

# RECOVERY OF CATHODE MATERIAL FROM LI-ION BATTERIES

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**Abstract:** This article focuses on the possibilities of recycling materials from spent Li-ion batteries, especially on direct recycling. Lithium-ion batteries (LIBs) are gradually replacing other types of accumulators from practical applications and further increase in their production is expected in the future. With high production, bigger amount of waste will have to be deal with. Recycling processes currently in use are not efficient enough and they have been developed mainly for one type of cathode material. Direct recycling is very promising in terms of efficiency, but it needs to be further enhanced. Direct recycling technology is discussed in the text as well as the recovery process for commercial Samsung 18650B-20R aged cell using different kinds of solvents.

**Keywords:** Li-ion battery, direct recycling, NMC

## 1 INTRODUCTION

Today, LIBs are used in many fields, from wearable electronics, smart phones, laptops, electromobiles to energy storage power stations. LIBs are in their principle, as well as other battery types, an electrochemical energy source. Due to the fact that they can accumulate energy in their electrodes, they are classified as secondary sources of energy.

LIBs are made of three main parts, cathode, anode and electrolyte. The cathode consist of aluminium collector and active material containing transition metal oxides and lithium, which ensures the battery function. The working principle of LIBs is called intercalation process. During the charging of the battery, lithium ions are deintercalated from the structure of cathode and migrate through the electrolyte to the anode, where they intercalate to the graphite. During discharging the process is reversed. Therefore, Li-ions are also referred to as rocking chair batteries [1], [2].

During the life cycle of the battery, due to the mentioned charging and discharging processes, there is a gradual decrease in capacity. Because of ions drifting between two electrodes, a certain deformation in the material structure occurs, capacity is decreasing leading to the end of life of the battery. Another reason for capacity loss is growing of SEI layer.

## 2 RECYCLING PROCESS OF LI-ION BATTERIES

Today, the efficiency of recycling is about 50%, and the processes themselves focuses on recycling the cathode material, which contains many important elements like lithium, cobalt, nickel, manganese etc.. Recycling is interesting mainly from the economic point of view, total energy costs and total emissions are reduced [3].

Recycling technologies of LIBs essentially consist of physical and chemical processes, with physical processes mostly used in the pre-treatment of batteries to separate the cathode material from the used LIBs. The chemical processes themselves are then used to recover the cathode material. Nearly all of the recycling techniques were created to recycle LCO (LiCoO<sub>2</sub>) chemistry concentrating on the metals contained [4].

There are three main technologies we distinguish in recycling, namely pyrometallurgical, hydrometallurgical processes and direct recycling. The main issue in recycling is the diversity of compounds which can be used in LIBs as active material and for which appropriate separation process must be designed.

Pyrometallurgical process is based on high temperature combustion. Energy consumption is very high and the second drawback is the emission of toxic gases which are produced during combustion. The material obtained afterward can be considered as a sort of intermediate product, meaning that he must be refined or otherwise processed. The biggest advantage remains the high recovery factor for cobalt. Second, hydrometallurgical way is a more environmentally friendly, leaching in various acids or bases is used. Leaching process must be adapted to the given battery chemistry. Using this method, we obtain precursors ready for the preparation of cathode material. In a lot of cases companies combine these two approaches to take advantage of both. The third type, direct recycling, is apart from the previous ones not based on separating the material into individual elements but tries to regenerate the active material as a whole [5], [6].

## 2.1 DIRECT RECYCLING

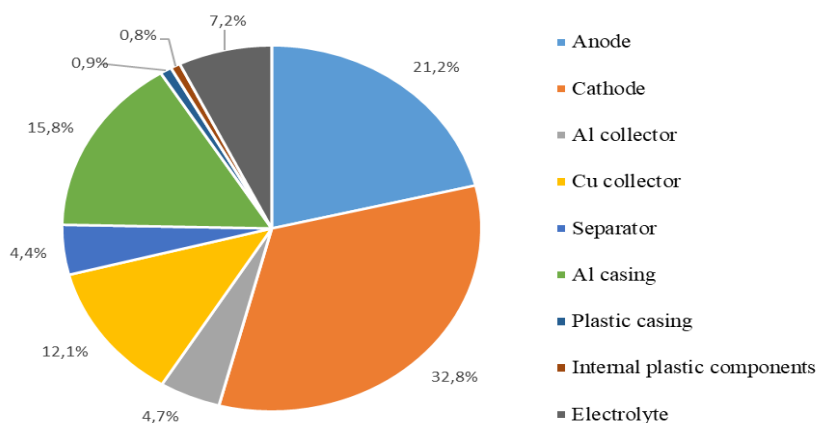
Effort is made to create a recycling method that would be less harmful to the environment and the obtained material could be directly used for the production of a new battery cell. Direct recycling is reaching this idea. Although it is still at level of research and not yet used commercially, it could theoretically give us high recycling efficiency rate (higher than 80%). It has the least steps to get final product, which can directly be used as a cathode material. In contrast to the other two methods mentioned, direct recycling is based on reactivation of capacity and other properties that were lost during life cycle of a battery. Defects in the active material can be fixed by relithiation process, meaning adding  $\text{Li}_2\text{CO}_3$  to the final product. Direct recycling cannot yet restore original properties of the materials fully, so the recycled material probably will not be as effective as it was in the beginning. Main advantages remain in less pollution and lower energy consumption. Also almost all of the materials from the accumulator can be restored, including aluminium [6], [7].

