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KYBURZ Direct Battery Recycling



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Summary

KYBURZ and Empa are jointly developing a direct recycling process for lithium iron phosphate (LiFePO_4) batteries. The project aims to recover high-quality materials from the batteries while minimizing energy consumption and maximizing the recovery rate. Instead of shredding the batteries, they are separated into individual components, which allows the active materials to retain the structural and electrochemical properties of the active materials to be reused to produce new battery cells. The focus is on a water-based separation process, along with thermal methods, to efficiently separate the active materials from the current collectors. Compared to the centrifugation method, filter press techniques have shown promising results in achieving solid recovery rates, and the wastewater analysis indicates that most elements are below disposal thresholds. Various analyses have been conducted on the recovered active materials, including elemental, structural, and electrochemical methods. The project aims to demonstrate a pilot plant for the water-based separation process and intends to refine and optimize the recovery techniques in the second phase, aiming for electrochemical properties comparable to pristine lithium iron phosphate batteries.



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1. Introduction

1.1. Background information and current situation

Lithium-ion batteries (LIB) are crucial for combating climate change by enabling low-carbon technologies like electric vehicles. As a result, the demand for LIBs and the need for sustainable solutions for end-of-life batteries are increasing. KYBURZ, a company with over 30 years of experience in electric mobility, has been exploring battery recycling early on. Conventional recycling processes are energy-intensive and require significant effort to reuse the battery materials. KYBURZ and Empa have developed a promising direct recycling method for lithium iron phosphate (LiFePO_4) batteries, which offers high materials recovery rates and reduced energy demand.

1.2. Purpose of the project

The project aims to advance direct battery recycling, a highly efficient and environmentally friendly method that retains the crystal chemistry of battery components. The pilot project connects various recycling steps, including discharging and disassembly, to the water-based separation processes for anode and cathode materials. Material purification and upgrading strategies are also explored. The ultimate vision is to directly incorporate recycled active materials into the production of new batteries, closing the material cycle and enhancing the sustainability of battery production and electromobility. KYBURZ and Empa are at the forefront of developing and demonstrating these processes, with support from the Swiss Federal Office of Energy under the P + D research unit.

1.3. Objectives

To ensure that the materials used in the batteries remain as intact and pure as possible when they are recovered, the gentle separation of active materials coating from the current collectors without intermixing the anode and cathode active materials is a critical step. The main objective of the project is to automate the water-based electrode separation process unit as an extension of the current pilot plant and the recovery of high-grade active materials from LiFePO_4 cells – with the following specific objectives defined in the project.

- To develop efficient water-based separation of active materials from current collectors by considering the reaction kinetics of the active material with water, safety, and corrosion effects of the electrode material/water suspension on the equipment,
- Develop a method to separate the suspension (active materials from water); and finally validate and demonstrate an optimal system with efficient active material recovery, best water management system, and water capturing and reintegrating capability into the process,
- Elemental and structural characterization and electrochemical performance assessment of the recovered material to assess its suitability for reusing in the production of new LiFePO_4 cells,
- Evaluation of the environmental impact of the proposed process, including energy monitoring through life cycle assessment (LCA).

2. Description of facility

2.1. Overview of the recycling process

Recovered LiFePO_4 batteries from Swiss Post delivery vehicles, with a 7 to 12 years usage period and an estimated cycle count of 2000-4000, were studied. Experiments primarily focused on powders obtained from end-of-life (EoL) batteries discharged to 2 V before disassembly, corresponding to 0% state of charge (SoC). These batteries had an average state of health (SoH) of 60%. Additionally, some experiments involved powders harvested from EoL batteries discharged to 0 V before disassembly, simulating a short-circuited battery scenario and corresponding to 0% SoC.



The already established KYBURZ cell disassembly process, developed by KYBURZ and Welthaubt, first removes the case lid of the cells. [1] Then, the cells are drilled at the back of the case, and the electrode packs are ejected using compressed air. The cell pack is steered across the roller to separate the electrodes (the anode and the cathode) and the separator.

