the process parameters to minimize the cost in the form of energy as well as raw materials. The effects of process parameters on the composition, structure, and electrochemical performance of the processed cathode materials were investigated using various physico-chemical characterization techniques and testing. They have also suggested that the cost can be reduced by replacing the typically employed 4 M LiOH solution with a mixture of 0.1 M LiOH and 3.9 M potassium hydroxide (KOH). The 4 M LiOH can be recycled and reused for the relithiation of spent Li-ion batteries without sacrifying the materials properties. The life cycle measurement of the processed materials suggested that the optimal condition is favourable in terms of reduction of energy consumption and emission of green-house gas, which leads to increased potential revenue. The schematic representation of hydrothermal relithiation, short annealing process, the effect of time, temperature, crystal structure and their electrochemical performances is shown in Figure 5(a–e) and Figure 6(a–h). Wang et al.[58] demonstrated the sustainable regeneration of high voltage LiCoO$_2$ from spent cathode materials using the hydrothermal route. The requisite amount

of spent cathode materials was kept in a Teflon-lined autoclave containing 60 mL of 4 M lithium hydroxide solution. The reaction mixture was washed properly with deionised water several times to get LiCoO$_2$ named HLCOE. Meanwhile, they mixed the powder with Li$_{1.4}$Al$_{0.4}$Ti$_{1.6}$(PO$_4$)$_3$ by ball billing in the stoichiometric ratio followed by calcination. This is firmly attached to the surface of LiCoO$_2$ which avoid an interfacial reaction between the electrolyte and LiCoO$_2$ resulting improved stability of LiCoO$_2$. When cycled under 4.4 V operation, the regenerated LiCoO$_2$ annealed at 800 °C shows a considerably increased discharging capacity of 166 mAh g^{-1} with an excellent capacity retention of 93 % at 1 C for 100 cycles, combining the foregoing advantages.

Shi and co-workers[32] developed a simple and efficient non-destructive approach towards the recycling and regenerating of LiCoO$_2$ particles from spent LIBs by combining hydrothermal and short annealing. The proposed process is efficient and eco-friendly in fully recovering exhausted cathode material without disturbing the original surface morphology and size distribution resulting in high capacity and cyclic stability. The chemical composition of recovered Li and Co of the cycled electrode material was tested by using an inductively coupled plasma optical emission spectrometer. They have added 5 % extra Li to compensate for the loss of Lithium during the sintering process. After regeneration of the morphology and phase of the electrode, the electrochemical performances have also been evaluated. The regenerated and non-treated LiCoO$_2$ powder mixed with PVDF with NMP in the mass ratio of 8 : 1 : 1 and resulting slurries were cast over the aluminium foil and allowed it to dry in vacuum oven for 6 h. They have also fabricated the coin cell using the same mass ratio, and their charge-discharge was carried out within the potential window of 3–4.3 V using Metrohm Autolab potentiostat. The resulting cell capacity retention was found around 74 % after the completion of 200 cycles. The electrochemical analysis revealed that the recovered material has a better charge-discharge capacity with better cycling stability and charge retention value. It has been proposed that this method is very much suitable in a large scale and can potentially be applied for other
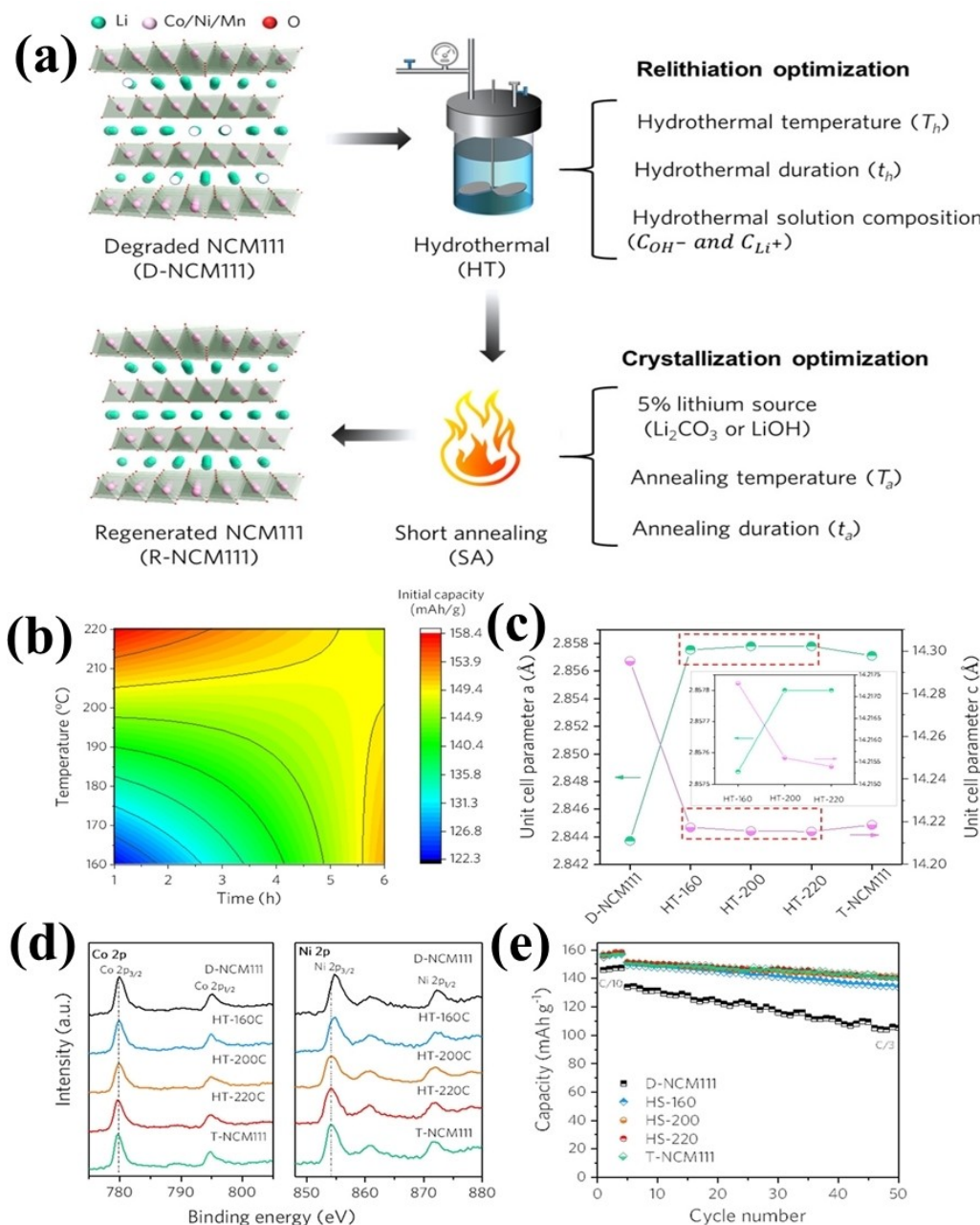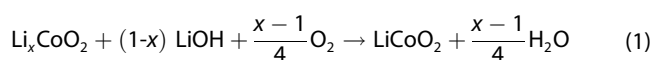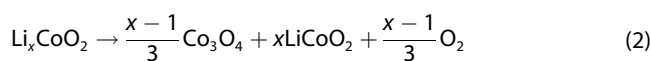
Figure 5. a) Schematic illustration of hydrothermal relithiation-based regeneration of D-NCM111. b) Contour map of the effects of hydrothermal temperature and time on initial capacity, c) unit cell parameters of a and c evolution, d) XPS spectra in Co 2p and Ni 2p regions, and e) electrochemical cycling stability of samples relithiated at temperatures of 160, 200, and 220 °C and control samples (T-NCM111 and D-NCM111). Reproduced with permission from Ref. [57]. Copyright (2021) American Chemical Society.

types of cathodes in LIBs like $LiMn_2O_4$, $LiFePO_4$ and $Li_xNi_yMn_zCo_{1-y-z}O_2$ ($0 < x, y, z < 1$). They have also proposed the possible mechanism for the regenerated cycled $LiCoO_2$. The following reaction steps taking place during the hydrothermal route is as follows.

$$Li_xCoO_2 + (1-x)\,LiOH + \frac{x-1}{4}O_2 \rightarrow LiCoO_2 + \frac{x-1}{4}H_2O \quad (1)$$

And for solid-state long-term sintering process following reaction steps taking place

$$Li_xCoO_2 \rightarrow \frac{x-1}{3}Co_3O_4 + xLiCoO_2 + \frac{x-1}{3}O_2 \quad (2)$$

$$2Co_3O_4 + 3Li_2Co_3 + \frac{1}{2}O_2 \rightarrow 6LiCoO_2 + 3\,CO_2 \quad (3)$$

where x ($0.5 < x < 1$) is the mole number of Li in the cathode. Li_xCoO_2 starts to release oxygen at 220 °C and forms Co_3O_4, which later reacts with Li_2CO_3 to form $LiCoO_2$ again.