Main method used in direct recycling is separating the active material from its current collector by using some sort of solvent, which can dissolve binder that hold everything together. In most of the cases NMP and DMSO are trusted organic solutions, effectively dissolving PVDF, which is commonly used binder in LIBs. One of the approaches uses cyrene as a solvent for separation the cathode powder from collector. It is a solvent derived from cellulose waste, which could be good alternative for toxic NMP and DMF. Another advantage is that cyrene itself can be recycled and used again [4], [8].

## 3 RECOVERY OF CATHODE MATERIALS

For this work, the battery which we chose to extract the cathode material from, was commercial Samsung INR 18650-20R (2 000 mAh) with NMC ( $\text{LiNiMnCoO}_2$ ) chemistry. Rate capability test was performed using a different C-rates between 0.1 C and 1 C before and after long term galvanostatic cycling for 500 cycles at 1 C at 80% depth of discharge (DOD). The capacity of the battery after 500 cycles decreased by 9%.

The degraded cell was firstly discharged, and then dismantled in a hood. All parts of the battery were measured and weighted. We can see bill of materials that made up the battery in the **Figure 1**. Understandably, the biggest part of the battery constitutes of cathode (32.8 wt.%) and then the anode material (21.2 wt.%). Aluminium casing is on the third place taking up 15.8 wt.% of the battery mass and copper collector taking up 12.1 wt.%. The amount of electrolyte was determined as the deviation of the weights of individual dried components together from the weight of the whole battery.



**Figure 1:** All parts of lithium-ion cell (in wt.%)

### 3.1 EXTRACTION OF ACTIVE MATERIAL

In this work, we investigated influence of the temperature to the dissolution process of cathode materials in four selected solvents, namely dimethylsulfoxide (DMSO), n-methylpyrrolidone (NMP), cyrene and ethyl acetate. DMSO and NMP were picked because they are widely used in industry. In the effort to find an alternative mainly to the toxic NMP, cyrene and ethyl acetate were picked as a promising candidates.

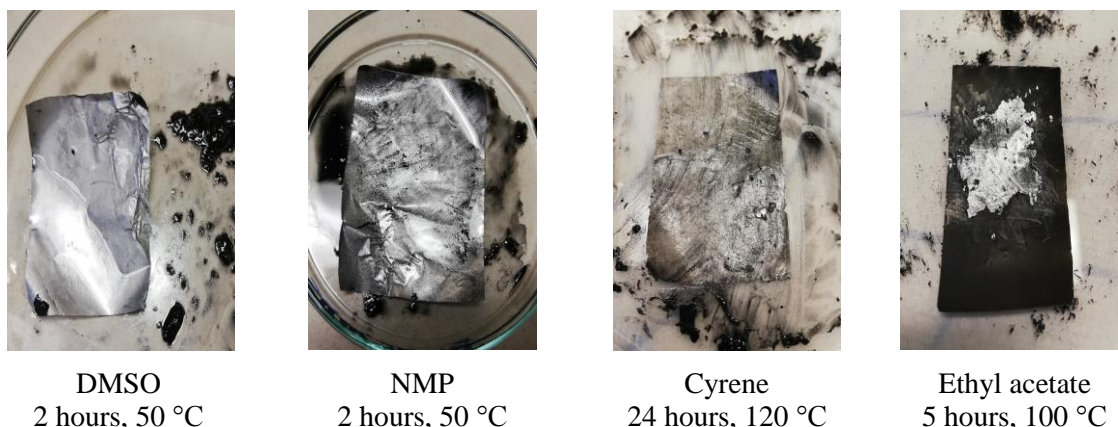
Cathode scraps were prepared and first test started at room temperature. Samples were continuously checked after 1, 2, 5, 10 and 24 hours. Same procedure was then repeated with the temperature at 50 °C, 75 °C, 100 °C and lastly 120 °C.