2.2. The water separation process

Preliminary experiments were conducted at KYBURZ to separate the positive and negative active materials coatings from current collectors by immersing in separate water baths. The resulting suspensions, consisting of the positive and negative electrode harvested masses, were sent to Empa St. Gallen in separate containers. The aqueous suspension of positive electrode harvested mass was decanted, and the water was appropriately disposed. The solid positive electrode mass was collected and dried at a specified temperature and time.

A small in-house reactor was developed to define the specification sheet for a pilot reactor to be tested at the University of Applied Science and Arts Northwestern Switzerland (FHNW), with the purpose of validating the scale-up process for a larger reactor. Inspired by the parameters of the small reactor, the reactor is developed with components and parameters such as a water inlet, an outlet for the active material suspension, a pump and motor, temperature monitoring, pressure control, a collection tank, and a control system. A basket with a mesh system was integrated into the reactor to separate current collector foils and the active materials suspension. The basket collects the foils while the suspension is released from the bottom and directed to the subsequent process unit.

Furthermore, the separation of the active materials from the water was also investigated in detail. Centrifugation experiments with graphite suspensions were conducted to obtain more information regarding the separability of graphite and water. A decanter centrifuge was also tested considering that the sedimentation process may lead to a more economical solution. In addition, tests with a filter press - after squeezing and drying - were tested and showed promising results.

2.3. Methods for characterization of recovered active materials

Li-ion batteries are assembled in a discharged state, meaning that the electrochemically active lithium is initially contained in the cathode. During the first life of LIB, a portion of the electrochemically active lithium inventory becomes irreversibly immobilized as secondary phases due to side reactions occurring in the cells. This includes the formation of solid and cathode electrolyte interphases. The gradual consumption of the initial lithium inventory is a common process that leads to capacity fade over time, resulting in the degradation of the battery SoH. To address this, and after confirming that this was the main cause of degradation in the active material, three different relithiation steps were performed to replenish the empty sites in the FePO_4 particles with fresh lithium, aiming to restore the material's initial capacity. These three relithiation routes were based on previous publications and included two solid-state reactions routes and one water-solution route.[2-5] For the solid-state routes, which consist in a thermal treatment in a tube furnace, lithium carbonate was used as lithium source. The difference between the two solid-state routes is the presence or absence of a reducing agent (glucose) during the thermal. The third route consisted of a water solution relithiation reaction with lithium hydroxide as lithium source and citric acid as reducing agent, also followed by an annealing step.

Throughout the various stages of the regeneration process, the active material underwent characterization using different techniques. These techniques included the analysis of the structure and



morphology of the material using methods such as X-ray powder diffraction, scanning electron microscopy, dynamic light scattering, and galvanostatic cycling measurements.

3. Activities and results

3.1. Current collector and active materials separation

Two separate in-house reactors were installed, one for the anode electrodes and another for the cathode electrodes, to study the detachment of active materials from the current collectors. The tests with an anode electrode showed a positive outcome that led to the design of the pilot reactor. In contrast, similar experiments were unsuitable for the cathode due to the rotation that the aluminum foils form a crumpled aluminum ball leading to the loss of materials. Therefore, it is planned to investigate and conduct further tests with the cathode materials in the pilot reactor.

3.2. Separation of active materials and water

Centrifugation experiments with graphite suspensions were conducted to obtain more information regarding the separability of graphite and water. Centrifuging the suspension results initially in very thin cakes¹ through which the liquid can still filter quite well, but such thin cakes do not seem economically feasible, and would require large filtration areas (i.e., several centrifuges would be required). With the increase in the cake thickness, the cake became so compact that the filtration rate was reduced, and the liquid remained on the cake surface, even after longer centrifugation.