Shi et al.[59] demonstrated a novel combined non-destructive hydrothermal with a short annealing process for the direct
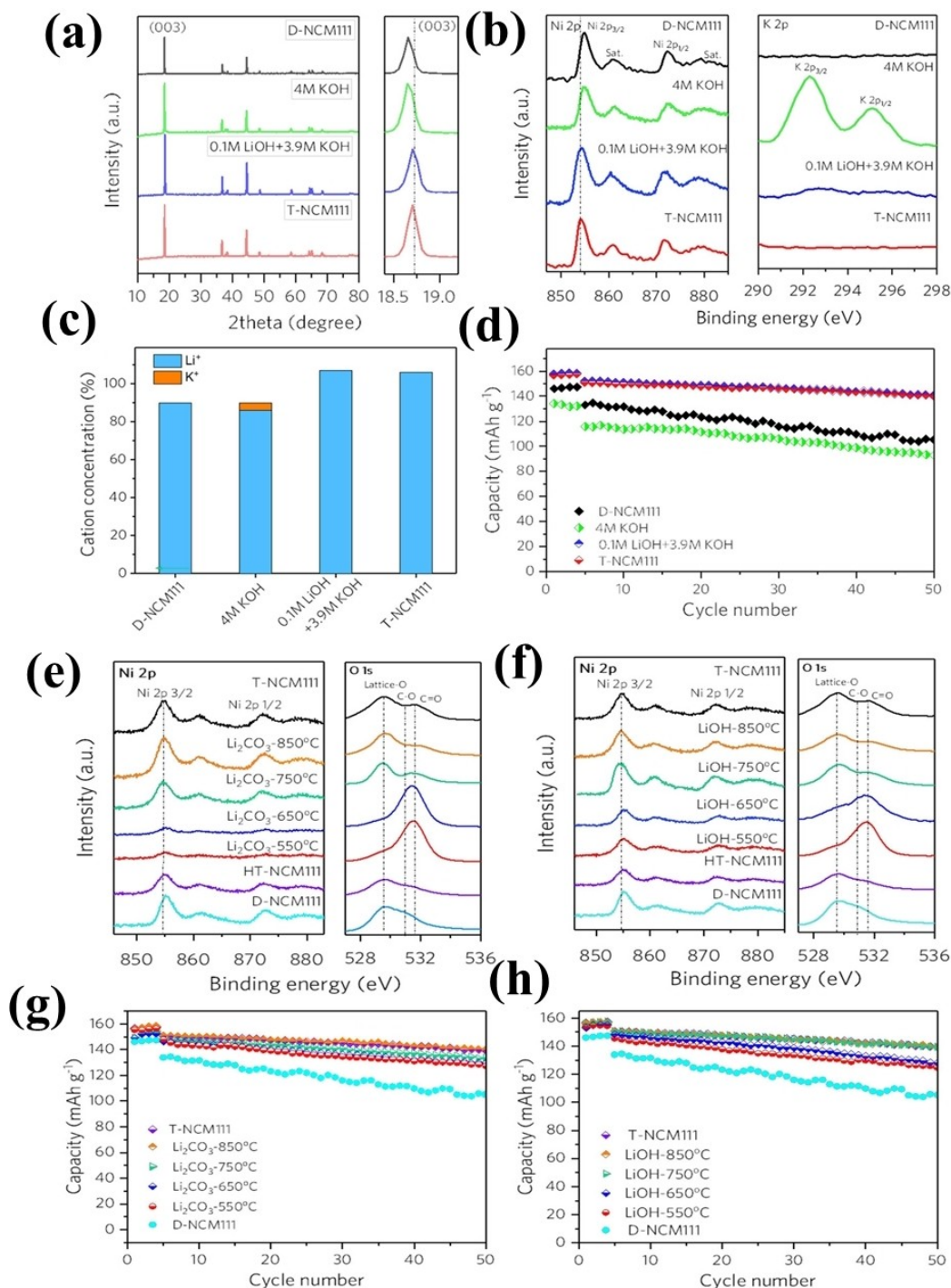
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Figure 6. Investigation of solution composition for hydrothermal relithiation. a) XRD patterns, b) XPS spectra, c) cation (Li$^+$ and K$^+$) concentration and d) comparison of cycling stability, e) XPS spectra of relithiated samples after annealing at temperatures of 550, 650, 750, and 850 °C with Li$_2$CO$_3$ and LiOH as the Li source. f) Cycling stability of relithiated samples after annealing at temperatures of 550, 650, 750, and 850 °C with g) Li$_2$CO$_3$ and h) LiOH as the Li source. Reproduced with permission from Ref. [57]. Copyright (2021) American Chemical Society. (XPS=X-Ray Photoelectron spectroscopy, D-NCM = Degraded Nickel Cobalt Manganese, T-NCM=Toda America Inc)

regeneration LiCoO$_2$ from tainted NCM cathode materials to make it new active cathode materials for further use. The severely damaged or deformed NCM111 and NCM253 cathode were recycled by adding a stoichiometric amount of lithium salts. The regenerated cathode materials show an excellent capacity, good cycling stability, and high-rate performances.

They have reported that after solid-state, sintering in the air can restore the cycling stability of NCM111 but not the NCM523 cathode due to the high concentration of nickel content. The oxygen partial pressure is required for stoichiometric restoration to convert the rock salt phase impurities to layered phase in NCM cathodes with high Ni concentration.

