International Conference on Resource Chemistry
March 08-09, 2021

# CHARACTERIZATION OF PROCESS WATER FROM LITHIUM-ION BATTERY RECYCLING

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## Motivation:

Lithium-Ion Batteries (LIBs) contain various elements and compounds, i.e. cobalt, lithium, phosphorus and natural graphite. These four are on the European Union's list of "critical raw materials" [1], thus making low-emission, cost-effective, and energy-efficient recycling processes essential. We are pursuing a mechanical recycling process for LIBs based on electro-hydraulic fragmentation (EHF). This process produces significant amounts of wastewater. The aim is to develop an efficient treatment and possibly recovery of the substances contained in the waste water.

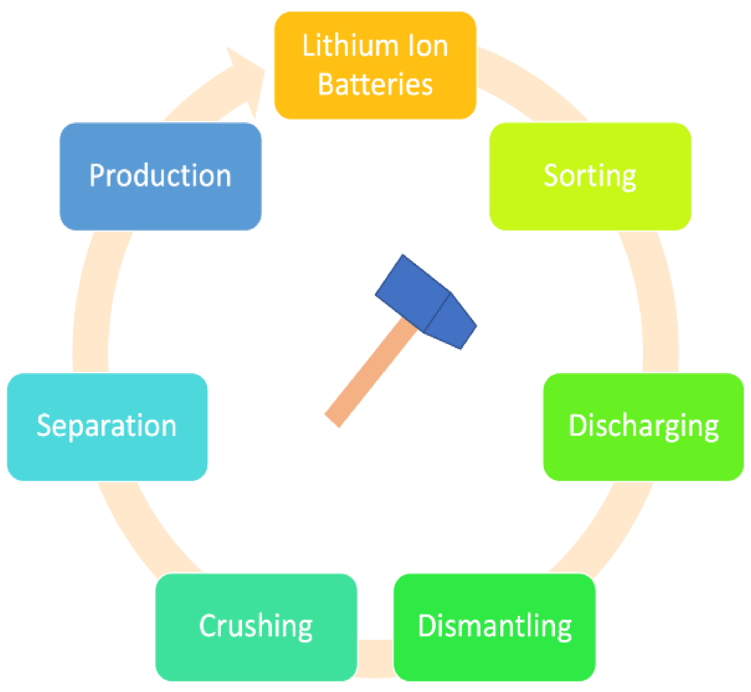

Fig. 1: Scheme of mechanical LIB recycling.

As a first step, we here present the results of the analytical composition of waste water from EHF in order to identify possible treatment technologies and estimate recycling potentials.

## Compounds expected in process water:

- The electrolyte of the LIB contributes to the majority of the load in the process water
- The electrolyte consists of several different organic solvents and the conducting salt $LiPF_6$
- Hydrolysis of $LiPF_6$ (equation 1 to 4) takes place slowly at room temperature [3] and leads to the formation of toxic/dangerous, hydrogen fluoride (HF) with a max. concentration < 0.7 g/L

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

$$POF_3 + H_2O \rightarrow HPO_2F_2 + HF \quad (2)$$

$$HPO_2F_2 + H_2O \rightarrow H_2PO_3F + HF \quad (3)$$

$$HPO_2F + H_2O \rightarrow H_3PO_4 + HF \quad (4)$$

➔ Organic solvents as contaminant in process water
➔ HF toxic in high concentrations
➔ Lithium not sufficiently retained by municipal wastewater treatment plants
➔ Recovery of lithium and fluorine as valuable salts

## Results & discussion:

- Process water is contaminated with organic and inorganic substances
- COD value reveals high organic load
  - Process water is poorly bio-degradable with $COD/BOD_5 > 2$
- High total fluorine concentration
  - Only about 12 % of the total fluorine is present as fluoride
- High total phosphorous concentrations
  - Phosphate is not detected in process water
  - ➔ At the time of measurement, hydrolysis of $LiPF_6$ is low
- Lithium ions only partially originate from the conducting salt
  - ➔ The mass balance shows that about 72 % of lithium ions are washed out from cathode material
- Magnesium and calcium from tab water precipitates
  - Composition of Magnesium and Calcium salts still has to be investigated

