New efficient Recycling Process for Li-ion Batteries

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***Abstract*—Lithium-ion batteries represent a key technology for the energy transition and electro mobility. Due to the growing battery market the amount of end-of-life batteries increases and thus a valuable source of raw materials. With a new functional and material specific recycling process, the battery materials shall be recovered, reconditioned and reused most efficient. At present energy-intensive metallurgical methods are used to recycle end-of-life batteries and production waste from battery manufacturing or automotive. With these methods only specific elements can be recovered. The added value depends on the market prices of the raw elements copper, aluminum, nickel or cobalt. The aspired recovery of the primal battery materials like Li-, Ni- and Co-containing chemical compounds and high-grade carbons for remanufacturing new cells, is more valuable instead of resynthesizing with high effort. The presented process of electrohydraulic fragmentation is energy- and resource-efficient and suitable for production residues as well as waste products.**

Keywords— Li-ion batteries; electrohydraulic fragmentation; funtional recycling; raw materials

I. INTRODUCTION

Mankind consumes as many raw materials as never before in history. Therefore it is urgently necessary to rethink raw material politics. Due to electric mobility and the growing market of electric cars and e-bikes, the demand for efficient battery systems for the automotive branch is increasing. In relation lithium-ion batteries have the highest potential and hold the largest market share at HV-battery cell sector with a steady growth. In 2012 the market volume was about 11 billion USD [2]. The return of waste lithium-ion batteries will be correspondingly high and the demand for efficient recycling technologies for the automobile industry will grow. The battery manufacturers need raw materials, especially ceramics made of Li, Ni, Co, Mn, Fe or Ti, carbons like graphite or conductive carbon black as well as metals and alloys of Cu, Al, Ni, Co, Mn and rare earths, which are classified as critical regarding to their supply reliability [3]. This is important for Germany, relating to its import economy. For a sustainable development the exploitation of additional raw material sources, the secondary raw materials, is needed. The classic metallurgical reconditioning processes for waste batteries and manufacturing residues particularly recover metals. But these processes are connected to a high effort of energy and process agents. Above all, only certain elements can be recovered with these methods. At present, expensive produced high-grade materials like carbon- and ceramic materials cannot be recovered. These

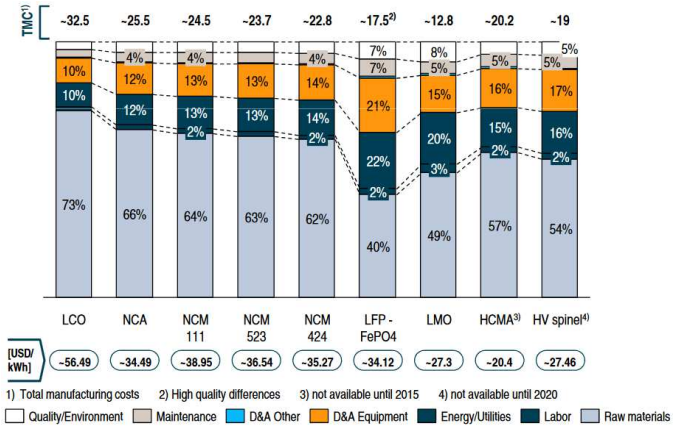

Fig. 1. Manufacturing cost calculation of main battery materials. Electrode material costs are largely driven by expensive raw materials like cobalt[1].

materials have to be produced elaborately out of the recovered basic materials. Related to that circumstance the added value depends on the market price of the containing elements like Ni, Co or Mn [4]. The recycling of battery types which contain only a small amount of these expensive elements (e.g. $LiFePO_4$ batteries) is not economically viable, because the metal value of the basic materials represents only a small part in the added value. With a view on the whole manufacturing costs of battery materials, which contain energy costs and material costs, the low material costs of $LiFePO_4$ (LFP) are compensated by high energy costs compared to $LiCoO_2$ (LCO) or Li(Ni, Co, Mn)O_2 (NCM). A recycling process that regains directly LFP, instead of recovering Li, Fe, and P, would entail eminent economic and ecological benefits (fig. 1).

