

RECOVERY OF COBALT AND LITHIUM FROM SPENT PORTABLE LITHIUM ACCUMULATORS AFTER INCINERATION

Martina Petranikova¹⁾, Andrea Miskufova¹⁾, Tomas Havlik¹⁾, Marek Vojtko²⁾

¹⁾Technical University of Kosice, Faculty of Metallurgy, Department of Non-Ferrous Metals and Waste Treatment, Letna 9, 042 00 Kosice, Slovak Republic

²⁾Technical University of Kosice, Faculty of Metallurgy, Department of Material Science, Letna 9, 042 00 Kosice, Slovak Republic

Abstract

Spent portable lithium accumulators (LiA) are secondary source of valuable metals such like: Co, Mn, Ni, Cu, Al, Li, etc. Sometimes the combination of thermal treatment and leaching is used to recover metals from spent LiA. Thermal treatment of black mass obtained from spent portable LiA can be used to remove carbon and organic compounds. In this work the effect of incineration at 300,500,700 and 900°C on cobalt and lithium extraction was studied. Samples without thermal treatment and after incineration were leached in 2M sulphuric acid with and without addition of hydrogen peroxide at 80°C. It was found out that incineration has a positive effect on cobalt and lithium extraction. Lower cobalt extraction occurred in case of leaching the sample incinerated at 900°C, because of presence stable phases with spinel structure, which were created during the incineration at this temperature

Keywords: hydrometallurgy, lithium accumulators, cobalt, lithium, incineration

1 Introduction

Portable lithium-ion accumulators (LiA) are the most used one among all available portable accumulators on the market. LiA serve as energy source for different kind of portable devices such: cell-phones, laptops, beepers, music players, etc [1]. More than 50% of LiA production is used for cell-phones [2]. 25% percent of produced LiA is used in portable computers.

LiA consist of two thin current collectors: the anode is made from metallic copper and the cathode from metallic aluminium. The cathode film is covered by an active material (LiCoO₂, LiNiO₂ or LiMn₂O₄) as a fine powder, aggregated with a polymeric binder PVDF (polyvinylidene fluoride) while the anode is covered by powdered graphitic carbon. In LiA, the anodes and cathodes are made from materials that allow the migration of Li-ions through an electrolyte solution. The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions [3]. The electrodes are separated by separator wetted by electrolyte. Spent portable LiA are valuable source of cobalt, nickel, manganese, lithium, copper and aluminium.

In general, spent portable LiA are recycled either by hydrometallurgical or combined way in laboratory and industrial scale. Thermal treatment is mainly used for organic compounds and graphite removal. Organic compounds used as binder cause problems during leaching and solid-liquid separation. Graphite causes a lower lithium extraction, because it acts as adsorbent for lithium [4]. There are some works, which used incineration for carbon and organic compounds removal before leaching in the Tab. 1.

Tab. 1 Summary of experimental conditions and obtained results from different authors.

authors	Incineration temperature [°C]	Leaching conditions	Co extraction before/after [%]	Li extraction before/after [%]
[4]	500	Distilled water / 90°C	-/-	20/90
[5]	700-900	1M HNO ₃ + 1.7 vol.% H ₂ O ₂ / 75°C	-/95	-/95
[6]	580-630	3M H ₂ SO ₄ + 3vol.% H ₂ O ₂ / 75°C	-/90	-/-
[7]	900	2M H ₂ SO ₄ + 15vol.% H ₂ O ₂ / 75°C	99/47	100/100
[8]	700	1.25M citric acid + 1vol.% H ₂ O ₂ / 90°C	-/90	-/100

It was found out, that calcination increased lithium recovery, because of carbon (adsorbent) removal [4]. In the work [7] it was noticed, that incineration decreased cobalt extraction from 99% to 47%, because of presence aluminium foils, which covered lithium cobalt oxide particles when became molten at high temperature.

Based on reported published works it is obvious that by thermal pretreatment carbon and organic binders are in general removed above temperature of 500-600°C and extraction of Li is consequently improved. On the other hand the effects of incineration on cobalt extraction have not been thoroughly and expressly examined in most presented studies. Thermal treatment was used only for pre-treatment of material without studying its influence on cobalt extraction.

In this work the possibilities of cobalt and lithium recovery from spent portable lithium accumulators after incineration were studied. The main aims were to observe effects of incineration on cobalt and lithium extraction and to determine optimal conditions for incineration and for following leaching of black mass from spent LiA.

