CIRP Annals - Manufacturing Technology 72 (2023) 13–16

Contents lists available at ScienceDirect

CIRP Annals - Manufacturing Technology

journal homepage: https://www.editorialmanager.com/CIRP/default.aspx

Direct recycling of lithium ion batteries from electric vehicles for closed-loop life cycle impact mitigation

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ARTICLE INFO

Article history:
Available online 12 April 2023

Keywords:
Life cycle
Analysis
Battery recycling

ABSTRACT

Direct recycling of lithium ion batteries from electric vehicles aims to close the loop of battery manufacturing. This study presents a novel process-based life cycle assessment model for studying the environmental impacts associated with the direct recycling for closed-loop production of lithium ion battery relative to the conventional open-loop battery manufacturing. A 66 kWh NMC-graphite battery pack is analyzed using directly recycled NMC and graphite for the closed-loop manufacturing. The results show that the closed-loop manufacturing via direct recycling can reduce environmental impacts by up to 54% over the conventional open-loop manufacturing of lithium ion battery for electric vehicles.

1. Introduction

The past decade witnessed the rapid growth of the lithium ion battery (LIB) market, particularly for electric vehicles (EVs). It is predicted that by 2030 the global demand of LIBs for EVs will reach 2900 GWh [1], while the global cumulative demand on LIBs will be increased to 9300 GWh [2]. It is expected that this trend will continue in the following decades as a result of the growing market penetration of EVs.

The huge demand and consumption of LIBs for EVs cause grave concerns about their end of life, due to their content of materials that may cause toxic impacts. On the other hand, obsolete LIBs carry good economic potential through recycling of those materials. Currently, pyrometallurgical and hydrometallurgical processes are adopted in recycling of LIB materials [3]. However, their economic values are not fully recovered due to the low-grade of materials that are recovered by pyrometallurgical and hydrometallurgical processes. In recent years, direct recycling techniques have been proposed and developed at lab scale to recycle the active materials in LIB cathode and anode for reuse in manufacturing of new LIBs. This will allow closing the loop of LIB manufacturing to develop a circular economy. Direct recycling involves separation of the active materials in both anode and cathode with high purity from spent LIBs and then regenerate their electrochemical performance through various mechanical, chemical and physical processes.

The direct recycling techniques are promising alternatives to conventional pyrometallurgical and hydrometallurgical recycling methods. Taking the most commonly used battery type, lithium nickel manganese cobalt oxide-graphite (NMC-G) battery, as an example, about 20% of the usable lithium is lost at the End-of-Life (EoL) of a commercial EV battery pack due to parasitic reactions, solid electrolyte interface formation, and particle isolation [4]. Without breaking the structure of the active materials in LIB electrodes, the direct recycling method can relithiate and regenerate the active materials, i.e. NMC and graphite in electrodes from spent LIBs and recover their electrochemical performance by restoring their capacities, eliminating surface vacancies, and hindering surface reconstruction.

As direct recycling introduces the use of extra materials and processes, their environmental impacts need to be systematically studied, understood in a life cycle perspective and improved. Several studies in literature have reported life cycle impacts of the direct recycling processes. Quan et al. conducted a comparative life cycle assessment (LCA) of different recycling technologies including the direct recycling [5]. Kallitsis et al. have performed a LCA of recycling options for automotive Li-ion battery packs including direct recycling [6]. However, no study has been conducted on cradle-to-grave LCA of the closed-loop direct recycling of spent lithium-ion batteries from EVs. In addition, no studies have considered the raw material saving potential of the directly recycled high-quality battery materials which can be used in manufacturing of new batteries for EVs. To fill the research gap, a novel LCA model has been developed to assess the potential environmental impacts of the regenerated NMC-G LIB pack retired from EVs using state-of-the-art direct recycling processes, and compare it to conventional open-loop recycling of an NMC-G lithium-ion battery pack using the hydrometallurgical recycling method.