Currently waste batteries are treated with pyrometallurgical and hydrometallurgical processes [5]. Disadvantages are on the one hand the energetic and chemical effort as well as the exhaust gas and chemical impact and on the other hand the fact that the wanted metals have to be extracted, whereby the metals become source materials at the end of the process. A new approach is the electrohydraulic fragmentation, which was so far only applied in mining industry. This process provides the possibility of a fractionized mechanical disintegration and is used for the first time for battery recycling. Shockwaves, which are transmitted in a fluid (commonly water) cause short but intensive impacts. Weak links are tackled by these shocks. The separation happens at macroscopic connections like bondings,

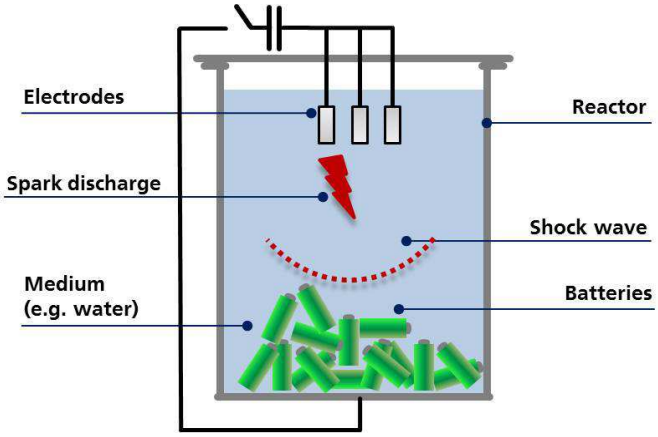

Fig. 2. Schematic operating principle of electrohydraulic fragmentation.

Fig. 3. Pilot plant at Fraunhofer IWKS location in Alzenau, Germany.

boltings and clampings or at microscopic interfaces like grain and phase boundaries. The technique can be used especially for hybrid materials to disintegrate them precisely at their material boundaries in order to separate different components. After the fragmentation of the different battery components (cathode, anode, electrolyte, separator, cell case and battery housing) the fractions can be collected material-specifically with efficient separation treatments. To receive purest materials, separation techniques are applied that use physical properties like different grain sizes or densities as well as chemical properties. Compared to conventional recycling processes the electrohydraulic fragmentation does not need high temperatures or critical chemicals and is further very energy efficient. Moreover singular components can be recycled functionally. On that electrode materials can be recycled and used for new products after a further treatment step [6].

II. Functional Principle Electrohydraulic Fragmentation

The centerpiece of the recycling process is the electro-hydraulic fragmentation treatment that uses a well-tried shockwave technology (fig. 2, fig. 3). This technique was already used successfully to disjoint electronic scrap. In that treatment, the material that should be processed is brought into a liquid medium. Shockwaves are generated by electric discharges between three electrodes and propagate in the medium. The shockwaves are impinging very homogeneously upon the material. With that technique it is possible to separate the basic materials contact-free at their boundaries. It allows an easy and gentle ripping of particles from electrode foil. The innovative fragmentation treatment developed by ImpulsTec GmbH uses mechanical shock waves, which are generated in a liquid medium, to disjoint a material. The shockwaves are caused by the electrohydraulic effect that occurs by igniting an electric arc in a liquid between two electrodes. Two capacitors are charged up to an operating voltage of up to 50 kV and then switched on the electrode system of the treatment reactor using a spark gap. Thereupon an avalanche generates a rapidly expanding plasma channel, what causes radially expatiating shockwaves. At the point of origin pressures of several thousand atmospheres occur, and decrease with the expansion of the shock front and the time. The electrohydraulic fragmentation treatment crushes the shredding material only with a shockwave. There is no direct contact between the material and other parts except for the reactor case. In contrast to ordinary milling treatments, the energy input location is not concentrated in one point, but a homogeneous energy input over the whole component surface [7]. Cracks and breaks occur at the weakest points of a composite. Furthermore there is a selectivity of the energy input relating to acoustic material properties. The shock wave acts similar to an acoustic wave inside the reactor and the shredding material. At boundary surfaces of materials with different acoustic impedances, increases of pressure occur by transmission and reflexion, which intensify breakage. Dependent on the algebraic sign of the impedance difference a phase inversion of the reflected wave sets in. This causes tensile stress at the material boundaries and initiates breakage at these interfaces. The third selectivity of shock wave generation takes effect on electro conductive components. In case of partially electro conductive materials the electric arc will be deflected through the conductive components. This effects an additional selectivity of the energy input on conductive areas of the shredding material. Related to its high material selectivity this technique is predestined for the use on complex composite materials. With ImpulsTec GmbH's universal shock wave fragmentation system "EHF 400" throughputs between 50-175 kg/h and processing costs between 0.15-0.75 €/kg can be realized [8].