2 Experimental

2.1 Material characterization

For experiments the lithium accumulators obtained from collection of spent portable batteries and accumulators at the Technical University of Košice were used. Total weight of used sample was 1027.19g. LiA without dismantling were crushed using a hammer mill SK 600. Samples for purpose of chemical analysis were obtained by quartation and following milling in vibration mill VM4. Chemical composition of sample with particle size less than 1mm after crushing and sieving is given in Tab. 2. Chemical composition of samples before and after thermal treatment was carried out by AAS analysis with Varian AA-20+. X-ray diffractometer PANalytical X'Pert PRO MRD (Co-K α) was used for qualitative phase analysis. Diffraction pattern of sample without thermal treatment is shown in Fig. 1.

Tab. 2 Chemical composition of sample after sieving (-1 + 0mm)

Element	Co	Li	Cu	Al	Ni	Fe	Mn
Content [%]	24.9	3.4	3.47	1.96	3.62	0.25	4.83
Element	C	As	Zn	Pb	Cr	Si	rest
Content [%]	43.2	0	0.07	0.05	0.013	0.215	14.02

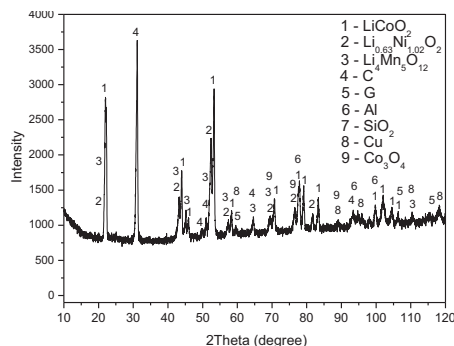


Fig. 1 X-ray diffraction pattern of sample

The active material such as LiCoO_2 , $\text{Li}_{0.63}\text{Ni}_{1.02}\text{O}_2$ and $\text{Li}_4\text{Mn}_5\text{O}_{12}$ were determined as well as phase of carbon and graphite in the sample by XRD analysis. Presence of aluminium, copper was also expected. SiO_2 is used as an addition agent. The phase of Co_3O_4 has origin in decomposition of LiCoO_2 , which occurs at elevated temperature or in the case when LiCoO_2 reacts with organic compounds during battery's life.

2.2 Experimental conditions

Incineration

Thermal treatment was carried out in the laboratory furnace. Samples were charged into the ceramic sampler and inserted into the furnace, which was heated up to required temperature. The air supply to the furnace was provided by compressor. Off-gas was cleaned by washing system, which consisted of five washing bottles. First of them was empty (safety reasons), the second one contained solution of 0.5M NaOH and the fourth one contained 0.5M H_2SO_4 . Distilled water was placed into the third and the fifth bottle. Experiments were carried out at the temperatures 300°C, 500°C, 700°C and 900°C for 60 minutes. Amount of sample was 5g. Loss on weight and chemical composition was determined after thermal treatment. XRD measurements of incinerated sample were also realized.

Leaching experiments

Leaching was carried out in glass vessel inserted in water bath. Required temperature was adjusted using thermostat Kavalier. For stirring the glass propeller was used. 2M sulphuric acid was used as a leaching agent. 30% hydrogen peroxide was used as reducing agent. Amount of hydrogen peroxide was 0vol.% or 15vol.%. Solid to liquid ratio was always 1:80. Experiments were carried out at temperature 80°C for 60 minutes. For leaching experiments the samples without thermal treatment and after incineration were used. Amount of sample was 5g. Liquid samples were analyzed by AAS (Varian AA-20+). Extraction values were corrected in compliance with loss of leaching solution due to sample off-take and solution evaporation.

3 Results and discussion

Thermodynamic study of incineration process

It can be assumed that during the heating LiCoO_2 decomposes to its oxides by following way: $\text{LiCoO}_2 \rightarrow \text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}$. During the decomposition the phase of Li_2O should be created together with oxygen gas. Seeing that sample contains relatively big amount of carbon, it

can reacts with oxygen and present oxides. Predicted reactions are described in Tab. 3 and the values of change of Gibbs free energy for reactions (1-5) are introduced in Tab. 4.