2. Method

In this study, a process-based LCA model has been developed to investigate and assess the cradle-to-grave environmental impacts of an NMC-G lithium-ion battery pack for a closed-loop production using the directly recycled and regenerated NMC and graphite, with

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https://doi.org/10.1016/j.cirp.2023.04.033
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both experimental results and literature data. The environmental impacts of a baseline NMC-G battery pack with the conventional hydrometallurgical recycling are also assessed for benchmarking. The two NMC-G battery packs are configured with the same mass (417 kg), capacity (66 kWh) and structure and compared on an equal mass basis. As shown in Fig. 1, the system boundary of this closed-loop cradle-to-grave LCA includes six stages: raw material extraction, material processing, electrode manufacturing, cell and pack assembly, battery use, and EoL treatment. The EoL stage for the baseline NMC-G battery pack uses the hydrometallurgical recycling method and pristine NMC and graphite are used to produce the electrodes of conventional lithium-ion battery pack. Meanwhile, the regenerated NMC and graphite for closed-loop battery production are from the direct recycling of spent LIBs from EVs at its EoL stage. Since the two

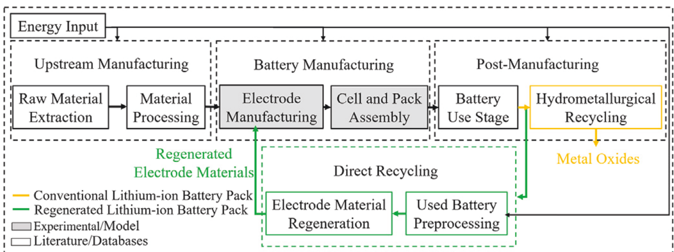

Fig. 1. Scope and system boundary for the LCA of the conventionally recycled and regenerated lithium-ion battery pack.

Battery types have identical functionality, weight and structure, the comparison is based on a reference flow of 1 kg of the NMC-G lithium-ion battery pack. In the life cycle inventory (LCI) analysis, the raw material extraction and material processing stages of the lithium-ion battery packs are modelled using the GaBi professional software with the data retrieved from the Ecoinvent database [7]. The battery manufacturing, and cell and pack assembly stages are modelled based on our industrial partner's battery pack manufacturing processes as reported in our previous study [8]. The battery pack use stage is modelled following our previous work [9]. In comparison, the baseline hydrometallurgical recycling method uses the validated industrial LCI from literature [3]. Both the baseline hydrometallurgical recycling model and the proposed direct recycling model have the same system scoping, from spent battery collection to material recovery and are modelled at industrial scale. In addition, the BatPac model developed by Argonne National Laboratory is used to design and simulate the baseline battery pack and the regenerated battery pack, which makes the results more comparable. The baseline hydrometallurgical recycling method can only recover metal in the format of salt. Meanwhile, the direct recycling method adopts the latest NMC and graphite electrode regeneration technologies and its end products can be directly used in battery manufacturing and close the manufacturing loop. The life cycle environmental impacts of the regenerated NMC-G battery pack are assessed using the ReCiPe method and compared with those of the baseline conventional NMC-G battery pack to show the trade-offs and environmental benefits of the direct recycling method.