III. Experimental

An experimental facility for electrohydraulic fragmentation of electronic scrap, type EHF-400 (ImpulsTec GmbH) is operated by the project group IWKS of Fraunhofer institute for silicate research ISC at their site in Alzenau. This shock wave fragmentation system was developed specially to recycle complex, hard breaking composites. The system complies with the EU machinery directive 2006/42/EC regarding safety- and health protection requirements. For experiments two reactor containers can be used with a volume of approx. 30 l or 40 l, respectively. Material volumes between 0.5 and 10 l and between 2 and 10 l can be processed per batch. The energy for the fragmentation is coupled into the reactor with three

Fig. 4. Processing of batteries including manual dismantling, elctrohydraulic fragmentation. segregation with sieving methods and purification.

electrodes arranged in a triangle above the material. Additionally a controller can regulate the distance automatically during the process. The Voltage can be adjusted from 25 kV to 40 kV for an under water discharge. In connection with the used capacitors an energy of 219 J (0.06 Wh) at 25 kV or 560 J (0.16 Wh) at 40 kV can be achieved theoretically per electrode. With every shredding batch an impulse frequency between 1 and 4 Hz can be set, which results in a relative energy consumption of 1.78 kWh/kg.

In the implemented test series battery cells of the type 18650 were investigated primarily. These cells were provided mainly by GRS from collections of waste pedelec battery packs [9]. The tests were run with the whole battery pack inclusive case and electronics, as well as with separated cells. The individual cells were removed from the package by hand (see fig. 4 top left). Battery cells with different states of charge (SOC) from deep discharged (SOC = 0%) to fully charged (SOC = 100%) were investigated. The states of charge were adjusted at Fraunhofer ISC under defined conditions. No differences in results or performance between discharged and charged batteries could be noticed after the first test series. Further tests were implemented with undefined states of charge. Current test runs showed that the results are getting better, if the process medium contains amounts of dispersed battery material. The aimed level of fragmentation of battery cells was achieved easier by usage of additives in the medium. The pictures in fig. 4 show the result of a test with ten single batteries type 18650. The cells were treated with ca. 1100 pulses and then valuated visually. The battery cells were fully opened after the treatment. The dispersed black mass inside the reactor was composed of active material and conductive carbon black. The mass could be separated by wet sieving. A light plastic fraction from covering and separator parts floated on the surface of the process medium. These parts could be separated mechanically the easiest way (fig. 4 top right). Metal fractions from shells and conductive materials remained on the reactor's ground or at a raw sieve (fig. 4 bottom left). After the fragmentation process the lithium-ion cells were torn into their components and could be categorized into a fine fraction and a coarse fraction. The coarse fraction especially included metal shells, separator foils and collector foils. The fine fraction mainly contained electrode materials like NCM (cathode) and graphite (anode) as well as conductive carbon black. This fraction was finely dispersed into the process medium and could be separated from the water by centrifugation or sedimentation (fig 4 bottom right). Related to the relative high amount of process medium of 27 l per batch it was more suitable to use the sedimentation process with decanting the water. The process medium rested for several days in a 60 l plastic barrel until all particles sunk down to the ground. The

Fig. 5. Wet separation table (left). Exhibits of coarse fraction (mid), battery housings (right) after fragmentation and separation.

