# INFLUENCE OF AMBIENT ATMOSPHERE TO ACTIVE MATERIAL OF DISASSEMBLED LI-ION ACCUMULATOR

**Katerina Karmazinova**

Doctoral Degree Programme (1.year), FEEC BUT

E-mail: xkarma07@vutbr.cz

Supervised by: Tomas Kazda

E-mail: kazda@feec.vutbr.cz

**Abstract**: At the present time the worldwide hot topic is recycling. How to deal with the product at the end of its life cycle? This paper is focused on recycling of active cathode material of lithium-ion accumulators. The research considers the influence of ambient atmosphere on different types of lithium-ion accumulators within a time period. As the recycling method was chosen the solvent extraction. The results show a comparison of two the most common used cathode materials for lithium-ion accumulators – $LiCoO_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$. At the forefront is the time period from disassembly the lithium-ion accumulator to extract cathode active material without structure changes due to the effect of the air atmosphere.

**Keywords**: Lithium-ion, LIBs, Recycling, Cathode, Active material, Battery, Accumulator, Solvent extraction, XRD analyze

## 1 INTRODUCTION

The lithium-ion batteries are currently the most used source of electric energy for portable electronic devices, electric vehicles or energy smart storage systems. With rising consumption of lithium-ion batteries go hand in hand the question of the end of their life cycle. Recycling is on the front burner also because the Earth´s sources are not unlimited and this has to be considered in every respect. From the point of LIBs recycling are highly valued contained heavy metals (as Nickel, Cobalt, Manganese). However, for absolute recycling, we also have to focus on active material and separation of lithium from this type of accumulators. Due to the different materials used and the complexity of the traction batteries, the development of recycling processes is a complex task that requires the interaction of different disciplines. Combination of mechanical, fluid process engineering and hydrometallurgical methods are used to achieve the highest possible recovery rates. Using the approach to recover as many recyclable materials with high yields as possible a high efficiency of the method can be achieved.

Commercial methods for recycling lithium-ion accumulators are based on pyrometallurgical process. During this process, the disassembled battery is subjected to high-temperature smelting procedures to recover cobalt and nickel as alloys, but this process does not lead to the recovery of lithium active material from the battery. For recovery lithium active material the several hydrometallurgical processes exist, although they are not used in the commercial sphere. The main problem, as written above, is the complexity of lithium-ion accumulators. For commercially viable process is necessary to optimize the whole recycling method that is able to use regardless of the type of cathode active material in lithium-ion accumulator.

This work follows on from diploma thesis “Possibilities of lithium-ion accumulators recycling” that was focused on an overview of existing methods of recycling and recycling of cathode material.

## 2 BATTERIES AGEING PROCESS

The lithium-ion battery works on ion movement between the positive and negative electrodes. In theory, such a mechanism should work forever, but cycling, elevated temperature and aging decrease the performance over time. These factors lead to material degradation which goes hand in hand with a decrease of sufficient battery capacity. Manufacturers take a conservative approach and specify the life of Li-ion in most consumer products as being between 300 and 500 discharge/charge cycles. After this number of the cycle the capacity decrease on 80-60% of their original capacity and for majority application this is insufficient. For example, this number of cycles reaches a regular cell phone user after two or three years of using a cell phone. However, performing real-life aging tests for every single application is an expensive and time-consuming process which cannot be done in every case. To achieve credible results all tested batteries were connected to the multi-channel potentiostat (Biologic VMP3) and analyzed by electrochemical methods – cyclic voltammetry (CV), galvanostatic cycling (GCPL), electrochemical impedance spectroscopy (EIS), then accelerated aging process of 300 cycles galvanostatic cycling was carry out. A potential window was set in the range specified in the datasheet of the tested battery. Charge/discharge current was set to 2 C provided an appropriate load. After cycling battery was again analyzed and then completely discharged.

On the following graphs is shown the decrease of capacity of Panasonic NCR18650RX Li-ion accumulator during galvanostatic cycling with charge/discharge current set to 2 C and potential window in the range of 2.75 – 4.2 V. Parameters of this battery stated in the datasheet are in Table 1.

