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Graphite recovery from waste Li-ion battery black mass for direct re-use

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ABSTRACT

Graphite was recovered from two leached (H₂SO₄ = 2 M, 60 °C, t = 3 h, Fe³⁺ = 2 g/L) Li-ion battery black mass concentrates with minimized energy consumption. One black mass originated from a mixture of mobile device and power tool batteries, and another from a single electric vehicle battery. The leach residues were pyrolyzed (800 °C, t = 1 h, Ar atmosphere) to remove the polyvinylidene fluoride (PVDF) binder and other non-metallic fractions. The black mass, its leach residue, and pyrolyzed residue were characterized using inductively coupled plasma-optical emission spectrometry (ICP-OES), ion chromatography (IC), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), thermogravimetric analysis (TGA), Raman spectroscopy, and N₂ adsorption/desorption. After hydrometallurgical recycling and pyrolysis, the main post-metallurgical black mass impurities were cobalt oxide, iron, acid-resistant boehmite (AlO(OH)), and silicon dioxide. The pyrolysis resulted in electrolyte and binder removal, affected the crystallinity of the remaining boehmite. The recovered graphite-rich residue with impurities identified was tested as an anode in half-cells vs. metal Li. The average specific capacities of recovered graphite-rich residues from both sources were 350 and 250 mAh/g at 0.1C and their capacity retention after 100 cycles was high (80 %) suggesting rather slow deterioration and hence the proposed recycling route being promising for the graphite reuse in new Li-ion batteries.

1. Introduction

The Li-ion battery (LIB) is currently the primary technology for powering electric vehicles (EVs), portable devices, such as mobile phones, power tools, and electric bikes. It is estimated that global EV sales could reach 21.5 million in 2030 compared to 4 million in 2020 (Or et al., 2020). The materials used in LIBs, Co, Li, Ni, Cu, and graphite, are considered critical in the EU (European Critical Raw Materials Act, 2023) due to insufficient mining activities and predicted growth of LIBs production (Jena et al., 2021), as well as demand in other industries. If the current mining trends for natural graphite continue, then by 2030 there will not be enough graphite to meet the future EV demands (Ballinger et al., 2019). A major part of available natural graphite is located in China, which produces ~ 65 % of all graphite worldwide (Ballinger et al., 2019). Flake graphite is found mainly in China, Brazil, Canada, and Africa (Wissler, 2006). Besides LIBs, the graphite supply issues can affect the chemical, nuclear, and electrical industries. However, the low recycling capacity of spent LIBs (SLIBs) is one of the issues related to a sufficient and stable supply of battery materials. Also, stockpiling and landfilling of SLIBs would cause a threat to the environment as LIBs contain toxic substances, such as solvents, fluoride compounds, and heavy metals (Ni, Co). Hence, metallurgical processing of the SLIBs will greatly benefit environmental protection and contribute to the supply of valuable battery materials (Jena et al., 2021).

LIB comprises an anode, cathode, separator, and electrolyte. The cathode layer consists of the active material coated on aluminum foil. The major cathode chemistries currently used in portable LIBs are $LiNi_xMn_yCo_zO_2$ (NMC), $LiCoO_2$ (LCO), $LiMn_2O_4$ (LMO), and $LiFePO_4$ (LFP) (Chernyaev et al., 2021b, 2021a; Zou et al., 2013). The anode is composed of graphite with some carbon black, both coated on copper foil. The anode material cost is approx. 5–15 % of the LIB cell total cost (Ma et al., 2019; Perumal et al., 2021; Thompson et al., 2021), whereas the cost of the cathode is over 60 % (Thompson et al., 2021). Due to its high porosity and stability (Al-Ani et al., 2020) with well-defined crystal structure, graphite can undergo repeated expansion due to the intercalation of Li^+ ions and thus, provide the high energy required in LIBs. Additionally, a LIB cell contains a separator (microporous polypropylene or polyethylene) that prevents direct contact between the

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cathode and anode layer, but allows sufficient Li⁺ migration between electrodes (Golmohammadzadeh et al., 2018; Velázquez-Martínez et al., 2019). The polymer binders, mainly PVDF, and other additives are used to adhere the cathode active material to the aluminum foil and graphite to copper to improve mechanical cohesion (Liivand et al., 2021; Liu et al., 2019; Sabisch et al., 2018). Carbon black is typically used as a conducting agent in the mixture with the binder in both anode and cathode (Or et al., 2020; Yu et al., 2018). Lithium salts (mostly LiPF₆, but also LiBF₄, LiClO₄, and LiSO₂) are dissolved in organic carbonate-based solvents (e.g. ethylene carbonate, dimethyl carbonate, diethyl carbonate or propylene carbonate) serving as an electrolyte (Golmohammadzadeh et al., 2018; Liivand et al., 2021; Velázquez-Martínez et al., 2019; Wang et al., 2019). Lithium salt (LiPF₆) is a toxic substance that can react with humidity in air and produce hydrogen fluoride (HF) gas, which is corrosive and harmful to human health (Larsson et al., 2017; Yu et al., 2021a) he mass distribution of battery components in different battery types (NMC, LCO, LMO) is similar but somewhat varied in graphite content. The mass fraction of graphite in LIBs can vary from 14 % (LMO) to 20 % in NMC (811). The active cathode material varies from 31 % (NMC 811) to 41 % (LMO). The plastics (separator) are typically 2 % and the PVDF binder is 3 % of the LIB mass (Ali et al., 2021). Generally, either natural or synthetic graphite or a mixture of both is used in LIBs. Natural graphite is mostly used in LIBs for consumer applications and artificial graphite for high-energy or high-power applications (Brückner et al., 2020). Natural graphite may gain a larger market share than synthetic graphite due to its lower price and improved quality. The purity of the graphite in the ore is between 5 and 40 wt% and can be increased up to 99.9 % through mechanical separation and flotation followed by chemical or thermal treatment, while additional chemical purification is required to achieve the \geq 99.9 % purity, required in battery applications (Al-Ani et al., 2020; Wissler, 2006). Synthetic graphite is prepared by subjecting unstructured carbon to thermal treatment at temperatures above 2500 °C to induce graphitization, an energy-intensive process based on fossil fuels (Gaines et al., 2010; Zhu et al., 2022). Among other LIB components, graphite is a significant contributor to the CO₂, NO_x, SO_x, and PM10 (<10 µm particulate matter) emissions in the industrial production of LIBs (Dai et al., 2019).

