THE POSSIBILITIES OF RECOVERY OF SELECTED METALS FROM LITHIUM BATTERIES BY PYROMETALLURGICAL WAY

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Abstract

Some recycling technologies are used to processing of waste lithium batteries. The treatment can be carried out pyro-metallurgically, hydro-metallurgically or both with respect to which metals must be obtained. Still looking for new ways to effectively process the waste Li batteries, so for example bio-metallurgy is also used. The Li-Ion batteries also contain other metals such as cobalt, copper, nickel and aluminium outside of lithium, which are very difficult to obtain. There are many types of lithium batteries, and the content of these metals is variable in each battery components. This paper is focused on the recovery of these metals by a pyrometallurgical process using a collector.

KEYWORDS: Lithium batteries, cobalt, pyrometallurgy, recycling, metals recovery

1. INTRODUCTION

Recycling of batteries and accumulators containing lithium is at the forefront of scientific interest. The recycling processes were initially focused on recovering only selected metals - cobalt, nickel, and manganese using pyro- and hydro-metallurgical techniques. The process of the mechanical separation of copper and aluminium or Fe was added later. Nowadays, numerous processing technologies for this type of batteries have been developed, including those aimed at obtaining lithium. Given the pressure to increase the share of battery recycling (increasing the proportion of materials used as secondary raw materials) and the increasing cost and demand for lithium, technologies are being introduced that enable obtaining both lithium and other metals as well as plastic materials. With the increasing production of electric vehicles and hybrid vehicles, the development of photovoltaic elements and EEE, the volume of lithium batteries will increase significantly. Lithium batteries contain hazardous components, and under certain conditions, they may be hazardous, which makes their recycling difficult [1-7].

Production of lithium batteries and accumulators continues to grow in the world, and more new types of batteries are being developed. Therefore, it is very difficult to determine the exact content of metals and other non-metallic components contained in them. Cobalt I highly valuable raw material, the gain of which is currently the most important economic parameter for recycling. As stated in [8], the lithium content in Li-Ion batteries (LiB) is in the range of 2-5 %, cobalt content in LiBs is up to 20 %. After separation of the electrode mass itself, the content of the metals of interest is higher in this fraction.

Given the processing technology used, the selected process conditions and the equipment used, it is possible to obtain various components that can be used as secondary raw materials. New and better technologies are still being developed in a number of already running research projects. In the case of new processes, an emphasis is also put on the possibility of repeated use of the recovered secondary raw materials for battery production.

2. DESCRIPTION OF THE EXPERIMENT

For the experiment, an electrode mass of Li-Ion batteries without a magnetic fraction was used. The batteries from laptops were crushed in a hammer crusher to remove magnetic particles. Subsequently, this material was screened, and a portion of undersize smaller than 0.4 mm was further used.

To obtain selected metals, a pyro-metallurgical process was used, in which copper was used as a collector. Copper was obtained after the processing of copper cables.

2.1. Preparation of the experiment

The electrode mass was annealed at 500 °C to constant weight. After annealing, a weight loss of about 13 % was found after a dwell of 40 minutes at a given temperature. The content of selected elements into LIB mass was determined by ED-XRF (Energy Dispersive X-ray Fluorescence) spectrometry, as in the initial state and after annealing. Charges contained 5, 10 and 15 wt% of LIB mass. The samples were made by induction melting and centrifugally cast into a graphite mould. The metal content in the castings was observed by OES (optical emission spectrometry) and ED-XRF spectrometry. After annealing, the metal content in the mass increased, and the cobalt content was then approx. 45 wt%. The determined contents of the selected elements are shown in **Table 1**.

Table 1 ED-XRF analysis of LIB material - annealing, 500 °C

Sample	An. No.	Co	Cu	Ni	Al	Si	Mn	Fe	Zn	Pb	Sn	Cd
		Content of metals (wt%)										
LIB 1	1	45.48	2.61	3.10	1.10	1.41	3.43	0.3608	0.6567	1.84	0.0297	0.0717
	2	45.47	4.15	2.86	1.83	1.40	3.01	0.3418	0.6301	1.96	0.0112	0.0505
	3	46.10	2.95	3.09	1.33	1.35	3.55	0.4184	0.8430	1.53	0.0154	0.0586
	4	43.82	6.31	2.86	1.60	1.46	3.33	0.3629	0.7382	1.48	0.0063	0.0992
LIB 2	5	46.67	2.01	2.95	1.04	1.43	2.94	0.4117	0.7176	1.53	0.0090	0.0648
	6	42.97	6.74	2.64	1.44	1.51	2.94	0.3628	0.8968	1.86	0.0089	0.0468
	7	46.31	2.38	2.96	1.04	1.38	3.21	0.4050	0.6465	1.56	0.0130	0.0586
LIB 3	8	48.55	2.49	2.77	1.31	1.42	3.04	0.3398	0.7162	2.02	0.0154	0.0467
	9	44.32	3.66	2.69	1.48	1.37	2.82	0.4783	0.7304	1.61	0.0249	0.0569
	10	45.19	2.47	2.84	1.15	1.45	3.08	0.3504	0.6543	1.53	0.0452	0.0535
	Avera-ge	45.49	3.58	2.88	1.33	1.42	3.14	0.3832	0.7230	1.69	0.0179	0.0607
	Devia-tion	1.50	1.59	0.15	0.25	0.04	0.22	0.0419	0.0828	0.19	0.0114	0.0148