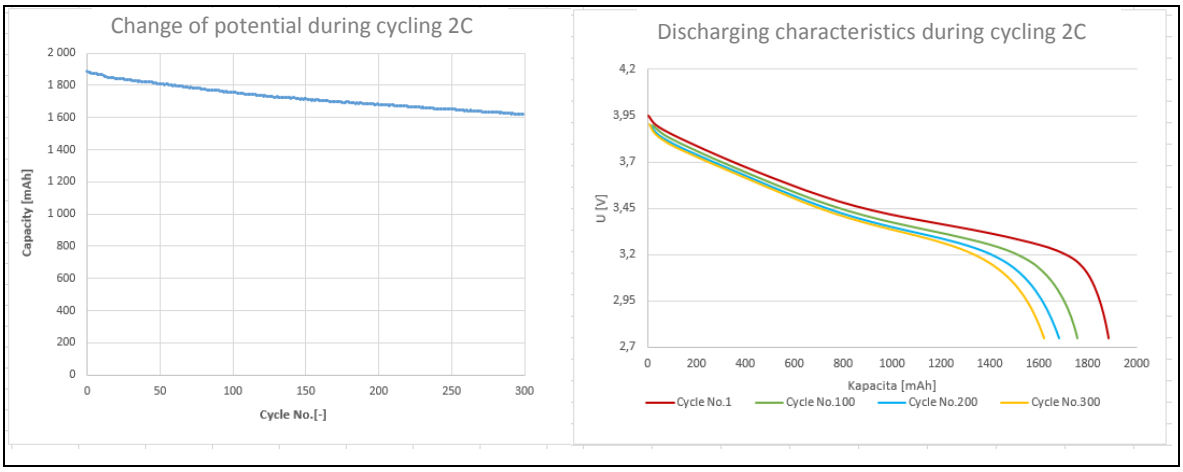


**Figure 1:** Battery characteristics during cycling

Before the beginning of the recycling process is important to completely discharge the accumulator. There is a risk of ignition during disassembly. Then each part of the accumulator can be recycled.

## 3 SOLVENT EXTRACTION

Dominated processes for recycling accumulators include the process of solvent extraction also known as liquid-liquid extraction, which increases the efficiency of metals recovery ratio. The process consists of the weakening of adhesive bonds of binder which are used to attach active material of electrodes to the current collector. During this process is necessary to choose the right organic solvent which is able to decompose binder as polyvinylidene fluoride or polytetrafluoroethylene.

For that application was chosen environment-friendly agent dimethyl sulfoxide (DMSO). Dimethyl sulfoxide is an apolar protic solvent that is generally used as a reaction medium and reagent in organic reactions. DMSO is well-nigh non-toxic and affordably priced in comparison with other commonly used solvents NMP (N-Methyl-2-pyrrolidone). The process has to be fully controlled

because each binder or each type of cathode has a different time to break down the adhesive bonds between aluminum foil and cathode material.

## 4 RESULT AND DISCUSSION

Obtained material from solvent extraction was dried overnight, pulverized in a ball mill and left in the ambient atmosphere. The prepared cathode material was separated into several samples that were continuously analyzed by XRD. For this research was used two types of cathode material for Li-ion accumulators. The influence of ambient atmosphere to degradation of active cathode material was investigated during measurements of samples for research recycling process of $LiCoO_2$ cathode material. It led to thinking if other types of commonly used lithium-ion cathode materials undergo the same range of degradation in the ambient atmosphere.

### 4.1 $LiCoO_2$ CATHODE MATERIAL

The $LiCoO_2$ active material was extracted from prismatic Li-ion accumulator. The XRD analysis was carried out within 24 hours and 4 weeks from accumulator disassembly. As shown in the following figures it was observed the material degradation. In time 24 hours after disassembly, the active material consists of pure $LiCoO_2$. The remeasure was performed after 4 weeks. The results (Figure 2) compare the XRD results. There are changes in the high and the positions of peaks. After 4 weeks was detected 91.02 % $Li_{0,35}CoO_2$ and 9.0 % $Co_3O_4$.