The regeneration of battery-grade graphite from spent graphite could be a relatively facile and efficient process, but the graphite recycling costs are still too high due to graphite regeneration at high temperatures, therefore, it is currently economically more feasible to use primary graphite in batteries (Zhu et al., 2023). The industrial LIB recycling consists of several unit processes, including mechanical pre-treatment, pyrometallurgical and/or hydrometallurgical processes (Ali et al., 2021). In mechanical pre-treatment the battery components can be separated and recycled directly (e.g. mechanical Cu separation after crushing) or decomposed and reacted chemically at high (e.g. smelting, roasting) or low temperatures (e.g. leaching). In pyrometallurgical treatment, Co, Ni, and Cu are recovered as alloys while Li, Al, and Fe form the slag (Jena et al., 2021) in smelting at 1400 °C with almost 50 % of battery weight (lithium, electrolyte, plastics, and graphite) lost (Ali et al., 2021), while lithium can be recovered from the slag hydrometallurgically. The alloy and slag are processed by hydrometallurgical methods to recover the metals. Currently, dominating recycling processes are described in more detail in the Supplementary material. During the industrial and lab-scale recycling processes, graphite is either used as an energy source or reductant for the pyrometallurgical stage of LIB recycling, where the graphite and organic components are burned away (Ma et al., 2019; Wang et al., 2021), or discarded as a leaching waste, containing some undissolved metals, binders, and electrolyte, after hydrometallurgical processing (Liivand et al., 2023; Niu et al., 2022; Rey et al., 2021; Velázquez-Martínez et al., 2019). Graphite recovery and reuse in LIB recycling have been explored by various researchers (Gao et al., 2020; Kayakool et al., 2021; Liu et al., 2020; Rinne et al., 2021; Rothermel et al., 2016; Vanderbruggen et al., 2022; Yi et al., 2020). Graphite separation from the active material and other

impurities in the black mass was shown to be enhanced by froth flotation (Rinne et al., 2021; Vanderbruggen et al., 2022). It was also demonstrated that high-temperature treated (over 800 °C) manually separated spent graphite exhibits good performance in new LIB cells (Kayakool et al., 2021). The electrochemical performance of graphite can be improved by doping, carbon coating, and composite materials (Huang et al., 2017; Niu et al., 2022). Spent graphite can be recycled to be used as a new functional material, such as a electrode material, absorbent, and catalyst (Niu et al., 2022). Several researchers have investigated the added value transformation of graphite from SLIBs into graphene oxide using the chemical oxidation (Hummers) method, which requires the use of strong oxidants, such as concentrated H₂SO₄ and KMnO₄ (Liivand et al., 2021; Liu et al., 2022). In this work, contrary to the manually extracted spent graphite and chemical purification, two industrially produced black mass concentrates, one prepared from an EV battery (NMC 111) and another from a mixture of LIBs from power tools (NMC, LMO, and LCO), were used to investigate the feasibility of graphite reuse from pyrolyzed black mass leach residue in a Li-ion battery. The concentrates were thoroughly characterized and compared, leached and subjected to pyrolysis to remove the organic impurities without additional chemical purification steps. The electrochemical testing of recycled and regenerated graphite from pyrolyzed leach residue was tested in the half-cells vs. metal Li configuration to compare the performance of graphite in residues of different black mass. This work demonstrates that a shorter recycling route - only leaching and pyrolysis - allows the black mass leach residue to be used as the anode in a new battery without additional purification steps, thus potentially saving the process costs.

2. Experimental

2.1. Battery waste raw material and characterization

In this study, two different black mass concentrates (denoted as DBM and ABM) were used as a source of graphite. Concentrate DBM was obtained from an industrially crushed EV battery whereas concentrate ABM originated from SLIBs of power tools and mobile devices. The specific industrial pre-treatment process employed to generate these black masses is undisclosed. Consequently, a comprehensive characterization of the industrial black masses was undertaken to gain more information. Nevertheless, it is noteworthy that the pre-treatment processes for black mass derived from mobile devices exhibit similarities to those described in our previous publications (Peng et al., 2019; Velázquez-Martínez et al., 2019). The concentrates were sieved (500 µm) to remove the large fraction consisting of separator, current collectors, casing, and wires. The underflow was used in leaching experiments. The metallic bulk composition (Ni, Mn, Co, Cu, Li, Fe), used in the extraction calculation in leaching, was determined by dissolving three samples $(\sim 0.5 \text{ g})$ from each sieve batch, in boiling concentrated aqua regia for 30 min, and analyzed by atomic absorption spectroscopy (AAS, Thermo Fisher, ICE 3000, USA). The black mass concentrate (\sim 0.25 g) was also dissolved in the mixture of HNO₃, HCl, and HBF₄ and treated in a microwave (Anton Paar Multiwave 3000) at 210 °C to dissolve the refractory components (e.g. SiO2, AlO(OH)). ICP-OES (Perkin Elmer Optima 5300 DV) was used to determine impurity metals Al, Ca, Na, Pb, Si, Zn, P, S. The F^- , Cl^- and PO_4^{3-} by digesting the sample in a mixture of concentrated HNO3 and H2SO4 using the abovementioned digestion method. The solution was analyzed using ion chromatography (Metrohm 881 Compact IC pro).