2.1. Direct recycling for closed-loop manufacturing of lithium-ion battery

The direct recycling processes studied for the closed-loop manufacturing of the NMC-G lithium-ion battery are shown in Fig. 2. The direct recycling for the closed-loop manufacturing of LIB for EVs is modelled on the actual operations and processes. First, the spent LIB packs are disassembled from the collected EVs. The EV collection rate is taken at the same rate as the conventional vehicles which is 91% as reported by Dunn et al. [3]. Energy consumption per kg battery removal is collected from Hawkins et al., at 0.083 MJ per kg lithium-ion battery pack [10]. Electricity energy is consumed to disassemble vehicles and spent battery packs are transported by 16–32-ton EURO5 lorries consuming fossil fuels [10]. Second, the LIBs are immerged into a salt solvent to fully discharge the battery. Dunn et al. estimated that 0.0036 MJ electricity per kg lithium-ion battery pack is needed to accomplish the discharging [3]. Third, the discharged battery cell is opened and the electrolyte is extracted from the battery cell using the carbon dioxide (CO_2) solvent. Liquid CO_2 is compressed into the battery cell at a flow rate of 15 L min^{-1} for 50 min, along with a 3:1 acetonitrile (ACN): propylene carbonate mixture at a rate of 0.5 mL min^{-1} for 20 min [11]. Liquid CO_2 will be transformed into gaseous CO_2 and then remove the electrolyte from the battery in the extract chamber (100 ml per pouch cell). Almost all CO_2 can be recycled and reused, except a small amount of gaseous CO_2 remaining in the extract chamber being counted as CO_2 consumption. The energy consumption of this step is the energy to compress CO_2 solvent into the battery cells, reported at 0.040 MJ per kg NMC-G battery pack [12]. Fourth, the battery cells without electrolyte undergo size reduction and final separation processes into anode and cathode strips, which consume 0.26 MJ and 0.023 MJ/kg battery pack, respectively [12]. All the electricity energy in the analysis is assumed produced by US. electricity grid mix combining all states and different voltage levels.

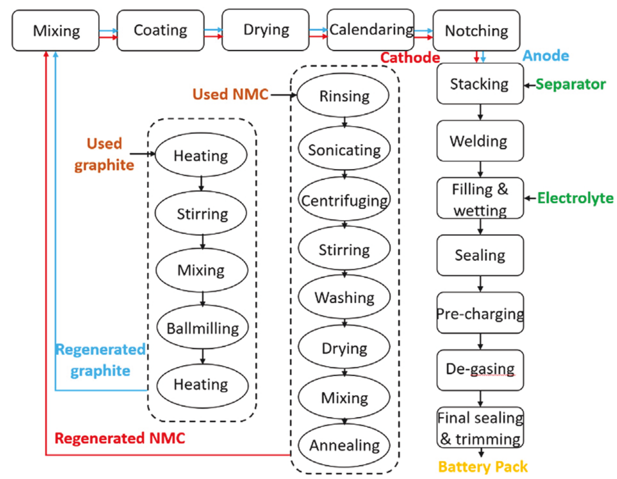

Fig. 2. Direct recycling processes for closed-loop manufacturing of LIB.

Prior to direct recycling of NMC from cathode, the binders including Polyvinylidene fluoride (PVDF), Carboxymethyl cellulose (CMC), etc., mixed in the cathode need to be removed. The first step is to sonicate the cathode strips in the NMP solvent to separate the NMC powder from the binders and carbon black (CB). In this step, the amount of NMP solvent needed is the same amount as used in the mixing of active materials for cathode production, which is 0.24 kg NMP as needed to remove the PVDF per kg battery pack. The energy consumption is 0.0064 MJ/kg battery pack.

The separated NMC cathode material can be extracted by centrifuging the sonicated solution (4.2×10^{-4} MJ/kg battery pack). After several rounds of washing with NMP and gravity precipitation, the remaining CB in the NMC cathode material is negligible (0.0036 MJ/kg battery pack). The most important step in the NMC regeneration is the relithiation process conducted to recover the electrochemical performance of the used NMC cathode material. During the relithiation step, the NMC powder is soaked and continuously stirred in the LiOH aqueous solution at a temperature of 90~100 °C (0.23 MJ/kg battery pack) [13]. Deionized water is used to wash the lithium salt and remove the residues (0.0036 MJ/kg battery pack). Finally, the NMC powder is mixed with excessive Li_2CO_3 (1.6×10^{-4} MJ/kg battery pack) after an overnight vacuum drying (0.22 MJ/kg battery pack) and thermally treated in oxygen for four hours at 850 °C to compensate for the Li loss in the post annealing process (0.18 MJ/kg battery pack) [13].