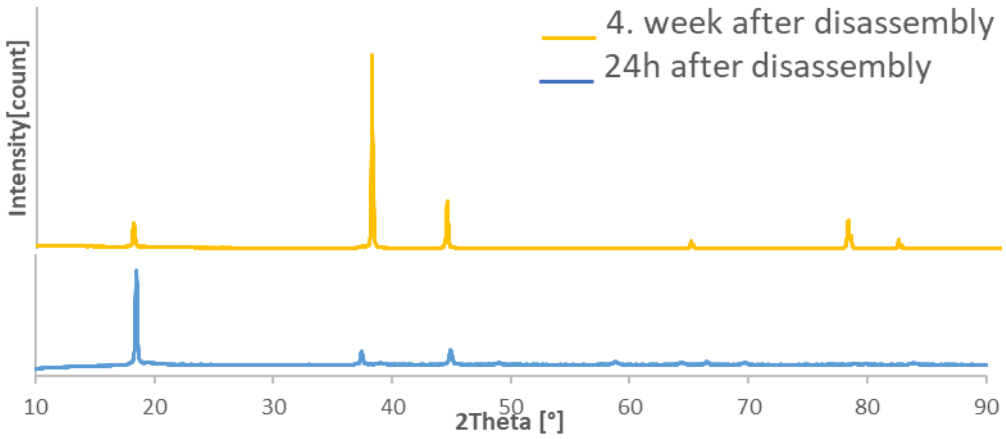


**Figure 2:** $LiCoO_2$ active material XRD analyze within 24 h. and after 4 weeks after extraction

The EDS analyze was also performed in that time period. And as shown on following pictures some structural changes are visible. Both examples have laminar structure, but in accordance to representation of detected elements of EDS analyze there are elements changes (Table 2.).

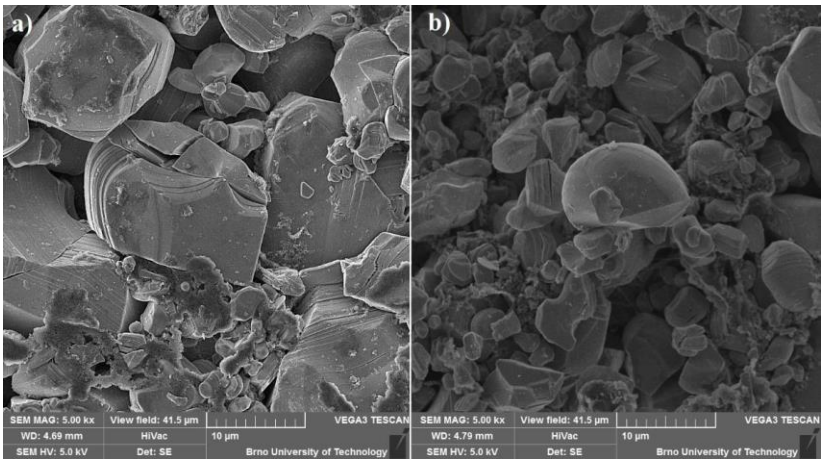


**Figure 3:** Electron microscope TESCAN VEGA3 - $LiCoO_2$ active material analyzed a) 24hours after extraction b) 4 weeks after extraction

| Element | AN | Series | Norm. C [wt.%] | | Atom. C [at.%] | | Error (3 Sigma) [wt.%] | |
|---|---|---|---|---|---|---|---|---|
| | | | 24h. after | 4.week after | 24h. after | 4.week after | 24h. after | 4.week after |
| Carbon | 6 | K-series | 11.51 | 8.38 | 24.12 | 19.77 | 5.46 | 4.27 |
| Oxygen | 8 | K-series | 33.20 | 28.07 | 52.25 | 49.69 | 12.57 | 10.78 |
| Cobalt | 27 | K-series | 55.29 | 63.55 | 23.63 | 30.54 | 4.57 | 5.25 |

**Table 2:** Comparison of EDS analysis of material 24 hours and 4 weeks after extraction

### 4.2 $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$

This is the currently most used type of active material in Li-Ion accumulators. The $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ active material was extracted from cylindric NCR 18650XR Li-ion accumulator.

The XRD analyze was performed within time period from 24 hours, to 20 days after disassembly. As is shown on figure, in comparison with $LiCoO_2$, the active material is not so influenced by the environment. During 20 days, when the material was exposed to the ambient environment and after remeasure, the composition of the material was not changed. The energy-dispersive spectroscopy of the sample (Figure 4) was performed on the cathode before extraction from aluminum foil. Electrode contain Ni, Mn, Co, conducting carbon and also elements from binder and electrolyte such as P and F.