As an alternative, a filter press method was employed and showed promising results. For this experiment, pressure and compressed air were applied to the sludge container (graphite suspension) to fill the filter press. The suspension was filtered by two filter clothes placed on either side of the filtration chamber. With regards to the cake dryness, the test after squeezing and compressed air drying showed promising results compared to the centrifugation experiments. Moreover, the water/filtrate could be integrated back into the preceding process unit and reused. The number of cycles the water would be reused will be optimized in the next phase of the project.

3.3. Wastewater analysis

To monitor the wastewater at the end of the anode and cathode water separation process, the wastewater samples were sent to the Office for Waste, Water, Energy and Air (AWEL) of the canton of Zürich, where they were analyzed. The result shows that wastewater from the anode is not suitable for disposal into the wastewater system due to the high concentration of copper (above the threshold limits) that is present in dissolved form. Further investigation is ongoing to remove the dissolved copper and regulate the pH in anode wastewater. [6] However, the wastewater from the cathode meets all discharge requirements for disposal to a water treatment plant, except for lithium which is present in high concentration and needs to be investigated as well.

3.4. Harvested mass characterization

After harvesting the positive electrode active material, preliminary characterization was conducted to determine the main causes of degradation. XRD analysis was employed to identify the crystallographic phases present in the material and estimate the fraction between the two main phases, LiFePO_4 and FePO_4 . The XRD pattern revealed additional reflections not found in pristine LiFePO_4 (Figure 1, green line), indicating the presence of FePO_4 and graphite (Figure 1, purple line). No other phase was observed in the material, indicating no detrimental effect to the crystallographic structure resulting from

¹ Cake = a layer of sedimented particles (here graphite)



the water-based treatment. The $\text{LiFePO}_4\text{:FePO}_4$ ratio was determined to be approximately 62:38 by XRD, which closely matched the nominal SoH of 60% of the EoL cells provided by KYBURZ. This suggested that 38% of the active material required relithiation to restore the initial capacity of pristine LiFePO_4 . The graphite reflection in the XRD patterns indicates its usage as an electrically conductive additive during manufacturing to allow high-rate capabilities. Further characterization of the harvested material involved analyzing its microstructure using scanning electron microscopy. The results indicated no significant changes to the microstructure following the water-based process. However, the presence of large aggregates was observed, attributed to remaining traces of binder in the sample. Additionally, the presence of graphite was confirmed, supporting the earlier finding. Moreover, the particle size of the LiFePO_4 particles was found to be around 200 nm which was confirmed also by dynamic light scattering.

After identifying the cause of the degradation of the material, the investigation focused on establishing a relithiation route. The two solid-state relithiation routes did not effectively result in the relithiation of the FePO_4 phase. Instead, XRD data revealed new reflections corresponding to compounds like lithium phosphate. On the other hand, the water-solution relithiation process showed successful results. The results clearly showed that the relithiated and annealed active material no longer exhibited reflections corresponding to FePO_4 (Figure 1, orange line), in contrast to the previously harvested material (Figure 1, purple line). Furthermore, no other secondary phases resulting from the relithiation process were detected. In addition to the successful results, this process showed several advantages over the other two methods: it could be performed at low temperatures, required only a few hours, and did not necessitate exact stoichiometric equilibrium between the lithium source and FePO_4 . These factors make the water-solution relithiation process favorable for scaling up to an industrial level.

The final test evaluated the electrochemical performance of the relithiated material in new cells, comparing it to the performance of original harvested and pristine material. Preliminary results showed that the electrochemical performance of the harvested material was not significantly affected by the water bath process resulting with an initial capacity in the same range as the nominal one. So far, the relithiated LiFePO_4 material has displayed a capacity lower than expected. One hypothesis to explain this low discharge capacity is the presence of remaining binder that blocks access to the material. Therefore, one of the activities during the second part of the project will be directed towards ensuring the complete dissolution of any remaining binder and achieving optimal performance of the relithiated and annealed LiFePO_4 material.