Tab. 3 Predicted reactions for process of incineration

$3LiCoO_2 + 3C + 2.75O_2(g) = Co_3O_4 + 1.5Li_2O + 3CO_2(g)$	(1)
$2LiCoO_2 + 2C + 1.5O_2(g) = Li_2O + 2CoO + 2CO_2(g)$	(2)
$2Co_3O_4 + 2C + O_2(g) = 6CoO + 2CO_2(g)$	(3)
$2CoO + 2C + O_2(g) = 2Co + 2CO_2(g)$	(4)
$Li_2O + CO_2(g) = Li_2CO_3$	(5)

Tab. 4 The values of change of standard Gibbs free energy for reactions (1-5)

Temperature [°C]	ΔG° [kJ]				
	(1)	(2)	(3)	(4)	(5)
300	-3058.474	-1967.100	-574.536	-403.073	-132.951
500	-3072.314	-1999.176	-643.917	-432.299	-103.356
700	-3088.051	-2032.481	-712.976	-460.854	-75.615
900	-3109.004	-2068.704	-780.184	-489.044	-57.679

The values of change of standard Gibbs free energy were calculated by HSC Chemistry 5.1. From values it follows that all reactions are possible from thermodynamical point of view and reactions tend to proceed along with creation of reaction products.

Of course besides proposed reactions, other side reactions of components such like $LiPF_6$, $AlPO_4$, Al, Cu, etc. could occur and in general the system of incineration is then more complicated.

Thermodynamic study of leaching process

XDR analysis has shown that lithium and cobalt are mainly present in the form $LiCoO_2$ in the input sample. The presence of Co_3O_4 was also confirmed. It can be expected that cobalt could be present in the form Co_3O_4 and CoO in the samples after incineration. Lithium can be present as Li_2O and LiF . LiF is the product of lithium salt ($LiPF_6$) decomposition. According to these predictions the possible leaching reactions were built up (Tab. 5). The values of change of Gibbs free energy for reactions (6-15) are introduced in Tab. 6.

Tab. 5 Predicted reactions for process of leaching

$LiCoO_2 + 1.5H_2SO_4 = CoSO_4 + 0.5Li_2SO_4 + 0.25O_2 + 1.5H_2O$	(6)
$CoO + H_2SO_4 = CoSO_4 + H_2O$	(7)
$2Co_3O_4 + 6H_2SO_4 = 6CoSO_4 + 6H_2O + O_2$	(8)
$LiCoO_2 + 1.5H_2SO_4 + 1.5H_2O_2 = CoSO_4 + 0.5Li_2SO_4 + O_2 + 3H_2O$	(9)
$CoO + H_2SO_4 + 2H_2O_2 = CoSO_4 + 3H_2O + O_2$	(10)
$Co_3O_4 + 3H_2SO_4 + H_2O_2 = 3CoSO_4 + 4H_2O + O_2$	(11)
$Li_2O + H_2SO_4 = Li_2SO_4 + H_2O$	(12)
$LiF + H_2SO_4 = Li_2SO_4 + HF$	(13)
$Li_2O + H_2SO_4 + 2H_2O_2 = Li_2SO_4 + O_2 + 3H_2O$	(14)
$2LiF + H_2SO_4 + 4H_2O_2 = Li_2SO_4 + 2O_2 + 4H_2O + 2HF$	(15)

Tab. 6 The values of change of standard Gibbs free energy for reactions (6-15)

Temperature [°C]	ΔG° [kJ]				
	(6)	(7)	(8)	(9)	(10)
80	-3272.03	-99.825	-311.02	-1996.57	-340.198
	(11)	(12)	(13)	(14)	(15)
	-275.696	-292.813	12.793	-533.186	-467.952

These values signify that almost all reactions are probable from thermodynamic point of view at given conditions and reactions tend to proceed along with creation of reaction products. Only reaction (13) has positive value of change of Gibbs free energy. LiF is very stable chemical compound and it doesn't react with sulphuric acid at the standard conditions.

3.1 Thermal treatment

Loss on weight by incineration

At temperature 300°C the mass sample was reduced by less than 10%. According to available data for average organics and carbon content in portable LiA, this temperature is probably not sufficient for burning out the organics and carbon. With increasing temperature the loss of weight increased. After incineration at temperature 500°C, sample weight was reduced by 25%. Around 40% of loss on weight was reached after incineration at 700 and 900°C.