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They have also compared the electrochemical properties of treated NCM cathode and non-treated NCM cathode materials within the voltage range of 3–4.3 V. The non-treated materials show poor cycling performances of around 86 mAh g^{-1} after 100 cycles. The treated NCM111 and NCM253 cathode show cycling performances of 145.1 mAh g^{-1} and 158.1 mAh g^{-1}, respectively after 100 cycles. Thus, it has been concluded that this approach has a distinct advantage in the direct recycling of spent cathode over the traditional methods. The process of hydrothermal lithiation, their surface morphology and of Li$^+$-ions and its electrochemical performances are shown in Figure 7(a–i). Yu and co-workers[60] demonstrated a safe and eco-friendly low-temperature hydrothermal relithiation (LTHR) process by redox mediation for the direct recycling of spent LIBs cathode. Three different NCM materials, including C-NCM111, D-NCM111, and C-NCM622, were successfully regenerated through the LTHR process. The degraded NCM cathode was stirred in 4 M LiOH aqueous solution with the addition of 1–3% (v/v) green solvents and treated it at 90 or 100°C for the relithiation. After that, the reaction mixture was washed several times to remove the residues of lithium salts and kept for drying in an oven. After complete drying the relithiated powder was mixed with 5 mol% excessive if Li$_2$CO$_3$ and was kept in the furnace at 850°C for 4 h with a ramping rate of 5°C per minute.
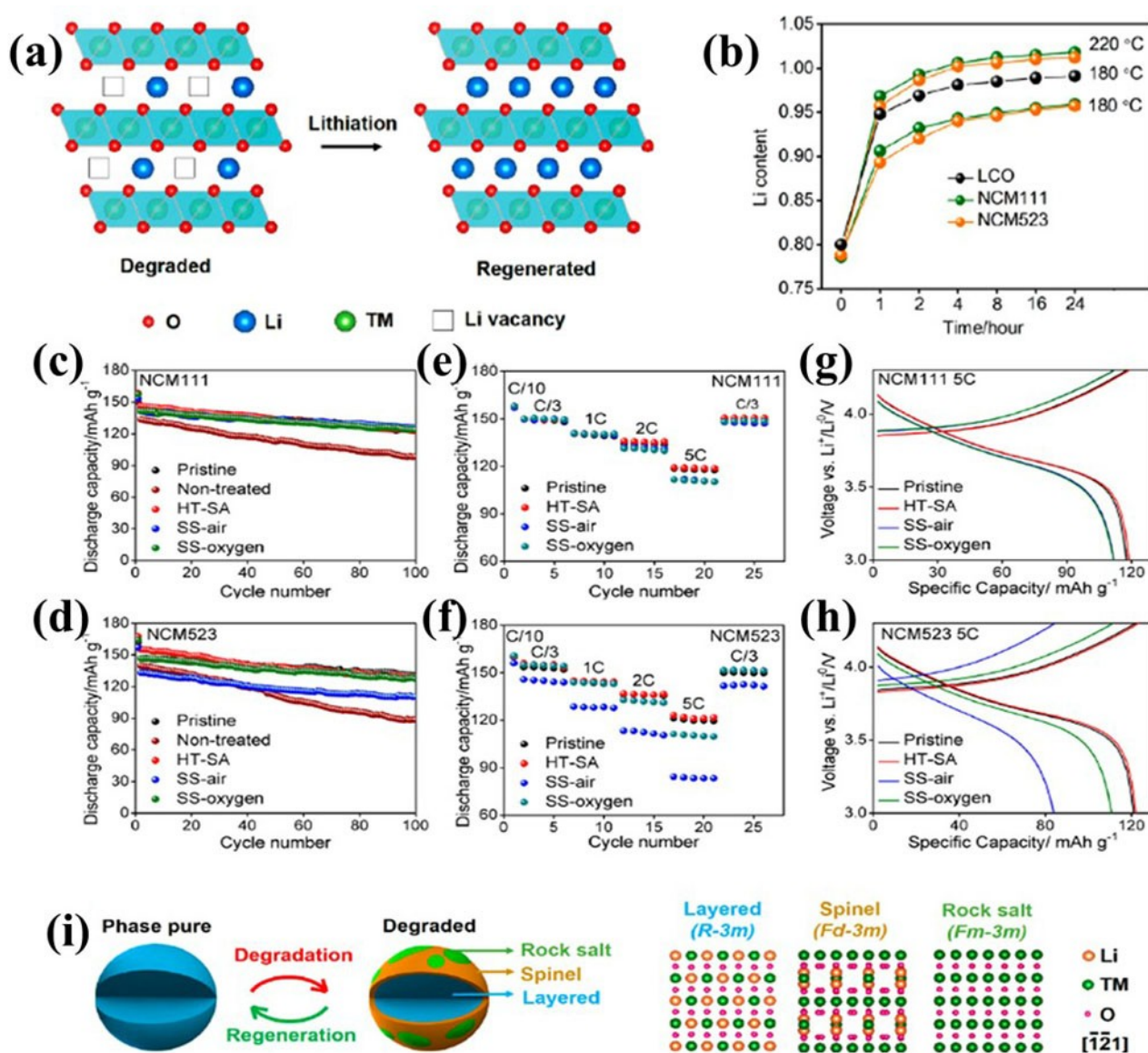

Figure 7. a) Hydrothermal lithiation process to restore the desired stoichiometry, b) kinetics of degraded cathode with different temperature and time, c) cycling performance of pristine, nontreated, and regenerated NCM111 samples at 1 C; HT-SA: hydrothermal treatment at 220°C for 4 h, followed by annealing at 850°C for 4 h; SS-air: sintering at 850°C for 12 h in air; SS-oxygen: sintering at 850°C for 12 h in oxygen. d) Cycling performance of pristine, nontreated, and regenerated NCM523 samples at 1 C. e) Rate performance of NCM111 samples. f) Rate performance of NCM523 samples. g) Voltage profiles of NCM111 samples at 5 C. h) Voltage profiles of NCM523 samples at 5 C. i) Illustration of the crystal structure change of NCM523 after cycling and regeneration. The right scheme shows the atomic arrangement of layered, spinel, and rock salt phases along the [$\bar{1}2\bar{1}$] zone axis. Reproduced with permission from Ref. [59]. Copyright (2018) American Chemical Society.

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The chemical composition of the relithiated powder was analyzed by AAS and ICP-OES spectroscopic techniques. The purity of phase and surface morphology was analysed by XRD and SEM techniques and surface composition with their oxidation state was also analysed by using X-ray photoelectron spectroscopy (XPS). They have also evaluated the electrochemical properties of degraded cathode materials and regenerated cathode within the potential window of 3 to 4.2 V. The degraded cathode reveals a capacity of 51 mAh g^{-1} due to the loss of 38% lithium in the system and the regenerated cathode exhibited a capacity of 155 mAh g^{-1} respectively. The regenerated cathode shows a cyclic retention of about 92% at C/3 after 60 cycles. Jiang et al.[61] demonstrated the successful relithiation of spent LiFePO$_4$ (LFP) batteries via the microwave-hydrothermal process. They have developed a new cathode material by refurbishing the spent cathode and microwave-reduced graphene oxide (MWrGO) anode for high electrochemical performances. The surface morphology, purity of phase, the oxidation state of elements and chemical composition of regenerated materials were analysed by SEM, XRD, XPS and ICP-OES spectroscopic techniques. The electrochemical performances were also evaluated by cyclic voltammetry, impedance, and galvanometric charge-discharge within potential ranges of 2.4 to 4.2 V. The regenerated LFP/MWrGO materials reveals a specific capacity of 150.5 mAh g^{-1} at 0.1 C. The enhanced specific capacity of 161.4 mAh g^{-1} with an excellent capacity retention of 94.9% was observed after 100 cycles by the successful introduction of 5% graphene on LFP/MWrGO composite. Thus, it can be concluded that this process provides a green facile method for the regeneration of spent LFP batteries and promotes the sustainability of Li-ion battery downstream technology. The only demerits of this method are the requirement of expensive autoclaves and facing difficulties in observing the crystal growth and repeatability of phases with all the spent cathode materials.

6. Ionothermal and Molten Salt Process of Relithiation

It is another method for the direct relithiation of spent cathode under mild condition. The ionic liquid supplies strong coulombic interaction between the ions, which subsequently served as both solvents and potential structure-directing agent in the solid.[33,62] Wang and co-workers[63] demonstrated novel ionothermal relithiation of delithiated NCM cathode using ionic liquids as recyclable solvents. The ionic liquids are the conventional molten salts leading to various advantages like negligible vapour pressure, negligible flammability, excellent thermal conductivity and much more flexibility in synthesis. For the direct relithiation they have used lithium halide as a precursor. The insertion of Li over the spent cathode material was investigated by crystal structure and chemical analysis using thermogravimetric analysis (TGA), XRD and inductively coupled plasma optical emission spectrometry (ICP-OES) measurement. The functionalised spent cathode material exhibits excellent