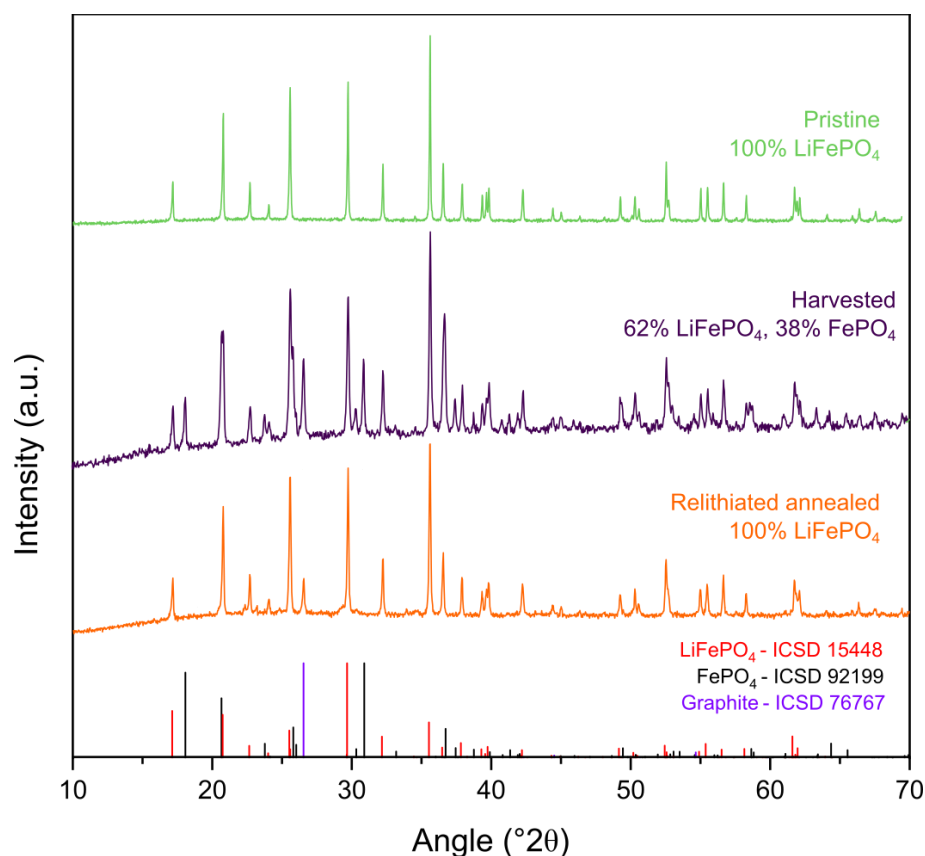


Figure 1: XRD patterns of pristine, harvested, and relithiated/annealed LiFePO₄. The stick patterns at the bottom of the plot correspond to reference patterns obtained from the ICSD database.

4. Next Steps

During the second phase of the project, the following main activities will be undertaken.

- Use the pilot reactor to separate the main materials from cathode electrode, and proper material selection for the scale up reactor will be conducted based on the outcome of the corrosion examination from the pilot reactor. In addition, pilot demonstration and scale up of the reactor vessels for separating of positive and negative active material coatings from their respective current collectors.
- Material characterization of the harvested graphite. In addition, improving the electrochemical performance of the relithiated LiFePO₄ will be addressed during the second phase of the project.
- A LCA will be calculated as soon as all the steps of the recycling process are validated. For the LCA analysis to be accurate, data (e.g., energy consumption for each step) from either the facility or the experiments will be used. This is required for each step of the recycling process, and this experimental optimization work is still being conducted.
- The data obtained from wastewater analysis showed a higher presence of lithium in cathode wastewater, and both lithium and dissolved copper in the anode wastewater. The goal is to implement efficient methods to treat and remove these trace metals.



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