For the direct recycling and regeneration of graphite anode material, the first step is to purify the used graphite since there are some impurities in the recycled graphite including metal elements such as

Al, Ni, Mn, Co, etc., and remaining binders including PVDF, CMC, and Styrene-butadiene rubber (SBR). These impurities may affect the electrochemical performance of the regenerated graphite when manufactured into the new battery. Here the impurities are removed by heat treatment (0.036 MJ/kg battery pack) and acidification (0.29 MJ/kg battery pack). The purified graphite is then coated with amorphous carbon made from pitch. Before the coating, the graphite without impurities needs to be heated in an argon atmosphere at 3000 °C (0.26 MJ/kg battery pack) to increase the graphitization degree and to mitigate the chance of defection [14]. Then the graphite is mechanically mixed with pitch at a mass ratio of 9:1 (5.8×10^{-5} MJ/kg battery pack). Finally, the regenerated graphite can be obtained by ball milling (0.013 MJ/kg battery pack) and heating the mixture to 1000 °C for 2 h (0.085 MJ/kg battery pack) [14].

After all the above steps, the directly recycled materials can be reused in the manufacturing of new LIBs with comparable electrochemical performance to the pristine battery [13,14]. In the half cell test, the initial capacity of pristine NMC reached 155 mAh/g at 0.1 C and remains 92% at C/3 after 60 cycles. Meanwhile, the regenerated NMC has the initial capacity of 154 mAh/g at 0.1 C and remains 91% at C/3 after 50 cycles [13]. In the half cell test, the pristine graphite can reach 292 mAh/g at 0.5 C for 250 cycles and the regenerated graphite can run up to 325 mAh/g at the same condition [14]. The directly recycled NMC and graphite powders can replace their pristine counterparts in the NMC-G battery manufacturing, through a series of battery manufacturing processes including mixing with binders, solvents, CB to produce the cathode and anode slurries. The cathode and anode slurries will then be coated on the Al and Cu foil current collectors. After drying, calendaring, and notching, the cathode and anode finally are made. They are stacked in layers with separators in between and welded together to form the structure of the pouch cell [15], which is then filled with $LiPF_6$ electrolyte. Finally, a single battery cell is produced with sealing, degassing, pre-charging, and final trimming [16,17].

2.2. Conventional hydrometallurgical recycling for open-loop EOL of lithium-ion battery

Hydrometallurgical recycling is commonly used in current EOL of LIBs from EVs. The hydrometallurgical recycling also starts from the collection and disassembly of spent LIB packs into battery cells. Then, the spent LIB cells are discharged and separated into anodes and cathodes. The current collectors are removed by warm NMP bathing at 100 °C for 1 h. The remaining cathodes are calcined, and the metals are leached by acid and hydrogen peroxide [3]. The obtained lithium oxides and other metal oxides are recovered by grinding, leaching, and filtration. Compared to direct recycling, the CB and PVDF are burned out in the calcination process instead of being recycled [3]. In addition, the active materials in solutions must be dried to collect them as powders, and they are in low quality and cannot be directly used in battery manufacturing.

2.3. Energy consumption in direct recycling of NMC and graphite

Energy consumptions are studied first on the direct recycling of NMC and graphite from the spent LIBs, since the energy consumption dictates the embedded carbon emissions from direct recycling processes. The contributions of each step to the energy consumption are shown in Fig. 3.

The energy analysis results show that 2.31 MJ of energy is required to produce 1 kg regenerated NMC in the direct recycling processes, to obtain comparable electrochemical performance from the used NMC. Among the 10 steps in the direct recycling of NMC cathode active material, stirring, drying, and annealing are the three most energy-intensive steps, accounting for 36, 34, and 27% of the total energy consumption, respectively. The stirring process is energy-intensive since it requires a large amount of energy to stir and simultaneously to heat up the NMP solution to 90~100 °C. The drying process is energy-intensive mainly because it takes 12 h to dry the powder which results in a large drying energy consumption.