➔ A subsequent treatment process can recover valuable materials such as lithium and phosphorous

| | Tab water | Process water |
|---|---|---|
| pH-value [-] | 8.1 | 7.7 |
| Conductivity $\left[\frac{mS}{cm}\right]$ | 0.6 | 2.1 |
| COD $\left[\frac{mg}{L}\right]$ | <LOD | 3,176 |
| $BOD_5$ $\left[\frac{mg}{L}\right]$ | <LOD | 563 |
| $COD/BOD_5$ | - | 5.6 |
| Fluoride $\left[\frac{mg}{L}\right]$ | <LOD | 84.5 |
| Total fluorine $\left[\frac{mg}{L}\right]$ | - | 695 |
| Phosphate $\left[\frac{mg}{L}\right]$ | <LOD | <LOD |
| Total Phosphorous $\left[\frac{mg}{L}\right]$ | < 2 | 215 |
| Lithium $\left[\frac{mg}{L}\right]$ | <LOD | 168 |
| Cobalt $\left[\frac{mg}{L}\right]$ | <LOD | 0.2 |
| Calcium $\left[\frac{mg}{L}\right]$ | 70.5 | 20.7 |
| Magnesium $\left[\frac{mg}{L}\right]$ | 12.7 | 1.3 |

## Electrohydraulic Fragmentation:

- An EHF process supplements the crushing process of LIB as the first step for recycling
- Fragmentation takes place in water
- Three cathodes are charged up to 40 kV
- Discharge results in the formation of shock waves
- Discharging frequency is between 1-4 Hz
- EHF process breaks up composite material at the interfaces
- LIB components can be recovered by sieving or sedimentation
- Dissolved substances remain in the process water (e.g. the electrolyte)

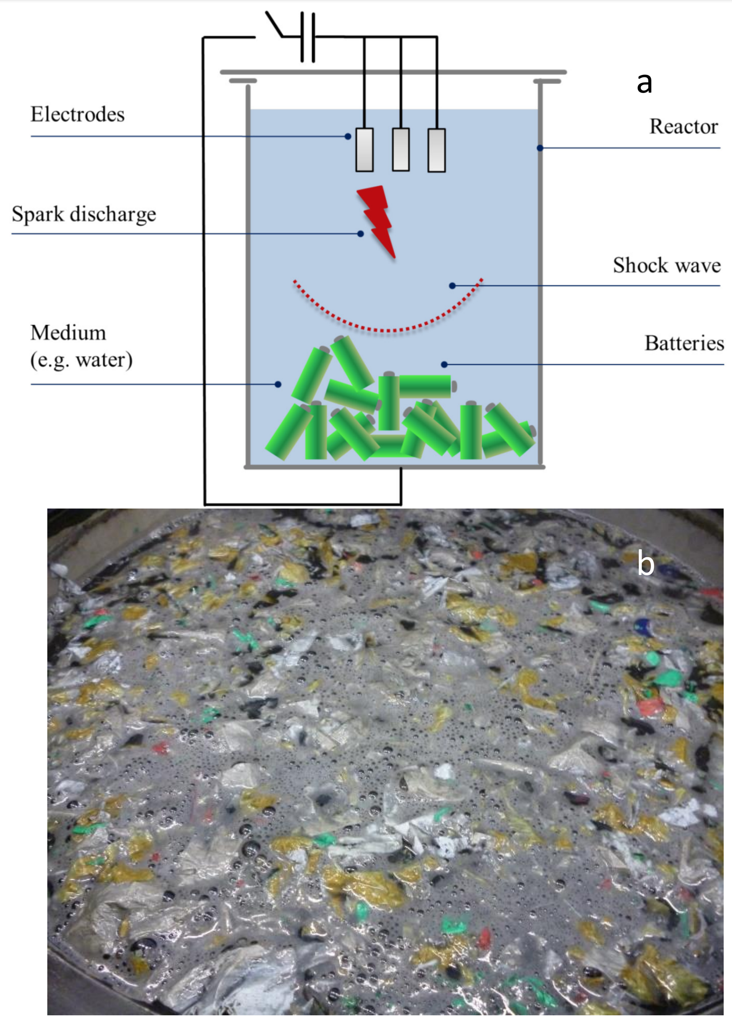

Fig. 2: a) Scheme of EHF process [2]; b) process water.

## Methods & parameters:

Chemical and biological oxygen demand (COD & $BOD_5$): These two sum-parameters for the organic solvents are determined by means of a cuvette test (LCK555 and LCK114) in a photometer.

Ion chromatography: Fluoride and phosphate is detected by a Thermo-Fisher ion chromatograph (Dionex 5000+). An AS11 with Guard AG11 is used as the column and the AERS suppressor is installed. A conductivity detector is deployed.