TABLE I. ICP-OES analyses of black mass samples out of end-of-life-batteries type 18650 and production waste.

	End-of-life batteries	**Production waste**			
	NCM/Graphite black mass (ca. 1100 pulses)	***NMC black mass (50 pulses)***	***NMC black mass (500 pulses)***	***Graphite black mass (50 pulses)***	***Graphite black mass (500 pulses)***
Element	mass-%	mass-%	mass-%	mass-%	mass-%
Ni	25.27	18.57	17.08	< 50 ppm	0.03
Co	5.14	18.45	16.77	< 50 ppm	< 50 ppm
Mn	4.80	16.70	14.95	< 50 ppm	< 50 ppm
Li	0.81	6.45	5.74	< 50 ppm	< 50 ppm
Al	5.94	4.14	5.51	< 50 ppm	< 50 ppm
Cu	2.77	0.09	0.16	0.37	5.45

water was carefully pumped out with a submersible pump. The remaining wet sediment was transferred into a 2 l beaker to be sedimented again. Afterwards the surplus water was drained and the sludgy fine fraction was dried completely in a compartment drier at 80 °C. The coarse fraction, including most metal parts and small amounts of plastics residues, could be separated from the fine fraction by sieving. This happened in two steps. At first the content of the reactor was poured through a 1 mm mesh sieve right after the electrohydraulic treatment. A large part of the raw fraction could be collected that way. The second step was to sieve the dried material fraction in a sieving tower with different mesh sizes of 48, 63, 125, 250 and 500 µm. The fine fraction could be taken in different particle sizes. The coarse fraction, received during the electrohydraulic fragmentation treatment was processes on a wet separation table (fig. 5 left) to separate metals from plastics. The metal-plastic fraction (fig. 5 mid) was placed on the table. Nozzles sprayed a thin water film upon the table and the separation trough began to vibrate. The heavy metal parts stayed on the table's surface. The vibrations conveyed the metals to the upper metal outlet. The light plastic parts floated upon the water surface and flowed downward to the water and plastic outlet. The plastic containing water flowed through a sieve into a tank to be pumped up to the nozzles again. The sieved plastics were transported off the sieve by vibrations as well. The housing of the battery cells that is largely free from plastics (fig. 5 right) could be recovered plainest. The output is nearly similar to conventional metal recycling outputs and it can be fed to common metal recycling.