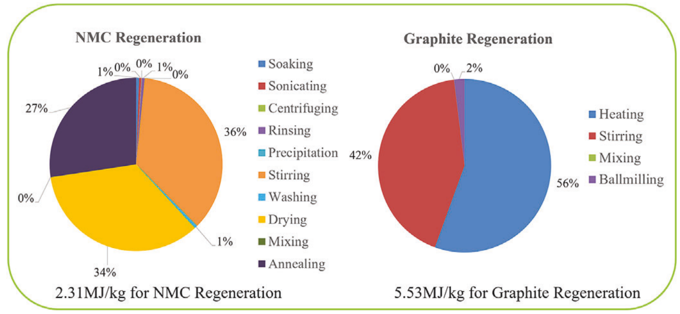

Fig. 3. Energy consumption in direct recycling of NMC and graphite.

The annealing process consumes a large amount of energy because it is conducted at 850 °C for 4 h. Nevertheless, compared to 14.4 MJ/kg energy intensity of the pristine NMC, the direct recycling of NMC offers a great energy saving.

The direct recycling of graphite requires more energy than the NMC. It demands 5.53 MJ to produce 1 kg regenerated graphite with electrochemical performance that is comparable to pristine graphite. The direct recycling of graphite consists of heating, stirring, mixing, and ball-milling. The two major energy consuming steps are heating and stirring, taking 56 and 42% of the total energy consumption, respectively, in the direct recycling of graphite. The heating process consumes 3.10 MJ/kg because it needs to heat up the temperature of the graphite mixture several times in argon and nitrogen atmosphere up to 3000 °C. Similar to the NMC regeneration, the stirring process in direct recycling of graphite is conducted in hot H_2SO_4 solution. The energy is mainly used to keep the high operating temperature instead of stirring itself.

3. Life cycle impact assessment and benchmarking

The life cycle impact assessment of the lithium-ion battery pack using the directly recycled NMC and graphite are conducted using the ReCiPe (v.1.08) method to evaluate 13 impact categories listed in Table 1 [18].

Table 1
13 impact categories in the ReCiPe method.

Impact categories	Abbreviation
Global warming potential	GWP
Freshwater eutrophication potential	FEP
Terrestrial ecotoxicity potential	TETP
Freshwater ecotoxicity potential	FETP
Human toxicity potential	HTP
Fossil depletion potential	FDP
Marine eutrophication potential	MEP
Photochemical oxidant formation potential	POFP
Marine ecotoxicity potential	METP
Metal depletion potential	MDP
Ozone depletion potential	ODP
Particulate matter formation potential	PMFP
Terrestrial acidification potential	TAP

The life cycle impact results for the regenerated NMC-G battery pack from the closed-loop production using the direct recycling processes are benchmarked against the results for the baseline battery pack from the open-loop production, across the 13 impact categories for the reference flow of 1 kg battery pack. The results are shown in Fig. 4, distinguishing the contribution from each of the six life cycle stages for all 13 life cycle impact scores. The impact scores are expressed in different units, and it is hence not advisable to compare across impact categories in Fig. 4.

As illustrated in Fig. 4, life cycle impacts of the NMC-G battery pack from the closed-loop production using the directly recycled NMC and graphite are lower than of the baseline NMC-G battery pack from the open-loop production, except for the MDP and MEP. The

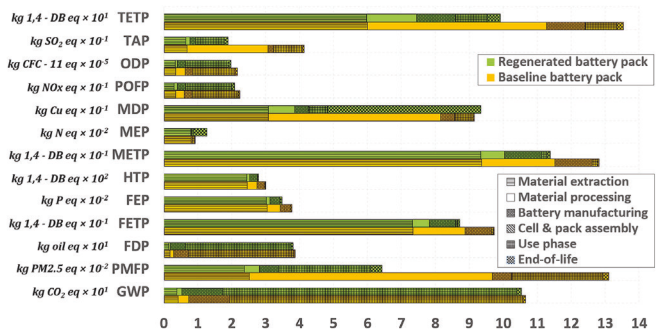

Fig. 4. Benchmarking of the characterized life cycle impacts of battery packs from closed-loop and open-loop productions.

main reasons are due to the savings of the environmental impacts being generated from the raw material extraction and the material processing phases of NMC and graphite by using the direct recycling for the EOL management of the spent EV LIB pack.