electrochemical performances as a pristine NCM in both half-cell and full-cell tests. They have also checked the cyclic stability using the charge-discharge cycle, where the curves of R-NCM almost coincided with P-NCM. The charge capacity of R-NCM exhibits 173.3 mAh g^{-1}, near to P-NCM 175.3 mAh g^{-1}, which is much higher than that of the D-NCM (145.9 mAh g^{-1}). Thus, the obtained results confirm the successful relithiation of spent cathode material, which can be used as raw cathode material for further battery fabrication. Molten salt is considered a novel electrochemical method for generating cathodes/anode for Li-ion batteries. Basically, it is employed for the preparation of a single phase of layered-structured with controlled morphologies.[64] The processing cost of getting anode and cathode from this method is relatively inferior compared to the conventional solid-state method.[65–67] Jiang et al.[68] demonstrated direct recycling of spent lithium-ion batteries by using eutectic molten salts of LiOH-Li$_2$CO$_3$ as lithium sources for direct regeneration of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$. The mixed material was heated at 440 °C for a sufficient time of 5 h for Li$^+$ diffusion. For the full regeneration, thermal annealing (850 °C for 12 h) was then performed to promote the crystallisation of the particles to form the original layered phase. The crystal structure and surface morphology of the regenerated materials were investigated by employing various physicochemical techniques like XRD, Scanning Electron Microscopy (SEM), and High-Resolution Transmission Electron Microscopy (HRTEM) etc. The battery materials get delithiated and the phase structure also deformed due to the significant high (006) and splitting of (004) peaks, respectively. They also found that the spherical structure was dispersed and formed cracks during the service. After relithiation the restoration of crystal structure and the surface morphology were confirmed by XRD and SEM techniques. The added lithium ions occupied the Li position again and Ni^{2+} was oxidized to Ni^{3+}, the NCM structure changed from rock-salt phase to layered phase and the cation mixing degree decreases. The electrochemical performances were investigated using CR2025 coin cell fabrication where lithium metal was taken as anode and Celgard 2400 as a separator. The cathode material was made up of active materials, P-conductive carbon and PVDF as a binder in the ratio of 8:1:1 and an adequate amount of NMP were also added to make the slurry. They assembled their batteries in the Ar-filled glove (Ar = Argon) box with water and oxygen concentration lower than 0.1 ppm using lithium hexafluorophosphate (LiPF$_6$) as electrolytic solvent by mixing it with ethylene carbonate, diethyl carbonate and ethyl-methyl carbonate in the ratio 1:1:1 respectively. The electrochemical performance was analysed within the voltage range of 2.8 to 4.3 V at a current density of 1 C. The regenerated cathode material shows the best cycling stability and shows a capacity of 130.3 mAh g^{-1} after 200 cycles, and the retention rate reaches 89.06%. The recycling method is safe, non-toxic, less energy-consuming, and suitable for large-scale practical application. The phase diagrams of LiOH-Li$_2$CO$_3$, electrochemical performances and the relithiation process of Li composition recovered by eutectic molten salts shown in Figure 8(a–f).
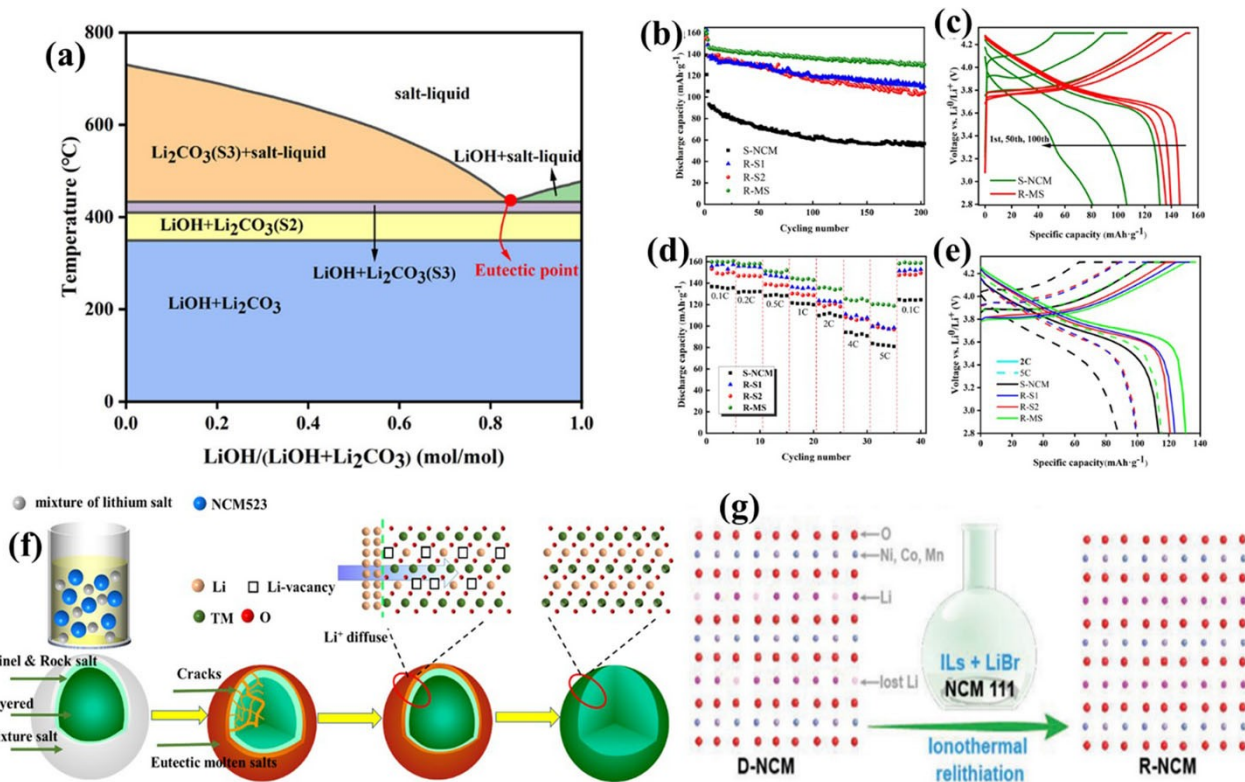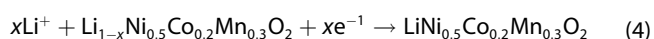
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Figure 8. a) Phase diagram of LiOH-Li$_2$CO$_3$, b) cycle performance of S-NCM and all regenerated materials, c) voltage-capacity profiles of S-NCM and R-MS, d) rate performance of S-NCM and all regenerated materials and e) voltage-capacity profiles of S-NCM and all regenerated materials at different rates, f) relithiation process for Li composition recovery by eutectic molten salts approach. (R = regenerated, S = spent) Reproduced with permission from Ref. [68]. Copyright (2020) American Chemical Society. g) shows illustration of the relithiation process for Li composition recovery via ionothermal approach. Reproduced with permission from Ref. [63]. Copyright (2020) Wiley-VCH.

Figure 8(f) depicts the plausible regeneration process for cathode material NCM523. First, a 0.86:0.14 mixture of LiOH and Li$_2$CO$_3$ was mixed with S-NCM. Second, the lithium molten salts penetrated through the gaps and formed on the surface of the NCM523 particles. Because Li$^+$ has a higher concentration than NCM523 particles have, it diffused onto their surface and regenerated their bulk while reacting with molten salts (at 440 °C). Lithium is then added to the lithium vacancies, and full regeneration is used to produce the NCM523 materials. Ma et al.[69] demonstrated the direct recycling/regeneration of the spent cathode of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (SNCM) using a one-pot molten salt-assisted method. The deficiency of Lithium and degraded crystal structure of spent SNCM cathode was restored with the conversion of the broken micron-sized spherical particle to submicron-sized single crystal in liquid medium of lithium-based molten salts. After treating with the molten salt of lithium, the chemical value was well matched with the theoretical values of cathode materials commercially available on the market. They evaluated the capacity and rate performances within the voltage range of 2.8 to 4.3 V by optimising the ratio of spent cathode and molten salts. The treated cathode reveals a capacity of 152.5 mAh g^{-1} at 0.2 C rate and cycling stability remains 86 % after the completion of 100 cycles. After charging-discharging cycles, the treated materials maintain a single stable crystal structure and surface morphology without owing any by-product. Shi et al.[33] reported the direct regeneration of degraded NCM cathodes through a eutectic Li-molten salt solution at ambient pressure. They have prepared eutectic molten salt solution by adding LiOH and LiNO$_3$ in the molar ratio of 2:3 for the effective relithiation of degraded NCM523 cathode at ambient pressure. According to their assumption, the eutectic solution has played an important role in relithiation as it contains a huge amount of lithium. The restoration of crystal structure, chemical compositions, and surface morphology led to the successful relithiation of degraded cathode and were well matched with the commercially available cathode. For the complete relithiation of the degraded cathode, they have heated the desired sample for 2–4 h at 300 °C. To evaluate the cycling stability and rate of retention after charge-discharge were well documented by the electrochemical process. The electrochemical properties were analysed by fabricating the coin cell leading to the Li storage capacity, cycling stability and an excellent rate capability within the voltage range of 3–4.5 V at a current density 1 C. This method can also be applied to regenerate other LIBs like LiMn$_2$O$_4$, LiFePO$_4$ and sodium-ion battery cathodes, e.g., Na-(Ni$_{0.60}$Co$_{0.05}$Mn$_{0.35}$)O$_2$. This method can also provide a unique pathway for the study of reversible chemistry in various solid-state ionic materials to develop green synthetic strategies for energy materials. Deng et al.[70] demonstrated a direct relithia-

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tion of ternary cathode material from spent LIBs through the molten salt process in the presence of acetylene black involving the impurities removal, Li compensation, structural and capacity recovery of cathode materials. For the relithiation the degraded $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) was taken, and after relithiation the NCM 523 particles can restore the $\alpha NaFeO_2$-type structure, and its specific capacity was compared with commercial materials. The restoration of the structure, surface morphology and faster relithiation process was due to the intrinsic network structure of acetylene black connected to ternary carbon by facilitating Li^+ diffusion into Li-deficient site. The relithiated cathode materials divulge a specific capacity of 160 mAh g^{-1} at 0.2 C. This method not only deals with the ternary carbon cathode material but is also useful in other structured-based cathode materials derived from sodium and aluminium ion batteries. The possible reaction mechanism during the process of relithiation has been discussed in Equations (4)–(8), where NCM 523 particles and acetylene black can be treated as an electrode which help in the reformation of crystalline structure.