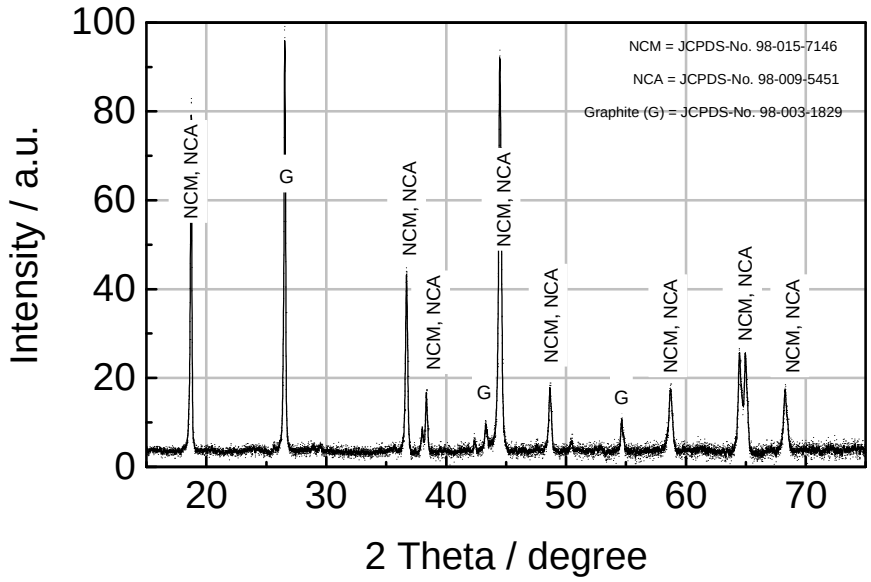

Fig. 6. XRD phase analysis of black mass from batteries type 18650 with highlighted NCM/NCA peaks (Measurement and edit by Fraunhofer ISC). Phase composition proves structural intactness of active material.

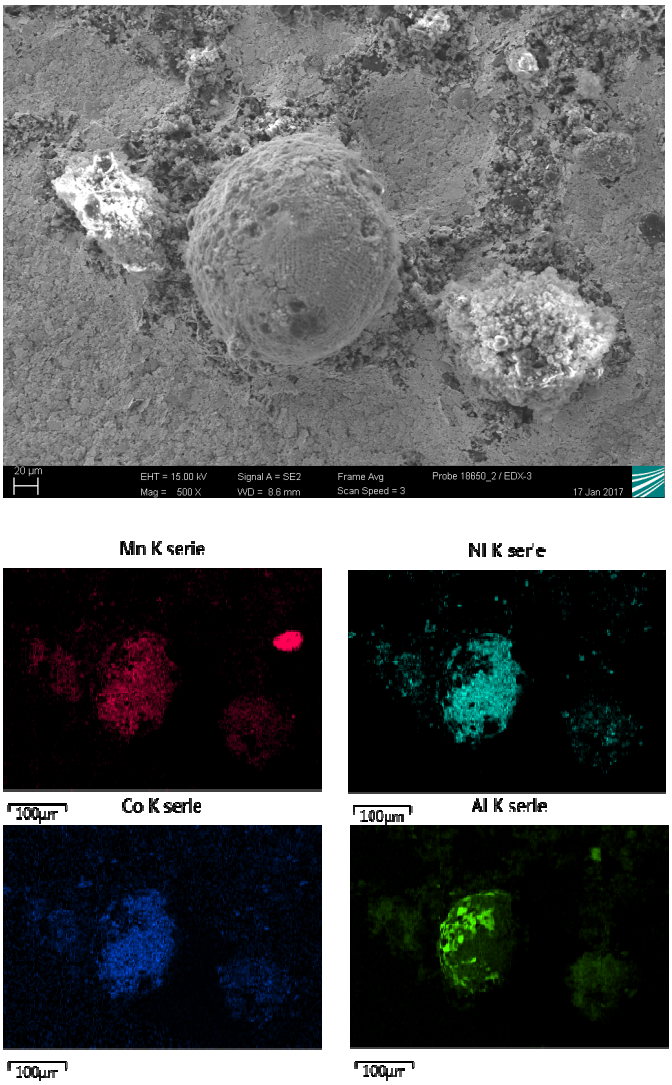

Fig. 7. SEM and element specific EDX mappings of black mass from battery type 18650 processed with ca. 1100 pulses. Separate monitoring of main cathode materials Mn, Ni, Co and Al in the same section.

