

Recycling of Lithium-Ion Batteries - The LithoRec Project

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The transition from combustion engine vehicle concepts to electric drive systems, and thereby electromobility, is seen as an important and highly promising way to reduce dependency on oil, decrease CO₂ emissions, solve the emissions problem in burgeoning megacities, particularly in Asia, and improve energy efficiency in the long term.

The battery is the fundamental building block and key technology of electromobility. Due to their energy and power density, only lithium-ion batteries are currently suitable to meet the high demands of electromobility. While lithium is found worldwide in ores, sedimentary rocks, stones, salt lakes, and seawater, commercial extraction is currently mainly feasible in geopolitically less stable regions in South America, economically protectionist China, and technically and economically viable Australia.

The current global political relevance of lithium is illustrated, for example, by the euphoric reporting on potentially large lithium deposits in Afghanistan [1, 2]. A detailed study on the forecasted consumption versus estimated reserves and resources suggests that it will be necessary to partially meet the rapidly growing demand for lithium and lithium components through recycling in the future [3].

I. The Lithium-Ion Battery and Its Components

Cells in lithium-ion batteries consist of many layers of cathodes and anodes, which are electrically insulated from each other by a permeable separator. Numerous layers of these electrode-separator assemblies are housed in a battery case, with the electrodes and separators being stacked or wound, depending on the manufacturer. The cases can be made of aluminum (hard case) or flexible aluminum-plastic (soft case or coffee bag). The cases are filled with an organic electrolyte solution and lithium salt between the electrodes. This electrolyte facilitates the exchange of lithium ions between the electrodes. During discharge, lithium ions migrate from the cathode to the anode, where

they intercalate into the metal lattice structure and accept an electron. The electrons are conducted to the current collector (anode-copper, cathode-aluminum) via the particulate composite structure of the electrode coating, which is connected to the battery's electrical contact.

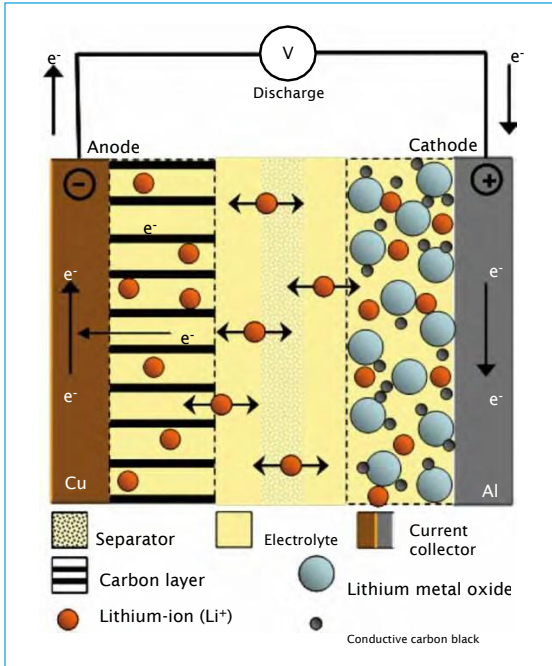


Figure 1:

Structure of a Lithium-Ion Battery

The charging and discharging processes cause electrochemical, chemical, and mechanical aging effects, which significantly impact battery performance. Given that batteries in electric vehicles are expected to last ten to fifteen years, corresponding to 4,000 to 5,000 charge-discharge cycles, these effects are of great importance.

On the anode side, porous graphite is coated on a copper current collector, while on the cathode side, lithium mixed oxides (e.g., $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, NMC) are state-of-the-art. These will thus be the first materials to be recycled. However, considerable efforts are being made to substitute the expensive transition metals cobalt and nickel in battery chemistry to reduce the raw material costs of batteries. For example, lithium iron phosphate-based battery cells are already being industrially manufactured and used today. Therefore, it is expected that future recycling processes may no longer be economically viable solely from the recovery of valuable metals such as cobalt and nickel.

2. Recycling of Lithium-Ion Batteries

There are numerous research and development activities and industrial experiences in the field of lithium battery recycling. However, previous approaches have mainly focused on recovering the valuable metals cobalt and

nickel from small batteries. These processes generally involve mechanically or thermally breaking down the entire battery system to recover the valuable metals using a combination of pyro- and hydrometallurgical methods. However, since traction batteries have a significantly larger proportion of active materials, targeted disassembly of battery systems, followed by the separate separation of active materials from the electrodes and the hydrometallurgical processing of the recovered coating, can be economically and ecologically advantageous.