Cathodic reactions

$$xLi^+ + Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + xe^{-1} \rightarrow LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 \quad (4)$$

$$NO_3^- + e^- \rightarrow NO_2 + O^{2-} \quad (5)$$

$$NO_3^- + 2e^- \rightarrow NO_2 + O^{2-} \quad (6)$$

$$O_2 + 4e^- = 2O^{2-} \quad (7)$$

Anodic reaction

$$C + 2O^{2-} - 4e^- = CO_2 \quad (8)$$

Yang et al.[71] develop a facile process for the removal of impurities and simultaneously for the direct relithiation of degraded $LiCoO_2$ using the optimised molten salt method. The complete removal of impurities (i.e., binder, carbon black, graphite and current collectors) from spent LIBs was treated with LiOH-KOH system in the molar ratio 3:7, where Lithium Nitrate ($LiNO_3$) and O_2 both supply as oxidants. Simultaneously, restoration of the crystal structure, chemical composition, and surface morphology of degraded cathode were analysed by XRD, SEM, TEM, XPS and ICP-OES spectroscopic techniques and compared with the commercially available cathode in the market. The degraded cathode materials were repaired by using a two-step heating process, i.e., 300 °C for 8 hours and 500 °C for 16 hours, respectively. After the successful restoration of degraded $LiCoO_2$ the electrochemical analysis was also performed and reported. It exhibited a high reversible capacity (147.3 mAh g^{-1} at 0.2 C), excellent rate performances (103.7 mAh g^{-1} at 5 C) and stable cycling stability after the completion of 100 cycles. Based on observed electrochemical properties, it was assumed that the regenerated $LiCoO_2$ has better performances than that of the newer cathode material. Li and co-workers[72] demonstrated an ambient air-relithiation using Li-molten salt along with the heat treatment to the

cycled lithium-rich layered oxide (LRLO) cathode and lead to the regeneration of material for both voltage and capacity. For the regeneration they have hand mixed the cycled layered cathode materials with an excessive amount of eutectic Li salts mixture with the help of a mortar pestle for 30 minutes. The molten salt solution containing the $LiNO_3$ and $LiOH \cdot H_2O$ in the molar ratio of 3:2 followed by heating the mixture for 15 hours and washed with distilled water several times to remove the excessive Li salts and kept in an air oven overnight for drying.

The electrochemical evaluation was carried out by mixing the regenerated cathode, conductive material and PVDF as a binder in the mass ratio of 8:1:1 in an appropriate amount of NMP and blend the mixture. They assembled the CR2016 coin cell inside the glove box in an argon atmosphere where Li metal acts as an anode, Celgard 2325 as separator and 1 M LiPF6 as electrolyte. The assembled coin cell was tested at room temperature using Neware Battery Test System (BT2000) instruments. The discharge capacity of heated and non-heated samples was examined and found that the discharge capacity of the non-heated sample was around 272 mAh g^{-1} and heated sample delivers 305 mAh g^{-1} respectively, showing a similar discharge capacity of pristine materials. The energy profile, voltage profile, phase structure and morphology of heated and non-heated samples shown in Figure 9(a–e). Tao Wang and co-workers[73] have developed a reciprocal ternary molten salts (RTMS) system for the direct upcycle of spent NMC 111 to Ni-rich NMCs by adding suitable salts of Nickel and Lithium in stoichiometric ratio. After refluxed with RTMS the Ni rich cathode material was achieved in ambient pressure in oxygen atmosphere. RTMS is having low melting point, which provides a source of Li^+ for the oxidation of Ni^{2+} to Ni^{3+} under high temperature to the system to get Ni-rich NMC 111. The successful upcycling of degraded NMC 111 to Ni-rich NMC exhibited an α-NaFeO$_2$-type layered material. This layered material restored the lithium concentration exhibiting the excellent electrochemical performance which is very much similar to that of the pristine material. The first charge/discharge capacities of Up-NMC 622 are larger than those of P-NMC 111 (charge capacity: 188.6 vs. 170.1 mAh g^{-1}; discharge capacity: 153.6 vs. 139.5 mAh g^{-1} at 20 mA g^{-1}). The D-NMC 111 does not exhibit electrochemical relithiation during the first discharge process, with a first discharge capacity of only 119.5 mAh g^{-1}, much lower than that of P-NMC Furthermore, during 100 cycles at a higher specific current of 200 mA g^{-1}, Up-NMC 622 outperformed P-NMC 111 and D-NMC 111 in terms of capacity. The surface morphology and electrochemical performance of degraded NMC and upcycle NMC is shown in Figure 10(a–j). Qin and co-workers[74] demonstrated a facile ternary molten salt approach for the effective regeneration of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$(NCM523) cathode of spent LIBs followed by annealing with oxygen in moderate temperature of 400 °C. They have successfully regenerated the cathode material by restoring Lithium loss and restored the degraded phases. The plausible mechanism for the relithiation process is depicted as follows.
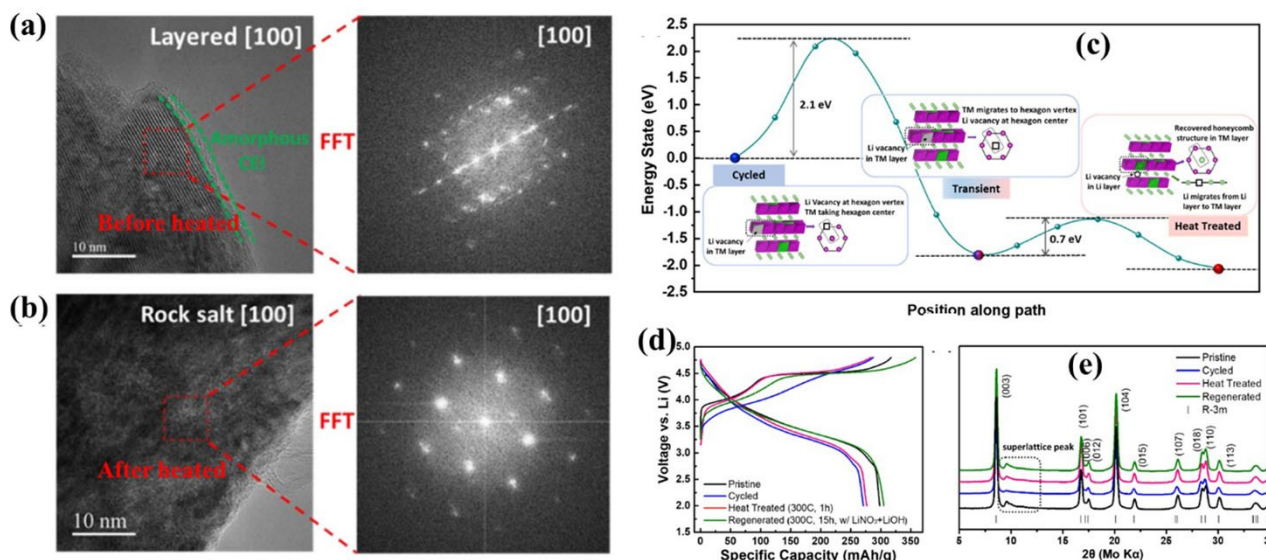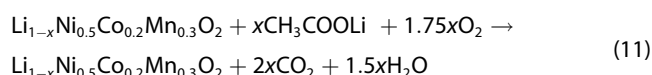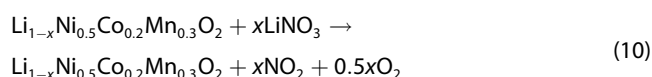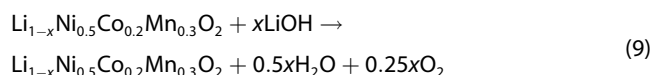
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Figure 9. a and b) TEM images of before and after heat treatment, c) energy profile of three states, d) voltage profile and e) XRD pattern of different regeneration conditions. Reproduced with permission from Ref. [72]. Copyright (2021) Elsevier.