The first-order (Raman) spectra were acquired from 1000 to 1900 cm⁻¹ using Renishaw in Via Qontor with a wavelength of 532 nm. The positions, height, and width of the disorder peak (D) and order peak (G) were measured to observe possible changes in graphite structure after pyrolysis. The I_D/I_G ratio was calculated using the spectra acquired from 5 different locations in the sample. D-band describes the degree of defects in the crystal structure while G-band describes sp² in-plane vibration. Additionally, D' band located at around 1609–1620 cm⁻¹ describes

the degree of defects in graphitic lattice (Al-Ani et al., 2020; Kayakool et al., 2021; Liivand et al., 2021). The mineralogy of the black mass was analyzed using XRD (Malvern Panalytical X'Pert3) with Cu K_{α} radiation (wavelength 1.54187 Å) at 40 kV and 40 mA, using a step size of 0.013 degrees. The mineralogy and texture of the samples were quantified through automated SEM-EDS analysis. The analysis was undertaken using a Hitachi SU3900 scanning electron microscope fitted with a single large area (60 mm²) Bruker SDD energy dispersive spectrometer and running the AMICS automated mineralogy software package. Beam conditions were optimized for analysis, therefore an accelerating voltage of 20 kV coupled with a beam current of approximately 15nA was used. The leach residue was analyzed using a scanning electron microscope (SEM, MIRA 3, Tescan, Czech Republic) equipped with an UltraDry Silicon Drift energy-dispersive X-ray spectrometer (EDS) and NSS microanalysis software (Thermo Fisher Scientific, USA). The surface area and textural characteristics of recycled graphite were determined using N₂ gas adsorption/desorption method (Microtrac BELsorp Mini II) carried out at -196 °C. The samples were degassed at 80 °C for 15 h to remove excess moisture.

2.2. Thermal characterization (Thermogravimetric-differential thermal analysis and single particle reactor)

Thermal analyses of the samples were conducted using a TA Instruments SDT Q600 simultaneous thermogravimetry differential thermal analysis (TG/DTA). The calorimeter was calibrated with the melting temperatures of high purity Zn, Al, and Au. The average measurement accuracies of temperatures were determined to be \pm 2 °C. Two calorimetric measurements were performed for the samples under the same experimental conditions. In all measurements, mass change and heat flow were measured simultaneously during continuous heating (10 °C/ min) to 800 °C. The measurements were performed in an inert atmosphere with 100 ml/min flow rate of N₂ gas (99.99 %) to avoid the decomposition of graphite. Al₂O₃ crucibles were used as sample holders and references. To measure the emitted gases (CO, CO₂, SO₂, and NO) and estimate the amount of time required to remove the organics from the samples at 300, 450, 600, and 800 °C, the sample was also thermally treated in a single particle reactor.

2.3. Leaching, pyrolysis and electrochemical testing

The flowchart experimental unit steps in the investigated process is presented in Fig. 1.

In two separate leaching tests aimed to obtain the leach residue with 100 % of metals dissolved the < 500 μ m fraction black mass concentrates (50 g) were added to pre-heated 500 ml of 2 M H₂SO₄ (stock VWR Chemicals, 95 %) and leached at 60 °C for 3 h. In the case of DBM, iron sulfate (Fe₂(SO₄)₃·nH₂O, VWR Chemicals, GPR Rectapur) was added to the lixiviant prior to leaching (Fe³⁺ = 2 g/L) to enhance the dissolution of metallic components and the active material, as iron serves as a mediator between Cu, Al current collectors and the active material (Chernyaev et al., 2021b). The 2 vol% (9.7 ml) of 50 % H₂O₂ (VWR Chemicals, GPR Rectapur) was added to the second hour of leaching to ascertain the complete dissolution of metals to obtain graphite-rich leach residue with minimum metal content.

After leaching, the leach residue was washed during the filtration with acidified water (pH 2) to remove all dissolved metal residues from the cake. To pyrolyze the dried leach residue, the material was placed in a silica crucible and inserted into the tube furnace (Nabertherm). The argon gas (99.999 %, Elme Messer) flow was initiated 5 min before the heating was started. Once 800 °C was reached, the sample was pyrolyzed for 1 h in Ar atmosphere. The sample was removed from the furnace after it cooled down to 60 °C.

The recovered and pyrolyzed anode material was subjected for electrochemical testing. Firstly, a slurry of 92 wt% active material, 2 wt % conductive carbon (Timcal Super C65), and 6 wt% PVDF (Solvay Solef



Fig. 1. Flowchart of the graphite recovery, pyrolysis and electrochemical testing.

5130) was obtained. N-methyl pyrrolidone (NMP, BASF Life Science) was used as a solvent with a solvent content in the slurries being 60 wt%. The slurry was mixed with a VMA-Getzmann GMBH-D-51580 Reichshof dispergator with a rotation speed of 500 rpm. Consequently, the electrode slurries were coated onto a copper foil with a loading of 1.5 mAh cm⁻². After overnight drying in a fume hood the coatings were heated in the oven at 80 °C for 4 h. After this, electrodes with 14 mm diameter were cut and then calendered using a pressure of 3000 kg cm⁻².