Figure 2 shows the practically feasible combinations of different processes for recycling lithium-ion batteries, ultimately recovering pure lithium salt for reuse in batteries. The different process paths always involve a combination of mechanical treatment, hydrometallurgy, and/or pyrometallurgy. With large vehicle batteries, dismantling at the modular or cellular level is required before materials can be fed into the pyrometallurgical process. Conventional battery recycling processes focus on recovering the valuable metals cobalt and nickel through a primarily pyrometallurgical process, which must be combined with hydrometallurgical methods to recover lithium (shown by the options on the right in Figure 2). Recovering a significant proportion of lithium with these methods is only possible with very high effort [4, 5, 6, 7], so the lithium-containing slag resulting from the pyrometallurgical process is currently used for other applications, particularly in the construction industry. However, in the LithoRec project, a process was developed on a laboratory scale in which, through purely mechanical and hydrometallurgical methods (leaching and subsequent precipitation of lithium), a significant portion of the lithium can be directly recovered alongside cobalt and nickel. Another advantage of the *LithoRec process* is that the recovered materials, when mechanically processed on a laboratory scale, have been proven to be of battery quality, thereby closing the loop on strategically important battery raw materials [8]. For example, lithium hydroxide was precipitated from lithium iron phosphate, and new NMC of battery quality was produced from lithium nickel manganese cobalt oxide (NMC).

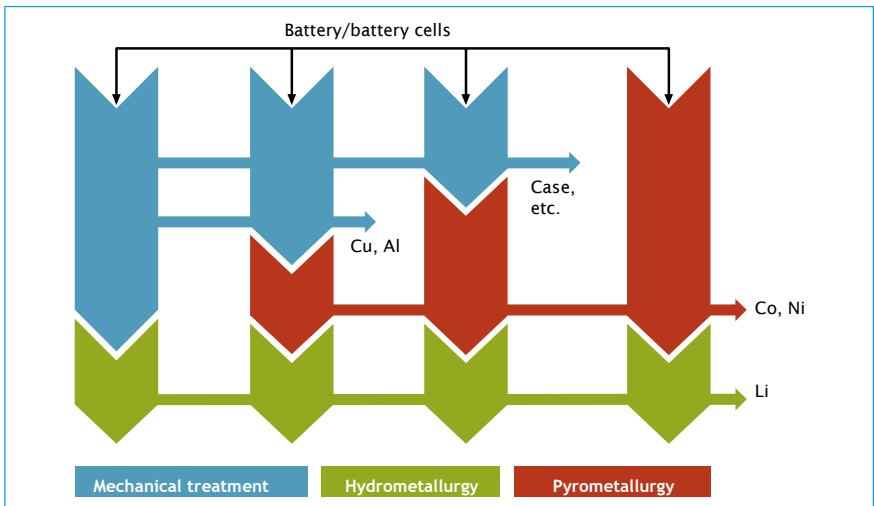


Figure 2: Basic Operations and Process Routes for Lithium Battery Recycling

3. LithoRec – An Approach to Recycling with High Lithium Recovery

Traction batteries for automotive applications can be divided into multiple system levels and thus dismantled at different levels, as shown in Figure 3:

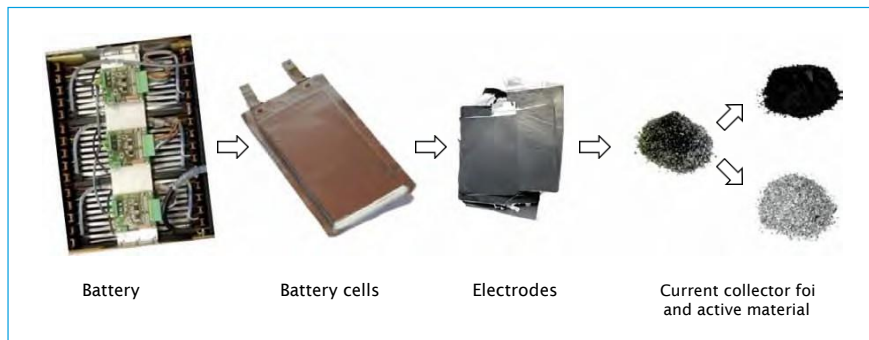


Figure 3: Mechanical Dismantling Levels of a Lithium-Ion Battery

The battery system removed from the vehicle must first be disassembled into its modules and individual cells. In LithoRec, the planning for dismantling battery systems down to the cellular level included not only system planning [9, 10] but also initial studies on the automation potential of the dismantling steps [11], including the prototype implementation of a gripper system for removing battery cells [12]. The automation of dismantling lithium-ion battery systems was also theoretically investigated in LithoRec. It was shown that specific dedicated dismantling steps, such as the removal of battery cells, have a high automation potential. Moreover, a gripper for cell handling with integrated state determination (voltage measurement and internal resistance determination) was developed as an example [13]. However, fully automating dismantling sequences of battery systems is unlikely due to the environmental conditions in dismantling factories, the variety and lack of standardization of the systems, and the qualification requirements.

After disassembly, the battery cells must be mechanically broken down through shredding processes to be further separated into fractions of cell housing/casing material (10 to 15%), an electrolyte (10 to 20%), other components (2 to 5%), separator/foils (about 3%), and electrodes (about 65%). A challenge in this processing step is the electrolyte, which can ignite quickly due to short circuits that occur when insufficiently discharged cells are shredded. Besides ensuring a complete discharge, inerting the shredder provides a safe way to shred the cells.

The electrode fraction consists of anode composites (15% copper foil and 31% organic coating) and cathode composites (8% aluminum foil and 46% active material coating – for example, lithium nickel manganese cobalt oxide (NMC)). To further hydrometallurgically process the active material, these composites must be separated from each other (Figure 4). Two alternative or combinable processes were developed for electrode separation: a wet chemical process and a mechanical process.

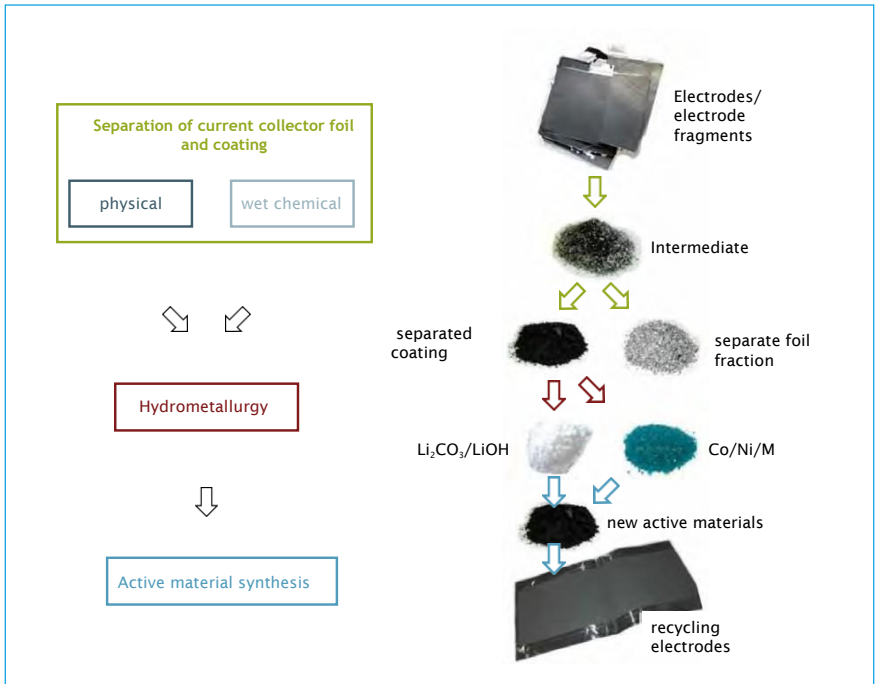


Figure 4: Process Path for Hydrometallurgical Recycling of Lithium-Ion Electrode Materials

The wet chemical process involves dissolving the polyvinylidene fluoride binder in the solvent N-Methyl-2-pyrrolidone, followed by separating the active material-laden suspension from the foil fraction. In this process, a separation efficiency of 96% of the active material introduced was achieved, which can still be optimized in processes with recirculated solvent [14]. Contamination of the active material fraction with aluminum from foil fragments was determined to be below 0.1% by weight using atomic absorption spectroscopy.

The dry separation method developed in parallel combines material pre-treatment, mechanical stress, sorting, and classification. It has achieved a separation efficiency of over 99% of the active material on a laboratory scale, with aluminum contamination of the recovered lithium salt below 0.1% by weight.