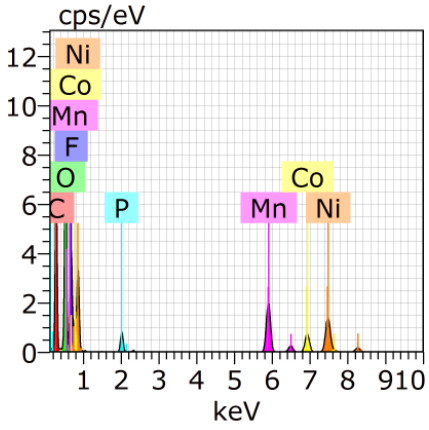


**Figure 4:** EDS analysis of cathode before process of solvent extraction

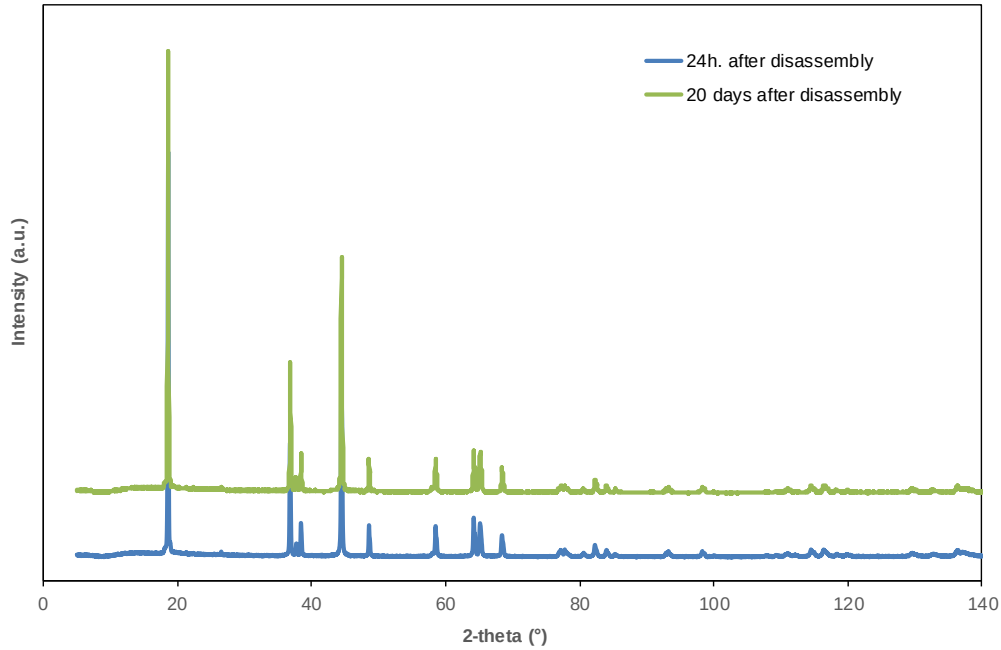


**Figure 5:** Comparison of XRD of active material $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ within time period

## 5 CONCLUSION

From the research that has been up to now performed, we can conclude that different type of cathode active material could be affected by the ambient atmosphere and other type is more stable in the surrounding environment. Until now the $LiCoO_2$ and $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ active cathode materials were tested within the time period to influence of the ambient atmosphere. $LiCoO_2$ undergo degradation in the environment. The origin chemical composition has changed with realizing the amount of $Co_3O_4$. Instead of this, the $LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ active cathode material does not change the chemical composition within 20 days after disassembly, so the process of next recovery can lead to better quality recycled cathodes. According to observed results is for finding comprehensive recycling process for lithium-ion accumulators necessary to know the exact battery composition and optimize the process of active material extraction.

## ACKNOWLEDGMENT

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## REFERENCES

[1] Karmazínová K., Kazda, T., Jandova, K., Li-Ion Batteries Recycling – Processes & Technologies, ECS Trans. 2017 81(1): 255-260; doi:10.1149/08101.0255ecst

[2] Conte, M., Conte, F.V., Bloom I., Morita, K., Ikeya T., Belt, J., Ageing Testing Procedures on Lithium Batteries in an International Collaboration Context; World Electric Vehicle Journal Vol. 4 - ISSN 2032-6653, 2010 WEVA p. 335-336

[3] Swain, B., Recovery, and recycling of lithium: A review. Separation and Purification Technology [online]. 2017, 172, 388-403; DOI: 10.1016/j.seppur.2016.08.031.; ISSN 13835866.

[4] Whittingham, M. ,Lithium Batteries and Cathode Materials. Chemical Reviews [online]. 2004, 104(10), 4271-4302, DOI: 10.1021/cr020731c. ISSN 0009-2665.