The electrodes were placed in an Ar-filled glovebox (Jacomex, with a level of O_2 and H_2O less than 0.3 ppm and 0.9 ppm, respectively) after drying in a vacuum overnight for further assembly of coin cells (CR 2016, Hohsen Corp.). 0.5 mm thick lithium metal foil (MSE Supplies) was used as a counter electrode. The electrolyte was 1 M LiPF₆ dissolved in a mixture (volume 1:1) of EC and DMC (battery grade, Sigma Aldrich). Glass fiber filters (GF/A grade, diam. 70 mm, thick. 0.26 mm, pore size 1.6 μ m, Whatman plc.) were used as a separator. The galvanostatic charge–discharge was conducted at room temperature on a LAND battery testing system CT2001A (Wuhan Land) at a constant current density of 0.03C – 5C mAh/g. The potential window was 0.01 – 1.2 V vs the lithium counter electrode. In the long-term measurements, the C-rate was 1C and the number of cycles was 100 at the potential window of 0.01–1 V vs. the lithium counter electrode. The measurement results were processed using the Origin 2021 software.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed in three-electrode cells ECC-Ref EL-Cell (EL-Cell GmbH). 18 mm diameter electrodes of the Cu foil covered by the active material composite made as described above were used as positive electrodes, 19 mm Li foil and 1 mm Li wire were used as negative and reference electrodes, respectively. EL-Cell GmbH separator and 1 M LiPF₆ in EC:DMC 1:1 electrolyte were also used for cell assembling in the Jacomex glovebox. Measurements were performed with a Biologic MPG-205 potentiostat (BioLogic). For CV measurements the potential range was 0.05–1.0 V vs. Li|Li⁺ and the scan rates were 20, 50, and 100 μ V s⁻¹. For EIS measurements, the frequency range of 10 mHz – 200 kHz and alternating potential amplitude of 10 mV were used. The measurements were done at the open circuit voltage (OCV) corresponding to the SOC of 50 %.

3. Results and discussion

3.1. Characterization of black masses

Both investigated black mass samples (ABM and DBM) were characterized in detail. The XRD analysis of black mass samples (Fig. 2) confirmed the presence of graphite, 3R (rhombohedral, ICDD PFD-4 04-007-2076) and 2H (hexagonal, ICDD PFD-4 04-014-0362) with their ratio being close to equal (Table S1). It indicates that both black mass concentrates mostly contain natural graphite, which is typically a combination of both 3R and 2H (3R usually being < 40 %), whereas synthetic graphite contains predominantly 2H type (Natarajan et al., 2022). ABM sample contained LMO (LiMn₂O₄, ICDD PFD-4 04-014-3549) and LCO (ICSD 98-016-0714) in addition to NMC 111 (ICSD 98-017-1750), confirming the varying origin of LIBs. Additionally, ABM contained a significant amount of SiO₂ (ICSD 98-010-0341), possibly silicon dioxide, as was found by Babanejad et al., 2022 in their work. Silicon dioxide could also originate from the graphite beneficiation processes as natural graphite is associated with quartz, feldspar, mica, and carbonate gangue in nature (Chehreh Chelgani et al., 2016; Jara et al., 2019), whereas Si can be also added in graphite anode (5–10 wt%) to increase anode capacity. In DBM, XRD analysis show the presence of graphite, NMC 111 and AlO(OH) (ICDD PFD-4 04-010-5683), which could originate from the ceramic-coated separator, as the ceramic layer can improve the mechanical properties, wettability, and thermal stability (Kefan et al., 2022; Xiao et al., 2022). Cu (ICDD PFD-4 04-003-2953) is found to be present in both samples which is expected as Cu foils serve as current collectors for graphite electrodes.

The initial elemental mapping results (Fig. S1 and Fig. S2) show the presence of Cu and Al foils in both ABM and DBM. ABM has graphite particles bound together into flakes (Fig. 3) separated from the current collectors after the pre-treatment processes. LCO exists separately from LMO and NMC according to Fig. S1. On the other hand, DBM consists only of NMC, widespread boehmite (AlO(OH)), and free graphite particles.

The bulk metal content in black mass is presented in Table 1. The EV battery (DBM) cathode active material is identified as NMC 111 as the atomic ratios of Ni, Mn, and Co is close to 1:1:1. Additionally, the amount of Al in DBM is significantly higher due to boehmite. An important feature of DBM is the absence of iron. ABM, on the other hand, has NMC, LMO, and LCO cathode mixture.

Also, the impurities were analyzed by ICP-OES in the black mass



Fig. 2. XRD diffractograms of investigated ABM and DBM battery black mass waste concentrates.

concentrates (Table 2). Additives like chloride and phosphorus likely originate from the electrolyte, and the fluoride comes from the binder (PVDF) and electrolytes. This could indicate that the ABM initial batteries contained the LIBs with a chloride-based electrolyte (e.g. LiClO₄). Additionally, the Si content in ABM is once again confirmed.

The elemental mapping and the quantification of phases suggest that the ABM black mass contains larger variation of different additives compared to DBM (Table S2).