The largest difference is in TAP impact. The TAP of the regenerated NMC-G battery pack from closed-loop production is 0.19 kg SO_2 eq/kg, while the TAP of the baseline NMC-G battery pack from the open-loop production is 0.41 kg SO_2 eq/kg, illustrating a 54% reduction from using the closed-loop battery pack over the open-loop battery pack. The main reason for this difference is the elimination of several lithium and other metal acidification steps in the material processing stage of the pristine electrode active materials.

Another large difference is in the particulate matter formation impact. The PMFP of the regenerated battery pack is 6.43×10^{-2} kg PM2.5 eq/kg, which is 51% lower than that of the baseline battery pack at 13.12×10^{-2} kg PM2.5 eq/kg. There are many reasons, first, in the open-loop battery system, the hydrometallurgical recycling burns out the carbon black and PVDF, and the insufficient combustion can cause the formation of particulate matters. Second, the direct recycling processes of the graphite from spent LIB pack produce much fewer particulate matters than the pristine graphite production since a larger amount of pitch is used in the pristine graphite production and the pitch involves petroleum refining [19].

The two battery packs also have a large difference in terrestrial ecotoxicity. The TETPs of the regenerated NMC-G battery pack and the baseline NMC-G battery pack are 9.92 kg 1,4–DB eq/kg and 13.55 kg 1,4–DB eq/kg, respectively. The TETP of the regenerated NMC-G battery pack is 27% lower than that of the baseline battery pack, mainly attributed to the high material recovery and reuse rate of the direct recycling.

Overall, the life cycle impacts of the regenerated LIB pack from the closed-loop production are lower than those of the baseline LIB pack from the conventional open-loop production. The MDP and MEP of the regenerated LIB pack are a little bit higher than those of the baseline LIB pack, mainly because the NMC direct recycling processes introduces need for Li_2CO_3 and LiOH. The life cycle impacts of the regenerated LIB pack can be further lowered in future since the direct recycling techniques are still under development at lab scale, and the associated material and energy consumption can be optimized in future.

4. Conclusions

A comprehensive life cycle assessment model has been developed for a 66-kWh NMC-graphite battery pack with 417 kg mass from closed-loop production using directly recycled NMC and graphite materials from spent LIB pack of electric vehicles. The life cycle assessment results are benchmarked against those of a conventional baseline NMC-graphite battery pack with exactly the same capacity, weight and structure but using hydrometallurgical processing as EoL treatment. The study found that the direct recycling processes require 2.31 MJ and 5.53 MJ energy to recycle the electrochemical properties of 1 kg NMC and graphite respectively. The life cycle impacts of the regenerated NMC-graphite battery pack using the directly recycled NMC and graphite are considerably lower than those of the conventional LIB pack, except for MDP and MEP, and it can be optimized and lowered in future scale-up processes. The direct recycling method has a great potential to close the loop of the EV battery manufacturing to build a circular economy around EV batteries in future.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support from the US National Science Foundation (CBET-2101129) is acknowledged.