Using DMSO as a solvent at room temperature was not efficient, the material was almost unaffected, as it was with the other solvents also. Although when heated up to 50 °C, the material started to separate from the collector after only one hour. Visible waviness was spotted on the surface as the layer was detaching itself. After another hour in the solution, most of the material fell off the foil, and the rest was removed using scalpel.

As for the NMP, it was the only solvent that could be used without using heating. At room temperature small pieces of active substance started to fall into the solution, and after five hours it was possible to remove it entirely from aluminium. With the temperature rising to 50 °C the process speeded, and it took active material only 2 hours to detach. No speeding in the procedure was observed with further raising the temperature. At 75 °C it also took 2 hours, but the substance was more dissolving into the solvent rather than detaching itself as a whole piece. It was necessary to filtrate the solution afterwards.

Cyrene was chosen as a green solvent and so an alternative not only to NMP but also DMSO. The results in the beginning were not promising. Until 75 °C almost nothing was happening with the material and it could not be scraped off, or it was much harder than with the other solvents. The temperature needed to rise up to 75 °C in order to remove the material, although it took 10 hours to release the bonding, 24 hours to completely separate. The big difference was observed at 120 °C, when only after 1 hour the layer started to break. From the places where the surface was little corrupted it was easy to remove, complete removal took 24 hours.

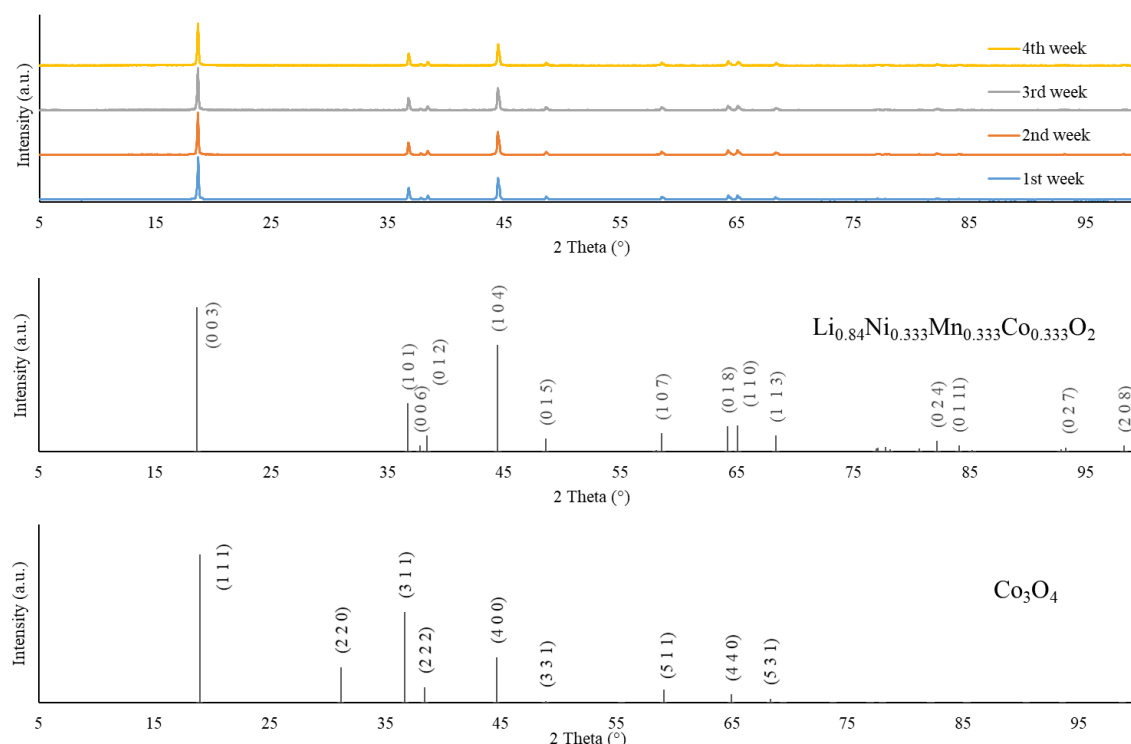
The last chosen solvent was ethyl acetate as it is less harmful for environment. This solvent was found out to be not as effective as the others. It evaporates very quickly and has boiling point of 77 °C. After crossing this temperature a little fall out from the scrap was observed, but it was probably due to boiling of the solvent which caused breaking of the cathode layer. There were visible cracks in the surface, the material was not dissolving in the solvent. Experiment was finished with the temperature of 100 °C, because it was hard to manipulate because of boiling solution.



**Figure 2:** Cathode scraps after dissolving in different solvents

In the **Figure 2** we can see photos of the cathode scraps after they were removed from the solvents mentioned above. It captures the samples at the time and temperature at which the best results were obtained for the specific solvent.