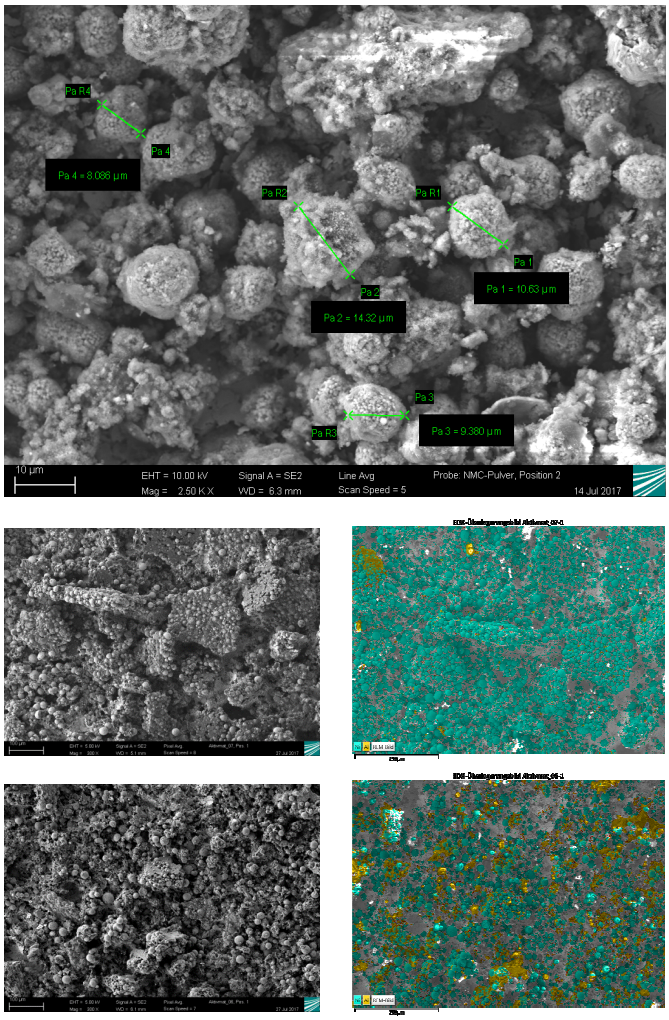

Fig. 8. Particle size determination of active material particles (top). SEM and EDX mappings of black mass from production waste processed with 50 pulses (mid) and 500 pulses (bottom). Distribution of active material illustrated by Ni and single Al-impurities are highlighted in color.

IV. Results & Discussion

Within the framework of material characterization following analytical methods were used to evaluate the results of the fragmentation and separation processes:

- Optical emission spectroscopy (ICP-OES)
- Scanning electron microscope (SEM)
- Energy-dispersive X-ray spectroscopy (EDX)
- X-ray diffraction (XRD)

A. *End-of-life batteries*

The separated fine fraction, gained after the elctrohydraulic processing of type 18650 battery cells, was sieved and purified. The result was a powder consisting of almost pure cathode and anode material. The most interesting aspects are the chemical and structural composition of the samples. The analyses were focused on cathode materials (so called black mass) like lithium-nickel-cobalt-aluminum-oxide (NCA), lithium-nickel-cobalt-manganese-oxide (NCM), lithium-cobalt-oxide (LCO) or lithium-manganese-oxide (LMO). The aimed elements were therefore, nickel, cobalt, manganese and lithium. Furthermore impurities like copper or aluminum particles from electrode foils are interesting.

1) ICP-OES

The black mass was analyzed with ICP-OES regarding to the element composition. The expected transition metal values of Co, Ni and Mn were detected. The elements Li, Ni, Co, Al and Mn indicate the presence of the cathode materials Li(Ni, Co, Al)O_2 (NCA) and Li(Ni, Co, Mn)O_2.(NCM). Al and Cu hint at fragments of the conductors of the cathode (Al) and the anode (Cu) (TAB. I).

2) SEM and EDX

SEM-images and EDX-mappings of the black mass were compiled to investigate the impurities (fig. 7). The EDX-

mappings evince that Ni, Co and Mn are spread nearly identically over the whole image area related to the composition of active material which is shown in detail on the element specific images on fig 7 bottom. Further the fine dispersed impurity of aluminum can be seen. The equivalent active material distribution leads to the conclusion that the synthesized cathode material is not been damaged by the separation process. XRD analyses should reveal, if the cathode material have the expected phases.