3.2. Leach residue characterization and pyrolysis

After leaching (more details in Supplementary material) the graphite remained in big agglomerates in the leach residue (Fig. 3). In ABM graphite is bound together in agglomerates, which have been separated from a current collector during mechanical pre-treatment, with remaining binder (Fig. 3A and Fig. S4). ABM leach residue contained little Co and Fe (Fig. S3A and Fig. S4). Additionally, the SiO₂ particles and magnetic iron-rich alloys are shown to be undissolved in ABM (Fig. S5). On the other hand, DBM is more homogeneous with free graphite particles, having fewer and smaller graphite agglomerates (Fig. S6), thus ABM could be subjected to grinding to break down the agglomerates. DBM contained a minor amount of silica fibers (possibly fiberglass) and has no iron, but it contains a significant amount of undissolved rhombic-shaped boehmite (AlO(OH)) particles. Ma et al., 2019 discovered the spread out Al₂O₃ particles after leaching the anode material in 5 M H₂SO₄ with 35 vol% H₂O₂ and assumed that they originated from a separator. The leach residue of DBM is shown to be free of valuable metals according to EDS and XRD analyses (Fig. S6 and Fig. 5B). Also, fluoride in both leach residues is evident due to the presence of the undissolved binder (PVDF) (Fig. S4 and Fig. S6).

The thermogravimetric analysis was carried out with leached residues to determine an optimal temperature for the following heat treatment, aimed to remove PVDF and other volatile compounds. The weight change, due to the loss of organic components, was recorded throughout the selected temperature range, while the graphite was expected to remain unreacted, due to its stability in an inert atmosphere and the lack of the active material in the leach residue for graphite to react with. In the black mass concentrates (Fig. 4, solid green line), the absorbed water, as well as the organic electrolytes (including LiPF₆), were removed at temperatures below 200 °C, indicated by the weight loss. LiPF₆, even without heating, can react with water and produce HF gas (Liu et al., 2019; Or et al., 2020; Teichert et al., 2020), according to Eq. (1).

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF\uparrow$$
(1)

At elevated temperatures over 60 °C LiPF₆ will decompose even further into HF and CO (Diekmann et al., 2018, 2017) with a complete decomposition between 200 and 250 °C (Ravdel et al., 2003). The organic electrolyte in LIBs is flammable and in the case of overheating, the gases may ignite immediately. In addition to HF, POF₃, and PF₅, LIBs release toxic gases, such as CO and CO₂ during burning (Larsson et al., 2017; Lombardo et al., 2021; Zhang et al., 2018).

The weight loss between 200 °C and 700 °C can indicate the melting and decomposition of PVDF as well as the simultaneous partial reduction reaction between the active material and carbon (Babanejad et al., 2022; Lombardo et al., 2021), resulting in the increased weight loss compared to the leach residue, which is free of the cathode metal oxides. The exothermic peaks (490 °C for ABM and 600–690 °C for DBM, solid blue line) were attributed to the transformation of the active material metals to their lower oxidation state (e.g. LiCoO₂ to CoO and Li₂CO₃) (Babanejad et al., 2022; Kwon and Sohn, 2020). A similar effect was observed by Kwon and Sohn, 2020.

In the case of leach residues (dashed line), free of the metal oxides, organic solvents and $LiPF_6$, the mass loss is lower compared to the original black mass. The initial stage of mass loss (100–300 °C) is not as sharp as in the original black mass and can be attributed to the removal



Fig. 3. Secondary electron micrographs of leached black mass concentrates (A) ABM and (B) DBM before pyrolysis.

Table 1

Average concentration (wt.%) of major metals in black mass samples determined
by AAS.

Element	Ni	Mn	Со	Li	Cu	Al	Fe
ABM	11.00	9.32	6.14	3.02	1.78	1.27	1.42
DBM	10.80	9.92	10.89	3.19	4.18	20.28	0.01

of moisture and residual electrolyte from the sample. The second stage of mass loss (300–525 °C) is caused by the PVDF decomposition as pyrolysis can effectively remove the organics at 500 °C (Zhang et al., 2018). The mass loss in ABM is higher compared to DBM, which could be due to the larger particle size (graphite agglomerates, Fig. 3A),

remaining residual LiCoO₂, and PVDF content, indicated by higher fluoride concertation (Table 2). In the third stage (525–800 °C), the mass loss in ABM residue is slightly more pronounced than in DBM. In this stage, the residual PVDF and oxygen groups are removed from the sample surface. Both black mass samples exhibited the emissions of CO and CO₂ (Fig. S10) during pyrolysis in single particle reactor as a result of the reduction of the active material by carbon with the emission of CO₂ (Lombardo et al., 2021; Perumal et al., 2021) as well as the evaporation of the electrolyte and decomposition of binder (Doose et al., 2021; dos Santos et al., 2019). Additionally, DBM exhibited the release of SO₂, indicating the presence of sulfur in possible electrolyte additives (Ma et al., 2015; Wang et al., 2014) or the active material as it could have been prepared from a sulfate-based precursor (Savina et al., 2020;

Table 2

Element	Ca	Na	Pb	Si	Zn	S	Р	F	Cl	PO43-
ABM	0.11	0.05	0.01	0.27	0.02	0.10	0.59	2.16	3.57	0.69
DBM	0.02	0.04	0.01	0	0	0.57	0.36	0.83	0	0.33



Fig. 4. Differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) curves for (A) ABM and (B) DBM black mass (solid line) and leach residue (dashed line), respectively.



Fig. 5. XRD diffractogram of (A) ABM leach residue and (B) DBM leach residue before and after pyrolysis.

Wijareni et al., 2022). Based on TGA results, it is concluded that 800 $^{\circ}$ C is sufficient for the pyrolysis with the aim to save energy.