$$Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + xLiOH \rightarrow$$
$$Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + 0.5xH_2O + 0.25xO_2 \tag{9}$$

$$Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + xLiNO_3 \rightarrow$$
$$Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + xNO_2 + 0.5xO_2 \tag{10}$$

$$Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + xCH_3COOLi + 1.75xO_2 \rightarrow$$
$$Li_{1-x}Ni_{0.5}Co_{0.2}Mn_{0.3}O_2 + 2xCO_2 + 1.5xH_2O \tag{11}$$

To aid ion diffusion throughout the regeneration process, the S-NCM was immersed in a homogeneous molten salt media at 400 °C, which is a naturally ionic conductor. The relithiation reaction [Equations (1)–(3)] was taking place homogeneously through the S-NCM particles in this favourable environment, accompanied by recrystallization. Thermal annealing (850 °C in O_2) was used after the reaction in molten salt to enhance the crystallisation of the particles into the required layered phase. The cathode powders were combined with a 5% excess quantity of Li_2CO_3 at 850 °C in an oxygen environment to compensate for Li evaporation at high temperatures. The electrochemical performances of regenerated material were analysed which delivers a reversible capacity of 160 mAh g^{-1} at 0.5 C with an excellent retention of 93.7% after 100 cycles. They have also found that the regenerated NCM cathode is comparably favorable to the fresh NCM cathode. Liu et al.[75] demonstrated the direct relithiation of spent LFP by using low-temperature molten salt method using lithium nitrate coupled with carbon environment. For the regeneration process they have taken spent LFP, $LiNO_3$ and FeC_2O_4 in the molar ratio of 1:0.5:0.1. The reaction mixture was heated at 300 °C for 1–6 h under argon atmosphere for relithiation, then quenched at room temperature and washed several times to remove the residue of lithium salt followed by centrifugation and allowed to dry at the oven for overnight. The dried sample was subjected to thermal annealing at 650 °C for 6 h to regain the

regenerated LFP. The chemical composition of the regenerated cathode was well evaluated by using ICP-OES spectroscopic techniques. The structural confirmation was done by using XRD, and the valence state/oxidation state of the elements were analysed by XPS spectroscopy. The electrochemical performances of the regenerated cathode have been carried out in coin cell which was assembled in an Ar-filled glove box Celgard 2400 separator and 1 M LiPF$_6$ in EC:DMC (3:7 by volume) as the electrolyte. The relithiated cathode materials obtain specific capacity of 145 mAh g^{-1} at current density 0.5 C within the voltage range of 2.5 V to 4.2 V. They have also compared with the spent LFP and found that the overall electrochemical properties were enhanced by 13% in then regenerated material. The schematic representation for the molten salt regeneration of sent LFP and its electrochemical properties are well documented in Figure 11(a–e).

Huan et al.[76] demonstrated a facile method to regenerate a brand new plate-like NCM622 cathode materials with well-matched {010} planes from the spent cathode NCM622 followed by molten salt strategy. The morphological, compositional, and structural restoration was investigated by using various physico-chemical techniques like XRD, XPS, FESEM and HRTEM. After the successful restoration of the damaged phase and morphology, they have also evaluated the electrochemical properties. The electrochemical properties were evaluated by cyclic voltammetry, and charge-discharge with the potential range of 2.6 to 4.3 V. The electrochemical properties reveal that regenerated cathode material delivered a high capacity of 155.1 mAh g^{-1} along with the excellent cycling stability of 94.3% capacity retention after 240 cycles at 1 C. These electrochemical properties of regenerated cathode might be attributed due to the insertion of Li$^+$ ions which help to repair the lithium defects as well as morphology. They have also proposed that this facile method can also be employed for regenerating SC523 and SC811 from the spent S523 and S811
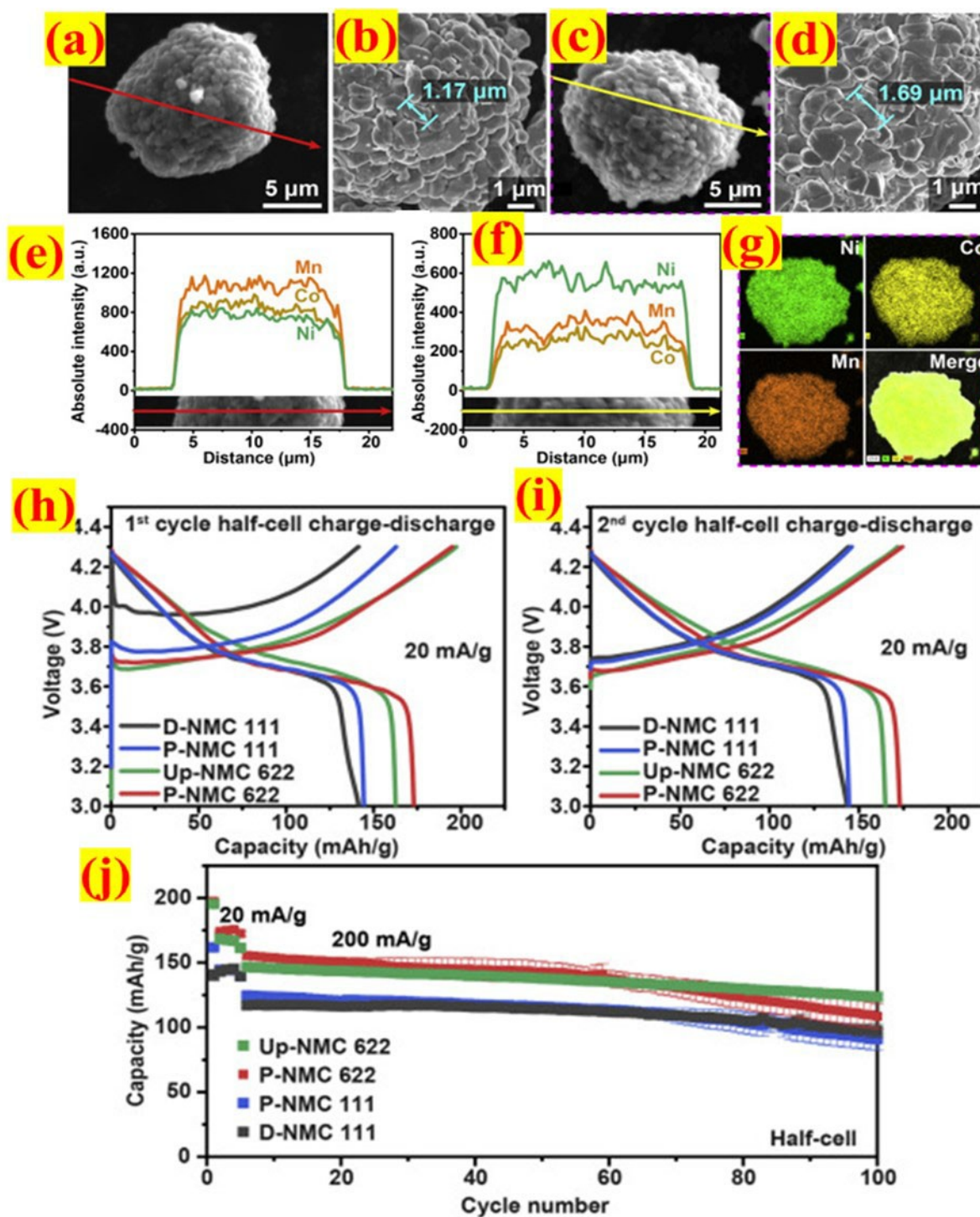
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Figure 10. A–D) SEM images of A and B) D-NMC 111 and C and D) Up-NMC 622. E and F) SEM-EDS line scans of E) D-NMC 111 and F) Up-NMC 622. G) SEM-EDS elemental mappings of Up-NMC 622. H) The first cycle and I) the second cycle charge/discharge curves of NMCs for full-cell tests, and J) Cycle performance of NMCs for full-cell tests (error bars are standard deviations). (D = degraded, Up- upcycle) Reproduced with permission from Ref. [73]. Copyright (2022) Elsevier.