References

[1] Rietmann N, Hügler B, Lieven T (2020) Forecasting the trajectory of electric vehicle sales and the consequences for worldwide CO_2 emissions. *J. Clean. Prod.* 261: p.121038.
[2] Roper W., 2020, High demand for lithium-ion batteries, Statista, https://www.statista.com/chart/23808/lithium-ion-battery-demand/ access date December 22, 2020.
[3] Dunn JB, Gaines L, Sullivan J, Wang MQ (2012) Impact of recycling on cradle-to-gate energy consumption and greenhouse gas emissions of automotive lithium-ion batteries. *Environ. Sci. Technol.* 46(22):12704–12710.
[4] Montoya AT, Yang Z, Dahl EU, Pupek KZ, Polzin B, Dunlop A, Vaughey JT (2022) Direct recycling of lithium-ion battery cathodes: a multi-stage annealing process to recover the pristine structure and performance. *ACS Sustain. Chem. Eng.* 10 (40):13319–13324.
[5] Quan J, Zhao S, Song D, Wang T, He W, Li G (2022) Comparative life cycle assessment of LFP and NCM batteries including the secondary use and different recycling technologies. *Sci. Total Environ.* 819:p.153105.
[6] Kallitsis E, Korre A, Kelsall GH (2022) Life cycle assessment of recycling options for automotive Li-ion battery packs. *J. Clean. Prod.* 371:p.133636.
[7] Zhang J, Ke X, Gu Y, Wang F, Zheng D, Shen K, Yuan C (2022) Cradle-to-gate life cycle assessment of all-solid-state lithium-ion batteries for sustainable design and manufacturing. *Int. J. Life Cycle Assess* 27(2):227–237.
[8] Yuan C, Cao H, Shen K, Deng Y, Zeng D, Dong Y, Hauschild M (2021) Water-based manufacturing of lithium ion battery for life cycle impact mitigation. *CIRP Ann.* 70 (1):25–28.
[9] Zhang C, Shen K, Yang F, Yuan C (2019) Multiphysics modeling of energy intensity and energy efficiency of electric vehicle operation. *Procedia CIRP* 80:322–327.
[10] Hawkins TR, Singh B, Majeau-Bettez G, Strømman AH (2013) Comparative environmental life cycle assessment of conventional and electric vehicles. *J. Ind. Ecol.* 17(1):53–64.
[11] Grützke M, Mönnighoff X, Horsthemke F, Kraft V, Winter M, Nowak S (2015) Extraction of lithium-ion battery electrolytes with liquid and supercritical carbon dioxide and additional solvents. *RSC Adv.* 5(54):43209–43217.
[12] Ciez RE, Whitacre JF (2019) Examining different recycling processes for lithium-ion batteries. *Nat. Sustain.* 2(2):148–156.
[13] Yu X, Yu S, Yang Z, Gao H, Xu P, Cai G, Rose S, Brooks C, Liu P, Chen Z (2022) Achieving low-temperature hydrothermal relithiation by redox mediation for direct recycling of spent lithium-ion battery cathodes. *Energy Storage Mater.* 51:54–62.
[14] Ruan D, Wang F, Wu L, Du K, Zhang Z, Zou K, Wu X, Hu G (2021) A high-performance regenerated graphite extracted from discarded lithium-ion batteries. *New J. Chem.* 45(3):1535–1540.
[15] Wang F, Ke X, Shen K, Zhu L, Yuan C (2022) A critical review on materials and fabrications of thermally stable separators for lithium-ion batteries. *Adv. Mater. Technol.* 7(5):p.2100772.
[16] Yuan C, Deng Y, Li T, Yang F (2017) Manufacturing energy analysis of lithium ion battery pack for electric vehicles. *CIRP Ann.* 66(1):53–56.
[17] Deng Y, Li J, Li T, Gao X, Yuan C (2017) Life cycle assessment of lithium sulfur battery for electric vehicles. *J. Power Sources* 343:284–295.
[18] Goedkoop M., Heijungs R., Huijbregts M., De Schryver A., Struijs J.V.Z.R. and Van Zelm R., 2008, A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level; report I: characterisation, Impact world.
[19] Engels P, Cerdas F, Dettmer T, Frey C, Hentschel J, Herrmann C, Mirfabrikikar T, Schueler M (2022) Life cycle assessment of natural graphite production for lithium-ion battery anodes based on industrial primary data. *J. Clean. Prod.* 336: p.130474.