Based on XRD analysis, the graphite peak at 26.5 (20 degrees) in leach residue before and after pyrolysis is significant (Fig. 5) in both the black mass leach residues and corresponds to the characteristic graphite peak with the hexagonal space group (P63/mmc). Structural parameters obtained from the XRD patterns analysis are presented on Table S3. The interlayer distance (d₀₀₂) for the ABM and DBM leach residuals after pyrolysis are 3.364 Å and 3.363 Å, respectively. Thus, both samples have disordered graphite structures that are additionally confirmed by the calculation of the degree of graphitization (88 % for ABM and 90 % for DBM) (Vlahov, 2021). The crystallite sizes La and Lc for the ABM sample are higher than for the DBM sample which highlights the different nature of these two leach residues. The presence of delithiated LCO and SiO₂ is evident in the ABM leach residue, whereas the spectrum of DBM residue indicates a significant amount of AlO(OH), suggesting it could not be dissolved in leaching. Boehmite is not present in the diffractogram of the pyrolyzed samples (Fig. 5B) as its crystallinity may have been partially altered. Boehmite is known to change its structure to Al₂O₃ with H₂O release at temperatures above 500 °C (Laachachi et al., 2009; Tsukada et al., 1999). According to Fig. S11, sharp edges in some boehmite particles are slightly smoothened by the pyrolysis. LCO in the ABM leached sample is not present in the XRD diffractogram anymore after pyrolysis (Fig. 5A), which could be explained by a partial reduction of LCO to Co_3O_4 by graphite.

The organic impurities or metals in leach residue could cause undesired reactions in the LIB during the cycling, therefore the pyrolysis was carried out to purify the graphite in leach residue for its reuse in new LIBs. In this work, trial pyrolysis tests carried out, at 600 °C and 700 °C demonstrated that these temperature settings were not sufficient to remove all the fluoride, i.e. decompose the PVDF completely. Similarly, Salces et al., 2022 and Vanderbruggen et al., 2022 observed that the pyrolysis carried out at 500 °C for 1 h in an inert atmosphere was not sufficient to remove all binder contrary to the literature (Yang et al., 2016; Zhan et al., 2021; Zhang et al., 2018). Additionally, Doose et al., 2021 mentioned in their work that PVDF could decompose at temperatures above 650 °C. Therefore, 800 °C was selected for the pyrolysis process aimed at the complete removal of PVDF, solid electrolyte interface (SEI) layer, and the oxygen groups from the graphite surface. The mass loss in pyrolysis for the leached ABM and DBM is 16 % and 9 %, respectively. The graphite agglomerates get partially broken down into individual particles in both black mass residues. According to microscope images, graphite particles remain intact after pyrolysis in both ABM and DBM (Fig. 6). During the slurry preparation, the ABM particles appeared larger than those in the DBM sample.

The EDS map (Figs. 7 and 8) confirms the removal of fluoride from



Fig. 6. Secondary electron micrograph of graphite particles after pyrolysis (800 °C, 1 h, Ar atmosphere) of (A) ABM and (B) DBM leach residue.

graphite rich fraction. The EDS mapping of pyrolyzed ABM (Fig. 7) indicated the presence of undissolved cobalt along with SiO₂. Additionally, the agglomerates of graphite in the fraction are found to be largely intact even after pyrolysis (Fig. S9A).

EDS map (Fig. 8) once again confirms more homogeneous nature of the DBM sample (ratio of agglomerates to free graphite particles) as it is produced from a single EV battery unlike ABM. The presence of Al particles spread out across the sample is evident in DBM after pyrolysis. The SEM-EDS DBM (Fig. 6B, Fig. 8 and Fig. S11) reveals aluminum oxide, likely aforementioned boehmite. With its size of $\leq 1 \mu m$ or smaller, it could potentially interfere with graphite cycling in LIB cells. It is expected that any minor remaining amorphous carbon black will remain in the residues along with graphite.

In Raman spectroscopy study of the residues, the positions, height, and width of graphite D and G peaks are at 1346 and 1576 cm⁻¹, respectively (Fig. 9). D' band in this case appears as a shoulder rather than a peak on the right side of the G band in all samples, meaning that the level of defects is low (Al-Ani et al., 2020; Kar and Maiti, 2021). The I_D/I_G ratios of graphites in the leach residues (0.4 for ABM and 0.25 for DBM) indicate a relatively low degree of defects and is in agreement with earlier literature (Xing et al., 2018; Yang et al., 2021). This suggests the presence of high-crystallinity graphite which may be beneficial for the lithium intercalation due to an increased amount of active sites in graphite. Based on Raman spectra, the difference between the samples is negligible.

After pyrolysis, the I_D/I_G ratio of ABM decreased to 0.3 because of the removal of organic impurities in the graphite fraction, whereas no clear change is observed for the DBM possibly due to lower content of various additives initially. Besides, the difference of the I_D/I_G ratios after pyrolysis remain within the variance error, therefore it is concluded that pyrolysis does not degrade nor improve the graphite quality. Besides, it is expected that both leach residue samples contain a minor amount of carbon black, which could not be identified with the methods used in this work. Carbon black may contribute to the increased D peak.

The N_2 adsorption/desorption isotherm (Fig. S12A) for both leach residues corresponds to the type IV or V isotherm (mesoporous

materials) according to IUPAC classification (ALOthman, 2012). The surface area of the leach residues corresponds to the typical surface area of battery-grade graphite, which is $2-6 \text{ m}^2 \text{ g}^{-1}$ (Gong et al., 2020; Liivand et al., 2021; Ng et al., 2009). The surface area of pyrolyzed graphite is higher than in battery grade graphite due to the expansion of graphite lattices by Li⁺ during its use in battery applications as well as leaching in acid resulting in possible defects on carbon framework. Also, higher surface area of the pyrolyzed graphite (26.24 and 18.98 $m^2 g^{-1}$ for ABM and DBM, respectively) compared to non-pyrolyzed (4.43 and 8.08 m² g⁻¹ for ABM and DBM, respectively, Fig. S12) can also indicate the successful removal of organic components and oxygen groups from the surface of the graphite. The results are in line with (Ma et al., 2019), who reported an increase in surface area from 6.4 m² g⁻¹ of unpurified graphite to 15.1 m² g⁻¹ after purification. For instance, the amount of pores at 0-2, 4, and 10-12 nm width (Fig. S12B) has significantly increased after pyrolysis, which can have a positive effect on lithium intercalation.