respectively. Wu and co-workers[77] demonstrated the successful relithiation and sodium ion doping in spent LIBs collected from local mobile shops. The stoichiometric amounts of suitable salts, i.e., Li_2CO_3 and Na_2CO_3 were grounded with ethanol to make it a homogeneous solid mixture with spent cathode followed by sintered in an air oven at 850 °C for 12 h. The

chemical composition of relithiated cathode materials was confirmed by employing the ICP-OES measurement. The XRD pattern shows the absence of Co_3O_4 phase in the regenerated cathode which was there before relithiation. The intensities ratio I_{103}/I_{104} was also very high, signifying the successful relithiation/repair of a layered structure of Li_2CO_3 and that
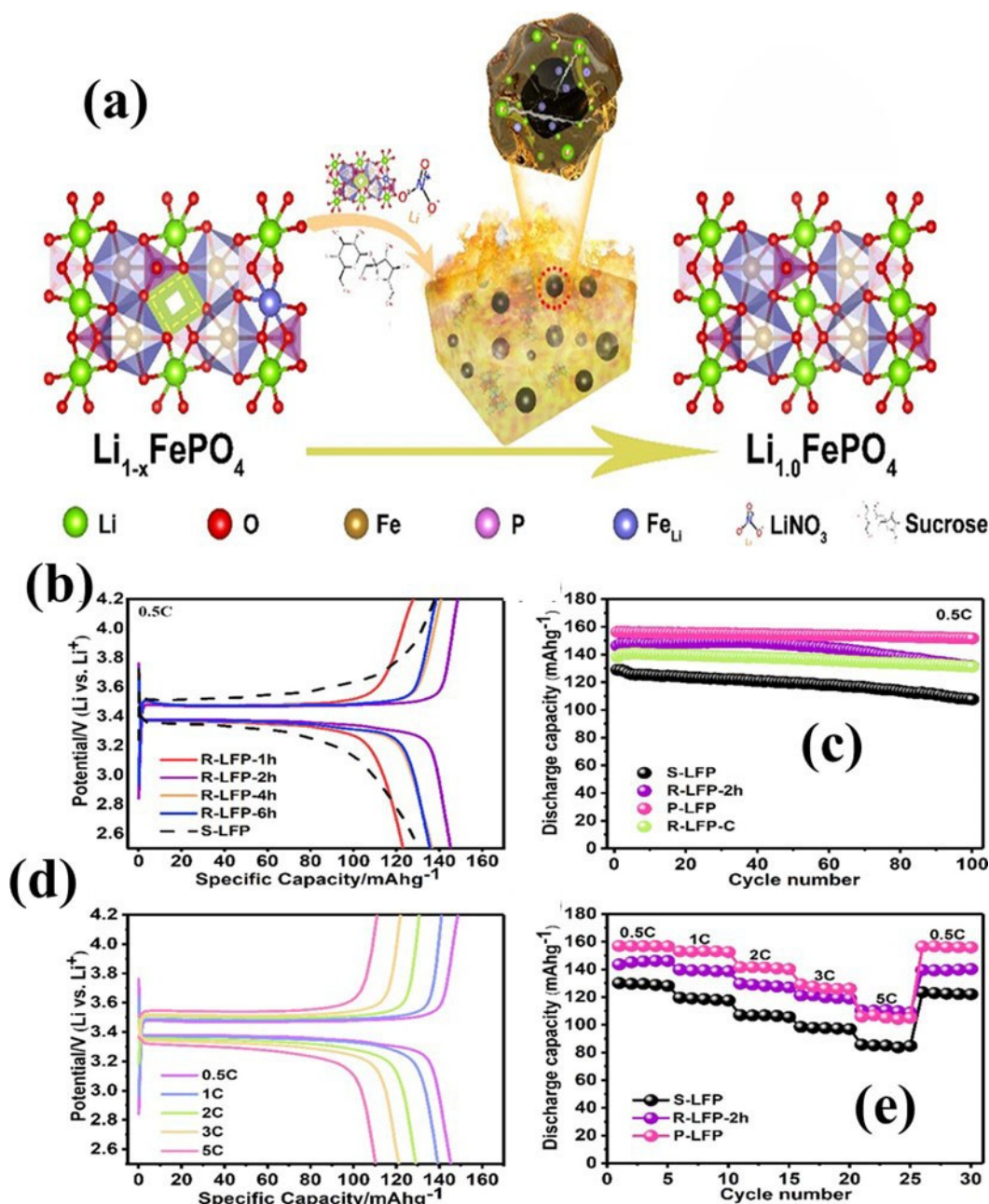
Figure 11. a) Schematic representation for the molten salt regeneration approach for spent LFP. Electrochemical performance of S-LFP and R-LFP: b) charge-discharge curves and c) cycling performance at 0.5 C. d) Charge- discharge curves of R-LFP-2 h and e) rate performance of S-LFP, R-LFP-2 h, and P-LFP at different rates. (S-LFP = spent Lithium iron phosphate, R-LFP = regenerated lithium iron phosphate). Reproduced with permission from Ref. [75]. Copyright (2022) American Chemical Society.

regenerated molecules. The existence of XRD results was also evidenced by HRTEM analysis, where the spinel phase of Co_3O_4 was missing and a clear lattice fringe was observed. Meanwhile, they have also examined the electrochemical properties of the relithiated cathode material using a 2025-type coin-cell where Li metal as an anode and 1 M $LiPF_6$ as an electrolyte which having mixed with Ethylene carbonate/Diethyl carbonate/Ethyl Methyl carbonate (EC)/DEC/EMC) in the volume ratio of 1:1:1. The electrode materials were prepared over aluminium foil by coating the desired amount of cathode material with PVDF and acetylene black in the weight ratio (80:10:10). After coating,

the electrode material was dried in an oven for the complete removal of solvent. The cathode material exhibits an excellent electrochemical properties of distinct discharge capacity 143.9 and 117 mAh g^{-1} at 1 C and 10 after 100 cycles. The retention rate is 95 % which is better than that of commercially available cathode materials. The improved properties are attributed to the presence of sodium, which helps Li-ions enter the surface of cathode material. This improved and strategic method can be treated as one of the most ecofriendly, and environmentally friendly and is economically viable for the relithiation of spent cathode without employing much labour and time. All the

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above literature provides deep insight into the greener and potential molten salt techniques for synthesizing cathode/anode material for the LIBs. The molten salt methods have advantages like easy reaction condition, simple process, low-pollution and relatively energy consumption draw the attention to the scientific community for the industrial implication. The major drawbacks of this method are wasting of resources which is ascended during the course of removal of unwanted salts after sintering. However, it is the big challenges for the scientific community to reduce the waste in the form of resources and provide a suitable and economical path to reuse further as it contains trace of metallic residues after sintering.