XRD analysis of incinerated samples

There are diffraction patterns of incinerated samples at 300 and 500°C are shown in the Fig. 2 and diffraction patterns of incinerated samples at 700 and 900°C are shown in Fig. 3.

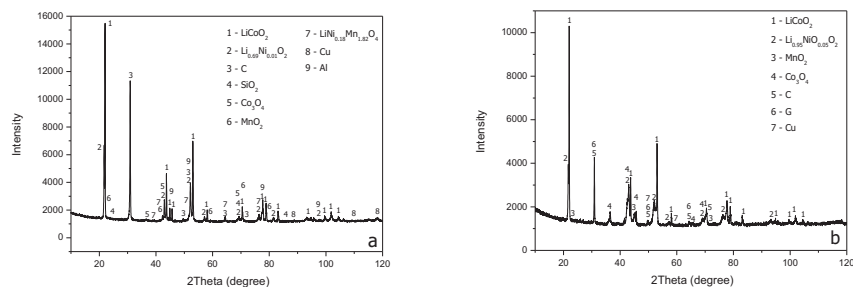


Fig. 2 X-ray diffraction patterns of sample after incineration a) at 300°C, b) at 500°C.

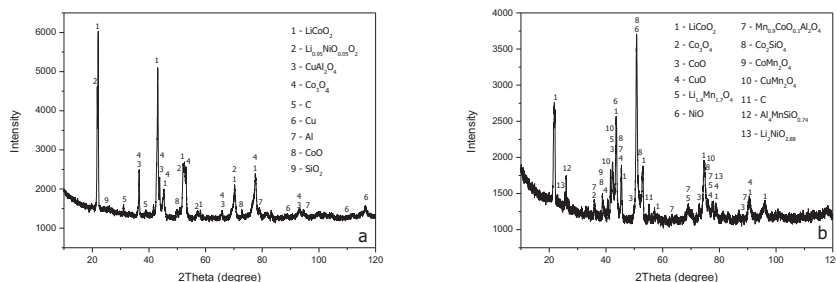


Fig. 3 X-ray diffraction patterns of sample after incineration a) at 700°C, b) at 900°C.

According to XDR analysis of the sample after incineration at 300°C (Fig. 2a) it is obvious that temperature 300°C is not sufficient for removal of carbon and LiCoO₂ decomposition. Partial decomposition of LiCoO₂ occurred at temperature 500°C, 700°C and 900°C (Fig. 2b, 3a, 3b). The phase Co₃O₄ was determined in the samples before treatment and after incineration. The phase CoO was found only in the samples after incineration at 700 and 900°C. As diffraction patterns show, carbon is still present in samples incinerated at relatively high temperature (Fig. 3b). The phases Li₂O and LiF weren't determine in the any samples. Some spinel and silicate phases (Al₄MnSi_{10.74}, CuMn₂O₄, CoMn₂O₄, Co₂SiO₄) were identified in the sample after incineration at 900°C.

Following the results of XRD analysis it can be said, that phase LiCoO₂ seems to be relatively stable under given conditions in the presence of the air and carbon up to around 700°C. It can be assumed that its partial decomposition can improve the leaching process. On the other hands the presence of different spinel phases can negatively affect the leaching of cobalt and lithium.

3.2 Leaching process

Untreated and incinerated samples were leached in 2M H₂SO₄ at 80°C without and with addition of H₂O₂. Kinetic curves of cobalt extraction under these conditions are shown in Fig. 4.

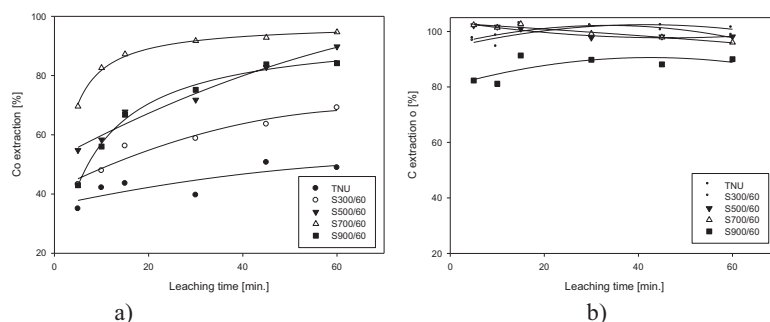


Fig. 4 Kinetic curves of Co extraction of incinerated samples in 2M H₂SO₄ a) without H₂O₂ and b) with 15 vol.% H₂O₂ at 80°C.