Combustion ion chromatography: With combustion ion chromatography (TOX 2100 H) the total fluorine content can be determined. The combustion program "volatile liquids" was selected. The fluoride determination is carried out by ion chromatography.

Optical Emission Spectroscopy (ICP-OES): The total phosphorous, lithium, cobalt, calcium and magnesium is detected by a ICP-OES 3800 Perkin Elmer.

**Experimental**

40 pre-damaged 18650 secondary batteries (1.64 kg) are treated with 2,000 impulses in 20 l tap water.

## Concept for combined treatment and product recovery:

- Biological wastewater treatment not advisable, as
  - Process water not biodegradable
  - Organic components partly volatile
  - Inhibitory effects on microorganisms not excluded

➔ Physical chemical methods better suited

- Recovery of Lithium
  - Electro-chemical deposition
  - Concentrate lithium, then precipitate
- Recovery of the organic solvents
  - Stripping process & membrane process

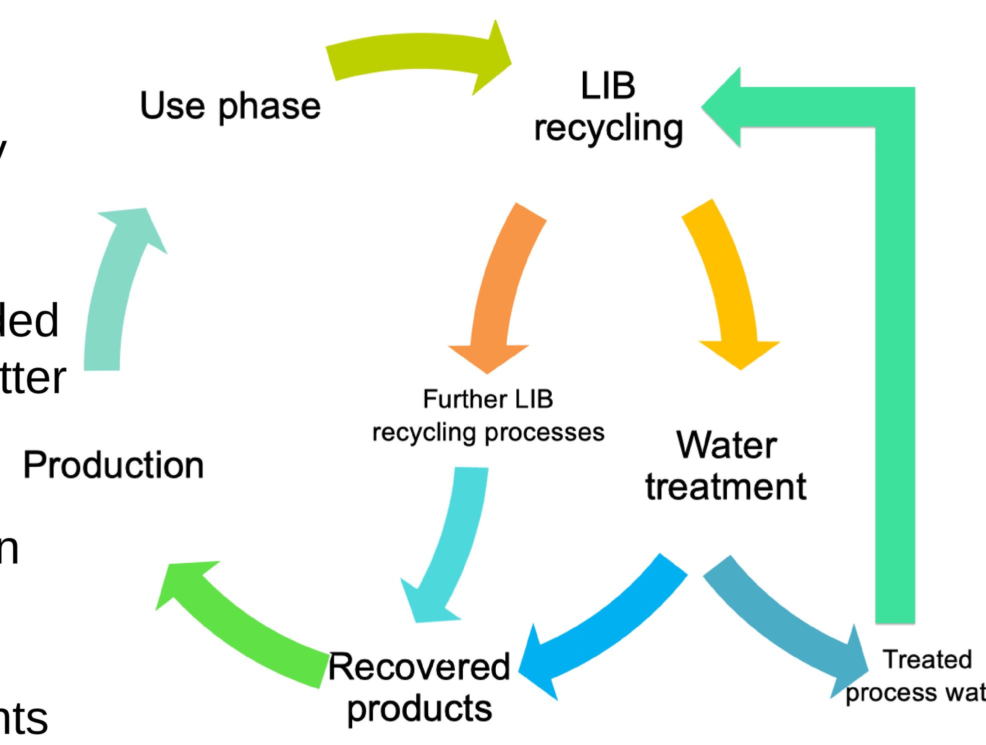

Fig. 3: Scheme of our overall concept for the treatment of process water from lithium-ion battery recycling.

➔ Minimization of water consumption via recirculation
➔ Preparing an energy balance to evaluate the planned treatment process
➔ Recovery of valuable materials e.g. $CaF_2$, $LiCO_3$, $Ca_3(PO_4)_2$

[1] European Comission, „Critical Raw Materials", 2020 Brussels Beglium, https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en
[2] J. Öhl, D. Horn, J. Zimmermann, R. Stauber, O. Gutfleisch, „Efficient Process for Li-Ion Battery Recycling via Electrohydraulica Fragmentation", Material Science Forum, 2019 Switzerland, doi:10.4028/www.scientific.net/MSF.959.74
[3] J. E. Harlow, X. Ma, J. Li, E. Logan, Y. Lui, N. Zhamg, L. Ma, S. L. Glazier, M. M. E. Cormier, M. Genovese, B. S. A. Camerin, J. E. Stark and J. R. Dahn, „A Wide Range of Testing Results on an Excellent Lithium Ion Cell Chemistry to be used as Benchmarks for New Battery Technologies", J- Electrochem. Soc., **166** A3031