For the hydrometallurgical processing of separated coating powders from lithium-ion batteries, a pilot plant was implemented at the Langelsheim site by Chemetall as part of LithoRec. Depending on the active material, 85 to over 95% of the lithium can be recovered from the separated cathode material here.

The transition metals cobalt, nickel, and manganese were delivered as concentrated solutions within the LithoRec project to H.C. Starck, which experimentally produced new battery active materials through precipitation, milling, and calcination processes. Ecological and economic balances based on laboratory or pilot-scale investigations showed positive results [15].

To evaluate the processes, the analysis of the products and yields of the individual process steps and the monitoring of the electrochemical performance of the produced recycling electrodes were used. Aluminum contamination of the separated coatings and their elemental compositions were determined by atomic spectroscopy, and a method for determining the binder content using thermogravimetric analysis was developed. The recovered materials and sections of the manufactured electrodes were examined using scanning electron microscopy, including energy dispersive X-ray spectroscopy. In addition, the particle size distributions of the recovered coating powders were determined by diffraction spectroscopy.

Evaluating aluminum contamination in the processed products was particularly important: During the mechanical disassembly, especially the shredding of battery systems, cells, and electrodes, contamination of the recovered active materials occurs, depending on the processing method, which can cause problems in synthesizing new active materials. For example, in LithoRec, difficulties arose during the synthesis of lithium nickel cobalt oxide from a solution intentionally contaminated with a significant amount of aluminum (1% aluminum by weight). The aluminum hydroxide co-precipitated during the hydrometallurgical process for the separation of the transition metals caused the spherical transition metal hydroxide particles to stick together. After calcination, these particles were highly aggregated and could no longer be ground without destroying the deliberately pre-set morphology. In addition, a contamination-induced change in particle morphology was observed after the re-precipitation from contaminated transition metal salt solutions.

To assess the recycling materials, test cells were manufactured and subsequently subjected to electrochemical tests. Figure 5 shows the electrochemical energy storage capacity of the test cells over the number of charge and discharge cycles. It is evident that the reference material and the slightly contaminated recycled material exhibit approximately the same cycle stability. However, the material that was artificially contaminated with 1% by weight of aluminum shows reduced current storage capacity and, most notably, significantly worse cycle stability.

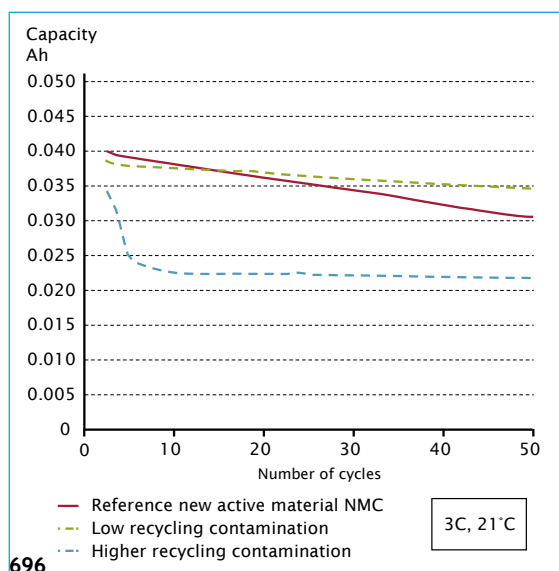


Figure 5:
Electrochemical Performance
of Recycling Materials

Initial ecological assessments provide an overview of the entire process chain (cradle-to-grave) with a focus on lithium-ion batteries [16, 17]. Within the framework of the two recently concluded BMU-funded projects LIBRI and LithoRec, the recycling technologies for lithium-ion batteries were ecologically evaluated [15]. Additionally, the potential economic viability of recycling large quantities of used batteries was demonstrated in LithoRec [18, 19].

4. Conclusions

In the context of the *LithoRec* research project, conducted by the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety, it was shown that the recycling of lithium-ion batteries based on mechanical and hydrometallurgical processes is technically feasible with high yield and purity, and is both ecologically and economically viable. As the transition metals cobalt and nickel are increasingly substituted by other materials in battery active materials, this alternative to the primarily pyrometallurgical processing becomes more attractive. A crucial factor for the utilization of the recovered lithium salt and transition metal solution as raw materials for the production of new active materials is the minimization of aluminum contamination. Under this condition, battery materials can be synthesized from the recovered metals, which, based on initial tests, exhibit the same properties, particularly cycle life, as standard battery materials from primary raw materials.

Acknowledgments

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