Cobalt extraction of untreated sample (TNU) is around 40% when H₂O₂ wasn't used. As follows from results Co extraction of samples after incineration is higher than Co extraction untreated samples at the same conditions. During the incineration partial decomposition of LiCoO₂ to Co₃O₄ occurred. Partial decomposition of LiCoO₂ to CoO happened at temperature 700°C and 900°C. Then higher cobalt extraction could be reached due to fact that Co²⁺ can be readily dissolved then Co³⁺. As follows from kinetic curves in Fig. 4a, cobalt extraction of sample incinerated at 300°C is also higher than cobalt extraction of untreated samples. The highest Co extraction value (almost 95%) was achieved with sample incinerated at 700°C. The cobalt extraction of sample incinerated at 900°C is lower than that one incinerated at 700°C. The presence of cobalt in the phases with spinel structure could cause this difference. Kinetic curves of cobalt extraction in 2M sulphuric acid with addition of H₂O₂ at 80°C are shown in Fig. 4b. The addition of hydrogen peroxide led to full extraction of cobalt in all cases except sample incinerated at 900°C. H₂O₂ is used as reduction agent and it causes the reduction of Co³⁺ to Co²⁺. From results of sample incinerated at 900°C follows that spinel phases created during the

incineration are stable and then cobalt wasn't leach out. Kinetic curves of lithium extraction are shown in Fig. 5.

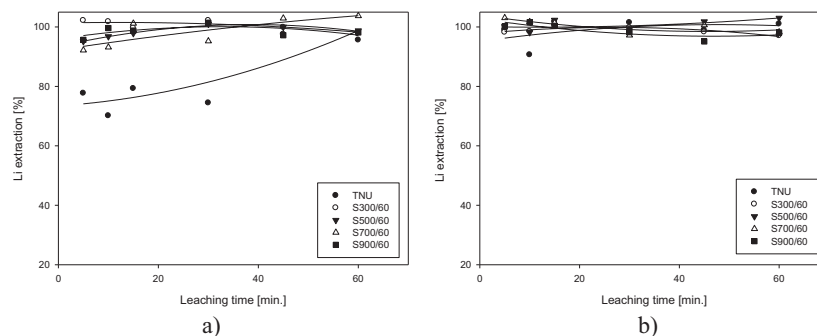


Fig. 5 Kinetic curves of Li extraction of incinerated samples in 2M H₂SO₄ a) without H₂O₂ and b) with 15 vol.% H₂O₂ at 80°C.

As follows from Fig. 5a and 5b incineration has no negative effect on lithium extraction, even full lithium recovery was reached after leaching of incinerated samples without addition of H₂O₂.

4 Conclusion

Possibilities of cobalt and lithium recovery from black mass from spent lithium accumulators were studied in this work. Samples of black mass were incinerated at 300°C, 500°C, 700°C and 900°C for 60 minutes. From results follows that partial decomposition of lithium cobalt oxide to Co₃O₄ happened at all temperatures of incineration. Partial decomposition of LiCoO₂ to CoO at 700°C and 900°C was confirmed by XRD analysis. On the other hand LiCoO₂ seems to be very stable, because it is still present in the sample after incineration at 900°C in the air and with the presence of carbon as reductant. Analysis also confirmed that even temperature 900°C is insufficient for graphite removal. Untreated samples and samples after incineration were leached in 2M H₂SO₄ at 80°C with and without addition of hydrogen peroxide. When untreated samples and treated samples were leached without addition of hydrogen peroxide, higher cobalt extraction was achieved from samples after incineration in comparison to untreated samples. The highest cobalt recovery (almost 95%) was achieved from sample after incineration at 700°C. When addition of hydrogen peroxide was used, total amount of cobalt was extracted from all samples except sample incinerated at temperature 900°C because of presence of spinel phases, which were created during the incineration. In general from results follows that thermal treatment has positive effect on cobalt and lithium extraction. Seeing that total cobalt extraction was reached only with using hydrogen peroxide, it is necessary further to study the influence of time on LiCoO₂ decomposition, because LiCoO₂ seems to be relatively stable compound and it is not easily dissolved. To confirm the total influence of incineration on black mass and cobalt and lithium extraction it is necessary to study its effects on the other elements and metals present in this material, mainly nickel and manganese, which are becoming a valuable part of this secondary raw material too.

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