3.3. Electrochemical testing

The electrochemical performance of the recycled graphite materials was investigated in the half-cells vs. metal Li. The potential window of 0.01 - 1.0 V for the long cycling and CV measurements and 0.01 - 1.5 V for the rate capability measurements were chosen to correspond the range achieved in real full-cell operation. Based on the rate capability (Fig. S13), both samples have high initial capacities of 395 mAh/g and 476 mAh/g for DBM and ABM, respectively. These values are above the theoretical specific capacity of graphite (372 mAh/g) (Zhang et al., 2021) due to either the formation of SEI during the first cycle, or remains of materials with a higher capacity in the recycled graphite. The specific capacity for both samples slightly increases at 0.1C and 0.2C due to the electrode-electrolyte activation (Zhang et al., 2022). For DBM, the specific capacity stabilizes at 0.5-2C and decreases at 5C and then increases at the last three cycles at 0.1C. Contrary, for the ABM regenerated graphite based electrode, the specific capacity decreases from 0.5C to 5C and then increases at the last three cycles at 0.1C. The average



Fig. 7. Backscattered electron micrograph and EDS map of the ABM pyrolyzed leach residue with wt.% of elements (800 °C, 1 h, Ar atmosphere).



Fig. 8. Backscattered electron micrograph and EDS map of the DBM pyrolyzed leach residue with wt.% of elements (800 °C, 1 h, Ar atmosphere).



Fig. 9. Raman spectra of (A) ABM leach residue and (B) DBM leach residue before and after pyrolysis.

specific capacitance at 0.1C is higher for DBM (350 mAh/g) than for ABM (250 mAh/g). It might be because of elements that are still presented in the graphite structure. The residues that are still presented in the graphite structure can affect the electrochemical processes and thus, the achieved capacities. Moreover, differences observed in the graphite structure can plausibly affect the lithium intercalation and hosting, as the DBM sample has a higher degree of graphitization and lower degree of defects according to XRD and Raman spectra analysis. Also, the presence of large particles in the ABM sample affects the uniformity of the electrochemical performance.

The specific capacities at the beginning of cycling at 1C (Fig. 10A) are somewhat low for both sample (161 mAh/g (ABM) and 228 mAh/g (DBM)) because reducing the potential widow from 0.01 to 1.5 V vs. Li|Li⁺ for rate capability measurements to 0.01 - 1.0 V vs. Li|Li⁺ for the long cycling measurements. The capacity retention after 100 cycles is in

the acceptable range for both recycled samples (ABM 70 % and DBM 80 %) indicating a rather slow degradation. Similar average specific capacity values for regenerated graphite, sourced from manually opened batteries, has been reported previously also by others, as 352 mAh/g (Yu et al., 2021b), 350 mAh/g (Li et al., 2022), and 250 mAh/g (Kayakool et al., 2021), with capacity retention ranging from 73 % to 97 %.

The EIS investigation before and after 100 cycles were conducted and the Nyquist plots with the equivalent circuit (Gholami et al., 2020.) for the ABM and DBM pyrolyzed residues are presented on Fig. 10B. The explanation of the equivalent circuit and the fitting EIS results (Table S4) are given in Supplementary materials. The SEI resistance R_{SEI} for ABM sample is significantly increased after 100 cycles from 3.5 to 4.2 Ω indicating an increase of thickness of SEI layer during the cycling. While for the DBM sample, this value is low and stable (2.8 Ω) before and after cycling, showing a good stability of the SEI layer. Moreover,



Fig. 10. The long-term cycling for the recycled graphite materials measured at 1C-rate at the potential window 0.01–1.0 V vs. the lithium counter electrode (A), the EIS for the ABM and DBM pyrolyzed residue samples before and after cycling (B), insert: the equivalent circuit. Experimental data is presented as dots and fitted data based on equivalent circuit as lines.

the DBM sample has higher Q_{SEI} -P values before (0.917) and after (0.946) cycling, which corresponds to a more uniform and homogeneous SEI layer kept even after 100 cycles. The charge-transfer resistance of the electrode/electrolyte interface is lower for the DBM (4.7 Ω) than the ABM (5.2 Ω) sample before cycling. After 100 cycles, for the ABM sample, the R_{ct} value dramatically decreased to 7.4 Ω indicating that the DBM sample has less degradation and better kinetic than the ABM

sample. The EIS results support the explanation of the difference in the specific capacities and the cycle performance between samples.

On the CV curves for both samples at the 20 μ V s⁻¹ on the first cycle (Fig. 11B and C), there is peak 1 at 0.8 V vs. Li|Li⁺ that corresponds to the SEI formation. As this peak is irreversible, indicating that the SEI formation mainly occurs during the 1st cycle. Also, on the CV curves, there are 3 more reversible peaks that correspond to the different stages



Fig. 11. The CV curves for the (A) ABM and (B) DBM pyrolyzed residue samples for the first three cycles at the scan rate of 20 μ V s⁻¹, dQ dV⁻¹ curves of the (C) ABM and (D) DBM pyrolyzed residue samples at different C-rates, insert: the magnifying charge curves.