3) XRD

The examination of the phase composition by X-ray diffraction confirms that NCM and graphite are available as active material after the electrohydraulic treatment (see fig. 6). The reflexes of NCM and NCA cannot be differentiated clearly with that method but NCA can be eliminated by element analysis. The chemical bonds of Fe, Cu, Cr, etc. are either x-ray amorphous or have a concentration less than 5 – 10 % by volume. As a consequence the black mass has to be composed of NCM and the sum of carbons consisting of graphite as anode active material, the graphitic conductive additives for cathode and anode and binder residues polyvinylidene fluoride.

B. *Production waste*

Furthermore, as a second recycling route, production waste in form of coated electrode foils was regarded. The scrap material was processed analog to end-of-life-batteries. At the end of treatment there was also a fine fraction of pure active material. Collected production residues have the advantage of a previous division in coated anode or cathode material without mixing them. With production waste the attention was focused on the shortening of process duration and estimation of exact pulse rates for the electrohydraulic generated discharges. To systematise the studies and ensure the comparability of the results the pulse count were preemptively set on 50 and 500 pulses per process.

1) ICP-OES

Similar to end-of-life batteries the ICP-OES analysis was applied to active material from production waste. The results of the ICP-OES analysis (TAB. I) show that the concentration of metal foil impurities (Al at NCM-cathode foil and Cu at Graphite-anode foil) increases at treatments with at least 500 pulses. The concentration of active material did not change. The enrichment of Al- and Cu-impurities is a result of a long process time and due to that a more intensive fragmentation. The foil particles are getting smaller and can be found in a higher concentration in the fine fraction.

2) SEM and EDX

The samples were analyzed analogously with a scanning electron microscope and characterized with an EDX-mapping. On EDX images of samples with a 50 pulse treatment (fig. 8 mid) only few impurities of aluminum (yellow) can be found. The active material here represented by nickel is marked green. A lot more aluminum impurities can be seen on the image of the 500 pulse treatment (fig. 8 bottom). The SEM images show fewer damages in the active material structure in samples with shorter process times or less pulses. Well illustrated due to the higher amount of circular nickel-rich particles that indicate NCA materials. At the sample that was treated with 500 pulses the agglomerates from the electrode material are more exposed, but broken active material particles can be found singularly, too.

Fig. 9. Recycled material fractions from electrohydraulic fragmentation process: metals (left), black mass (front), plastics (right).

Fig. 8 top shows an additional SEM image from NCM-cathode material sample recovered by the project partner ImpulsTec GmbH. The components exist in particle sizes between 8 and 15 µm. In that scale a separation of cathode material and graphite is not possible with mechanical methods. Related to this a separation should use a floatation principle. Classic floatation agents have a very low level of efficiency at particle sizes <10 µm. As part of the ongoing project, possibilities should be investigated to find a satisfying separation rate of the components.

V. CONLCUSION

The innovative recycling process based on electrohydraulic fragmentation technology offers a lot of potential applications due to its high separation selectivity. The performance can even be enhanced by adjusting the process parameter like pulse rate or operating voltage on the respective input materials. The technology is suitable for different kinds of waste material as well as end-of-life products. The outcomes for battery cells type 18650 can be seen in fig. 9. Metals and plastics can directly be fed to common recycling chain, while the black mass can be remanufactured in battery cell production cycle. An additional separation is not needed. Depending at which point the recovered black mass should be reintegrated in the process, it has to be differently reconditioned. As secondary material in cell manufacturing, enrichment with new additives (e.g. binder) is necessary. In case of other applications, further hydrochemical treatment according to the desired compounds or elements is required. The exposure and concentrating of valuable components of complex compounds in a directly reusable form will enable new ways to recycle batteries in the future and makes recycling in total more efficient.

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