The structure of the cathode material was also observed using XRD analysis. The aim was to find out how the material would change when exposed to air for longer period of time and if it will make any structural changes. The studied material was the one obtained from scraps immersed in NMP for two hours at the 50 °C. Due to analysis, the material was identified as NMC111, meaning that molar ratios between the metals are 1:1:1, formula  $\text{Li}_{0.84}\text{Ni}_{0.333}\text{Mn}_{0.333}\text{Co}_{0.333}\text{O}_2$ . This material was found to have less than 1% of impurities, which most likely are formed by  $\text{Co}_3\text{O}_4$  (0.61%) based on structure analysis. Sample was measured during four week period, each measurement took place after one week. In the **Figure 3** we can see the comparison of all four diffractograms. As we can see, there are no considerable changes in the structure during long time measurement. This information is important in the sense of storage of the recycled material. Also, if the battery would undergo some damage, there would be no changes in the material itself, as it is not reactive and do not degrade.



**Figure 3:** Diffractograms for NMC material

## 4 CONCLUSION

Direct recycling as one of the approaches for recycling of spent Li-ion cells is discussed. With high recycling rate and lower ecological impact could replace economically and energetically demanding pyro and hydrometallurgical processes. Four different solvents were demonstrated to separate active cathode material from current collector. NMP and DMSO were most sufficient, NMP working without using heat. Since NMP has many disadvantages related to environment and health, using DMSO would be a better option. It breaks the binder similarly to NMP solvent, although slightly higher temperature must have been used (50 °C). Cyrene performed well and successfully separated active layer, but the lowest temperature was 120 °C. Material structure was analysed using X-ray diffraction and was defined as NMC111. The material appeared to be stable, does not react with air and no considerable degradation was observed, which is favourable material feature.

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## REFERENCES

- [1] Lithium-ion battery overview. KORTHAUER, Reiner. *Lithium-Ion Batteries: Basics and Applications*. 1. Berlin: Springer Nature, 2018, s. 13-19. ISBN 978-3-662-53071-9.
- [2] KAZDA, Tomáš. *Modifikace materiálů pro kladné elektrody lithno-iontových akumulátorů*. Vysoké učení technické v Brně. Fakulta elektrotechniky a komunikačních technologií, 2015.
- [3] PAGLIARO, Mario a Francesco MENEGUZZO. Lithium battery reusing and recycling: A circular economy insight. *Heliyon* [online]. Elsevier, 2019, **5**(6), 1-7. ISSN 2405-8440. Dostupné z: doi:10.1016/j.heliyon.2019.e01866
- [4] ZHANG, Xihua, Yongbing XIE, Hongbin CAO, Faheem NAWAZ a Yi ZHANG. A novel process for recycling and resynthesizing LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub> from the cathode scraps intended for lithium-ion batteries. *Waste management (Elmsford)* [online]. Elsevier, 2014, **34**(9), 1715-1724. ISSN 0956-053X. Dostupné z: doi:10.1016/j.wasman.2014.05.023
- [5] WANG, Yuqing, Ning AN, Lei WEN, Lei WANG, Xiaotong JIANG, Feng HOU, Yuxin YIN a Ji LIANG. Recent progress on the recycling technology of Li-ion batteries. *Journal of energy chemistry* [online]. Elsevier B.V, 2021, **55**, 391-419. ISSN 2095-4956. Dostupné z: doi:10.1016/j.jechem.2020.05.008
- [6] PIĄTEK, Jędrzej, Semih AFYON, Tetyana M. BUDNYAK, Serhiy BUDNYK, Mika H. SIPPONEN a Adam SLABON. Sustainable Li- Ion Batteries: Chemistry and Recycling. *Adv. Energy Mater.* 2020, 2003456. <https://doi.org/10.1002/aenm.202003456>
- [7] KIM, Hee-je, Kamran ZEB, Vinodh RAJANGAM, Sangaraju SAMBASIVAM a Ihab OBAIDAT. A Comprehensive Review of Li-Ion Battery Materials and Their Recycling Techniques. *Electronics* [online]. Basel: MDPI, 2020, **9**(7), 1161. Dostupné z: doi:10.3390/electronics9071161
- [8] BAI, Yaocai, W. Blake HAWLEY, Charl J JAFTA, Nitin MURALIDHARAN, Bryant J POLZIN a Ilias BELHAROUAK. Sustainable recycling of cathode scraps via Cyrene-based separation. *Sustainable Materials and Technologies* [online]. Elsevier B.V, 2020, **25**, 1-7. ISSN 2214-9937. Dostupné z: doi:10.1016/j.susmat.2020.e00202