of Li⁺ ions insertion into the graphite structure (Li et al., 2019). The peak 2 at 0.19 V vs Li|Li⁺ corresponds to the stages of intercalation LiC₂₄ which is the IV stage with four graphene layers between layers with intercalated Li ions (Xu et al., 2017a). Then peak 3 at 0.08 V vs Li|Li⁺ (ABM) and at 0.09 V vs Li|Li⁺ (DBM) is the formation phases of LiC₁₈ and LiC_{12} , respectively, which is correlated to the stage III with three and stage II with two graphene layers between Li ions layers (Li et al., 2019; Xu et al., 2017b). The peak 3 at 0.04 V vs. Li|Li⁺ is attributed to stage LiC₆ (stage I), with the highest achievable lithium content in graphite (Xu et al., 2017a). On the anodic sweep, these three peaks are observed between 0.07 and 0.3 V vs. $\mathrm{Li}|\mathrm{Li}^+$ and are related to the deintercalation processes. The CV curves at different scan rates (Fig. S14 A and B) show that the intercalation/deintercalation processes stay reversible. Also, the peak currents increase with increasing the scan rate. For the DBM sample, the peaks are sharper indicating the fast kinetic of the intercalation processes so that the DBM sample has a more uniform crystal structure with a well-layered structure. While for ABM, peaks are not clearly pronounced, and the phase changes are not so visible, so the ABM sample has some structural issues that block the pathway for Li⁺ ions intercalation, such as graphite bound together in layers.

For the detailed analysis, the charge–discharge profiles at different C-rates (Fig. S15) are differentiated and the obtained curves are presented on Fig. 11C and D. The peak 1 corresponding to the SEI formation is present only at 0.03C rate as shown in the CV analysis. Also, the dQ dV^{-1} plots three more peaks correspond to the intercalation of Li ions into the graphite structure and correlate with the peak analysis of the CV curves. Moreover, at 0.2C-rate for the ABM sample peaks 4 and 3 are not separated. For both samples, at the C rates higher than 0.5C only one wide peak is presented on the charge curves. For the ABM sample peaks shift towards the high potential region with the increasing C-rate suggesting low kinetic. All this confirms that the ABM sample has more disordering structure than the DBM sample as shown also in CV analysis.

In conclusion, the cycling performance shows high stability during 100 cycles for both recycled graphite materials (70 % for ABM and 80 %for DBM). In terms of average specific capacities, the ABM sample has lower values (250 mAh/g at 0.1C) than the DBM sample (350 mAh/g at 0.1C). Based on the characterization, the former has a low degree of graphitization and more disorder structure. Additionally, the ABM sample has a wider particle distribution and particularly some larger particles lead to non-uniform electrodes. The EIS analysis indicates that this sample has less stable and non-uniform SEI than the DMB sample, which also affects the electrochemical performance and capacity retention. The less pronounced peaks on the CV curves and peak shifting with increasing C-rates on the dQ dV⁻¹ plots indicate slower intercalation/deintercalation kinetics and structural disordering. Summarizing, these factors contribute to the observed lower specific capacity of the ABM sample. On the other hand, the DBM sample has a higher degree of graphitization and less defects based on the XRD and Raman analysis. The EIS also shows that the DBM sample has a uniform and stable SEI layer and ages less during the cycling. Additionally, the CV and dQ $\mathrm{d}\mathrm{V}^{-1}$ curves confirm that the DBM sample has fast intercalation/deintercalation kinetics and a more organized graphite structure. Overall, based on the electrochemical performance, these recycled graphite materials are promising for further use in LIBs.

4. Conclusions

In this study, for the first time, two industrially produced Li-ion battery black mass concentrates of different origin (power tools/mobile devices vs. EV batteries) and their leach residues were thoroughly characterized and compared as a part of the same scientific work aimed at recycling and reusing graphite. The origin and homogeneity of black mass concentrates is found to significantly affect the electrochemical performance of recovered graphite.

The black mass samples were leached (H_2SO_4 = 2 M, 60 $^\circ C,$ t = 3 h, Fe^{3+} = 2 g/L), pyrolyzed (800 $^\circ C,$ 1 h, Ar atmosphere) and the

performance of pyrolyzed residues in an electrochemical cell as anode was compared. The novelty of this process lies at the core of leaching industrially produced black mass concentrates followed by 1 h long pyrolysis and omitting the additional intensive chemical purification steps of graphite to save energy, characterizing the residues and recognizing the remaining impurities in the residues: SiO₂, Fe-Ni alloy and minor undissolved cobalt oxide in the power tools/mobile devices based black, with a significant amount of refractory boehmite (AlO (OH)) impurities found in the EV black mass residues. Additionally, it was found that the black mass pre-treatment steps carried out by battery recycling operators leave the graphite agglomerates present in the black mass, which were not broken-down during leaching nor in pyrolysis, which may lock up useful graphite surface and decrease the electrochemical performance of graphite in anode, thus more mechanical processing may be required. In the case of EV battery black mass, the residue's electrochemical performance was superior to that of black mass originated from mobile phones and power tools. Despite the nonhomogeneity and impurities in the graphite that remained after leaching and pyrolysis, this study demonstrates that the graphite quality in the residue is sufficient for use as an anode in new Li-ion cells. This finding suggests a promising avenue for further graphite valorization from battery waste leach residue.

CRediT authorship contribution statement

Alexander Chernyaev: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. Anna Kobets: Conceptualization, Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – review & editing. Kerli Liivand: Conceptualization, Methodology, Supervision, Writing – review & editing. Fiseha Tesfaye: Methodology, Validation, Writing – review & editing. Pyry-Mikko Hannula: Methodology, Writing – review & editing, Tanja Kallio: Funding acquisition, Supervision, Writing – review & editing. Leena Hupa: Project administration, Funding acquisition, Writing – review & editing. Mari Lundström: Project administration, Resources, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2024.108587.

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