7. Beneficial Aspects of Direct Recycling Methods

The overall cumulative energy consumption, safety, environmental impact in term of emission of greenhouse gasses and revenue has discussed in Figure 12(a–d). Figure 12(a) reveals that the hydrometallurgical route is anticipated as the highest energy consumption techniques because of significant amount of material input. The EverBatt model considers the energy used in the upstream manufacturing processes of these chemicals when performing the full life cycle analysis. In
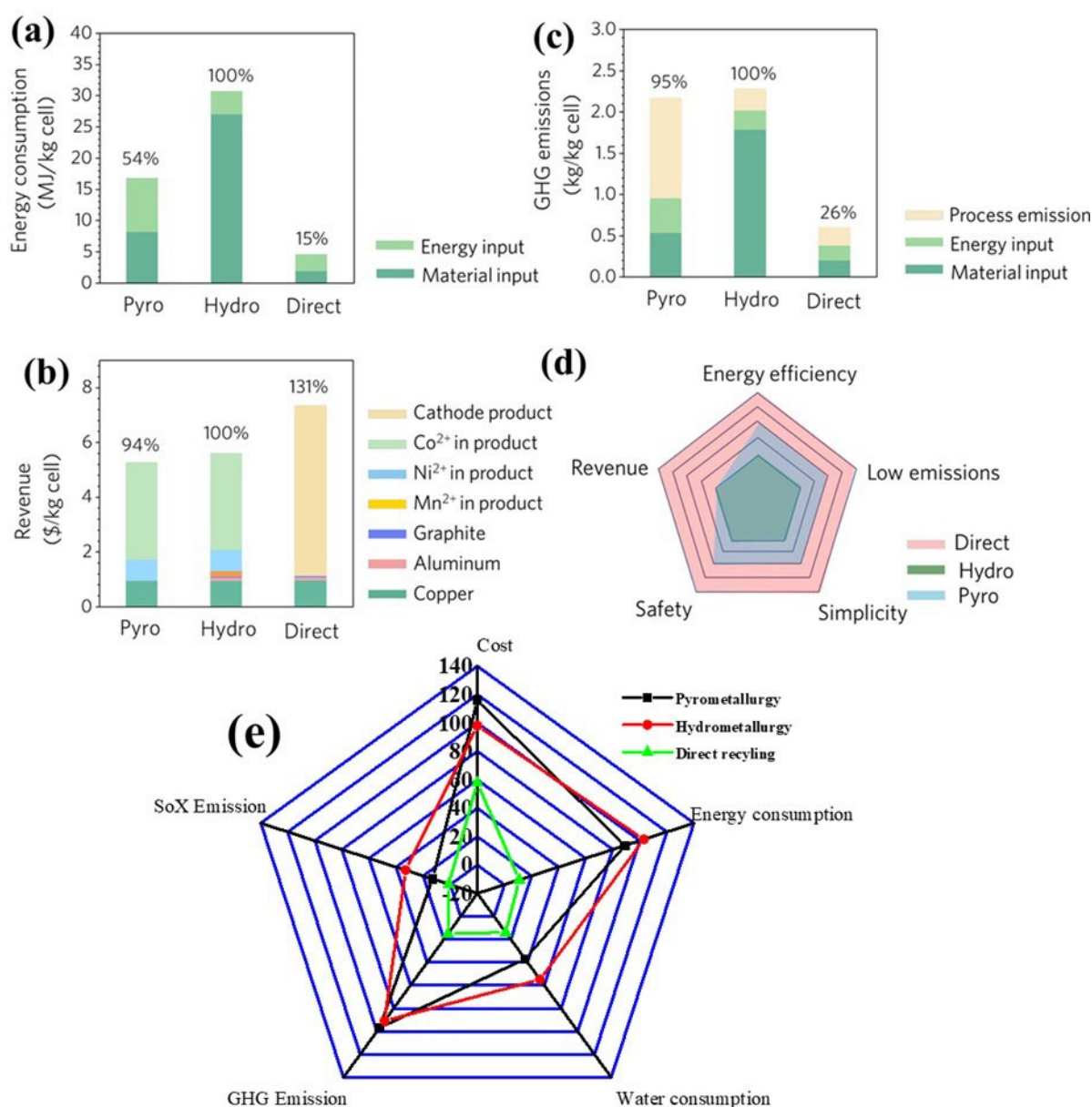

Figure 12. Life cycle analysis of pyrometallurgical (Pyro), hydrometallurgical (Hydro), and direct (Direct) recycling methods. a) Energy consumption, b) GHG emissions, c) potential revenue from outputs produced, and d) spider chart comparing various features of Pyrometallurgy, Hydrometallurgy, and Direct recycling methods. Reproduced with permission from Ref. [57]. Copyright (2021) American Chemical Society. e) The comparison of the cost, energy consumption, and environmental impacts of producing 1 kg NMC11 cathode and recycling them with different technologies (namely, pyro/hydrometallurgy and direct recovery). (Sources has been taken from Reference [78]).

Pyrometallurgical route high temperature required in the smelting step caused the energy consumed to be estimated to be higher than that in hydrometallurgy when only the energy input in the recycling processing itself was taken into account. Evidently, the primary inputs connected to raw materials and equipment are the leading factors ascribed to the modelling outcomes. The only raw material used in the direct recycling process is LiOH, the amount of which is determined by the Li loss of the used cathode materials. In this regard, direct recycling eliminated the requirement for energy-intensive machinery like that required for pyrometallurgy and hydrometallurgy as well. Moreover, the direct recycling process avoided the requirement of high energy consuming equipments like in other two process. Therefore, direct recycling required just 4.5 MJ of energy to recycle 1 kg of wasted LIBs, 15% less than hydrometallurgy, and was made possible by less chemicals and kinder processing conditions. Figure 12(b) shows that the GHG emission is relatively higher in Hydrometallurgy and Pyrometallurgy than that of the direct recycling method. Notably, for the direct recycling of 1 kg of spent LIBs, only 0.6 kg of GHG was released, which is significantly lower than those of pyrometallurgy (2.16 kg) and hydrometallurgy (2.27 kg). In addition to having low energy consumption and GHG emissions the direct regeneration process is anticipated to generate the highest revenue as shown in Figure 12(c) because the recycled cathode output can be used directly to create new LIBs, which are more valuable than the precursors obtained in pyrometallurgy and hydrometallurgy method. With a total revenue of $6.90, the manufacturing of regenerated cathodes (light yellow bar) promises to amount to $5.80. Cathodes, on the other hand, are broken down into elemental components for pyrometallurgy and hydrometallurgical recycling. A comprehensive comparison above three different recycling methods are elaborated in Radar plot form as shown in Figure 12(d). The graph shown a clear picture for the benefit of direct recycling method in terms of energy efficiency, emissions, and revenue generation. Furthermore, the direct recycling method is safer because it does not employ a corrosive acid/alkaline chemicals or high temperatures above 1000 °C. The direct recycling method are easy to operate rather than the conventional route followed by leaching and precipitation and ample of tedious courses. Because of high efficiency, high economic return, environmental friendliness, and high safety is thereby embodied by direct regeneration. We have also provided the comparative data in the form of Radar plot of the existing techniques from very recent published paper. The data for the Radar plot has been taken from the source[78] which provide a more clarity towards the beneficials of direct relithiation to maintain the circular economy as shown in Figure 12(e). The direct recycling of spent LIBs is considered as an emerging technology to maintain the original chemical structure and process value of battery materials by recovering and reusing directly.[79]

8. Future Perspective and Outlook

This paper provides a general overview of the regeneration/relithiation of cathode material from spent LIBs along with comparative economics of all existing process. Additionally, the authors have provided a summary of the direct relithiation procedure employing a variety of methods and resources. The direct regeneration process has attracted a rising attention because of its environmental friendliness, economically viable, no valuable material loss, no secondary waste, low energy consumption and maximum profit compared to the conventional methods. However, there is always a space for optimising and improving method/technology for industrial beneficiation and high economic returns. From the above-mentioned work/literature following conclusions are drawn:

- The degraded valuable materials are recovered from spent LIBs.
- The valuable metals in the cathode can be restored directly without any further separation during regeneration.
- The incorporation of suitable salts can maintain the stoichiometric ratio of the degraded materials.
- The regenerated cathode materials show almost similar or sometimes better than that of the pure materials or commercially available in the market with equivalent electrodes.
- Micro-level elements remained in the cathode material, which improves the electrochemical performance. Still, it is necessary to maintain the impurities level below its threshold value during the regeneration/relithiation of the spent cathode.
- Lithium scarcity should be known among sellers, distributors, consumers, and developers globally.
- Government should be more focused on recycling of spent LIBs and provide basic infrastructure to develop the pilot-scale plant.
- More accurate and scientific process should be developed for recycling of spent LIBs in the coming future.
- To maintain the stoichiometric of spent cathode several steps have been followed for the incorporation of Ni and Li. Thus, it is required to develop a universal method for the recycling of all types of NCM cathodes.
- The ionothermal route of direct regeneration has to be explored more both in lab scale as well as pilot scale for the commercialisation of techniques in the near future.
- The remaining techniques are on the verge of commercialisation like conventional methods (hydrometallurgical and pyrometallurgical route) as it is user friendly, eco-friendly and economically viable.

There are several drawbacks and difficulties that limit the actual application and commercialization of wasted cathode materials together with all these positive aspects and strategies. The impurities present in the cathode are taken positively to improve the electrochemical properties, but the practical application is not favorable as battery industries needed the impurities in the controlled chemical composition. It is still a challenge for the recovery of impurities within a cost-effective

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manner for its practical application and to develop the closed-loop process for the recovery of the spent cathode from LIBs without losing the valuable components. The coupling mechanical and chemical approaches are the most suitable process for closing the loop for several materials. To be safe and environmentally friendly, it is a big challenge to eliminate the potential hazards during the treatment of spent LIBs like a binder, separator, residual electricity and electrolyte etc. The removal of organic contents from the spent cathode leads to water pollution by increasing the concentration of biological oxygen demand (BOD) and chemical oxygen demand (COD) in the free-flowing water and groundwater also. Therefore, much attention should be paid to the recovery of valuable components and to develop a short route and close system for the efficient extraction of Lithium and circular economy.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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