Copper with a purity of min. 3N6, which was separated after the processing of copper cable waste, was used as a collector. Charge - Cu and annealed LIB mass - is shown in **Figure 1**. Pure copper and annealed LIB mass were used for the charge. Charges of copper and LIB masses containing 5, 10 and 15 wt% were prepared for the heats. Castings made of copper and LIB mass are hereinafter referred to as LIB5, LIB10 and LIB15. The castings made of pure copper are referred to as Cu 1 and 2 - wire. The melting point was chosen for pure Cu at 1200 °C and for mixture of copper and mass at 1550 °C. The charges were approximately 80 g with respect to the size of the crucible.

Figure 1 Charge - Cu and annealed LIB mass

2.2. Pyro-metallurgical process of metals recovery

The heats were performed in the equipment SUPERCAST 13 by the method of induction melting in an argon atmosphere, and then they were centrifugally cast into graphite mould (**Figure 2**). In this way, the cylinders with a diameter of 25 mm (**Figure 3**) were obtained. The castings were machined, cut at given points, and the chemical composition was determined by optical emission spectrometry (OES) using a SPECTROMAXx spectrometer. Control measurements were performed by the ED-XRF method using a Delta Professional spectrometer, acquired within the frame of the RMSTC project. The chemical composition of selected metals determined by both methods is comparable. The values of metal content determined by the OES method are shown in **Table 2**.

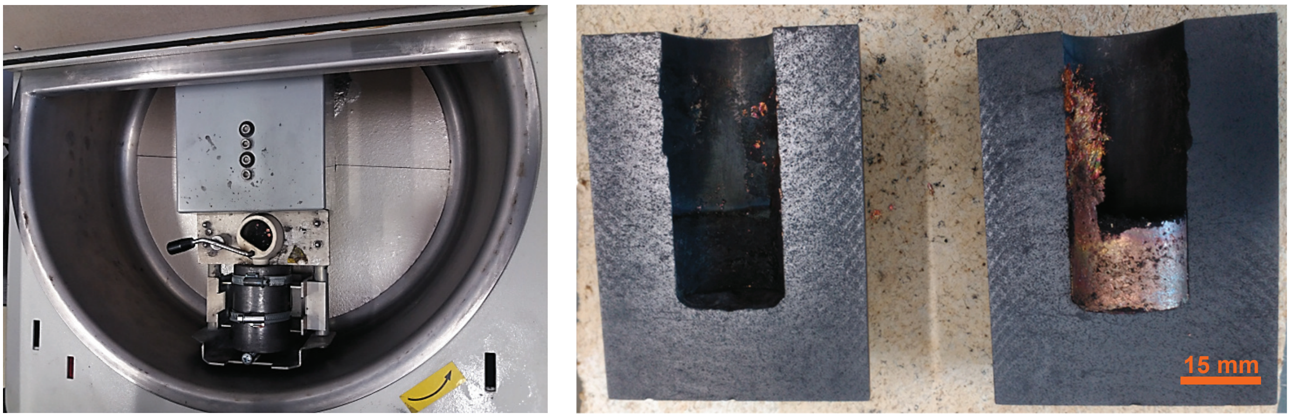

Figure 2 Melting and casting equipment, casting in a graphite mould

Figure 2 shows on the left the inside space of the furnace with the prepared charge in a corundum crucible and a graphite mould. The figure shows on the right the final casting in the mould. **Figure 3** shows on the left one of the castings cleaned from the rest of the LIB mass, and on the right 2 samples already prepared for chemical analysis using the OES method (**Figure 4**) and ED-XRF.

The measurement was performed at 3 points of the casting - in the upper, middle and bottom parts of the casting. The points of measurement are shown in **Table 2** as upper, middle and bottom. It can be seen from **Table 2** that the contents of the selected metals are similar at all three points of measurement and the castings are therefore homogeneous.

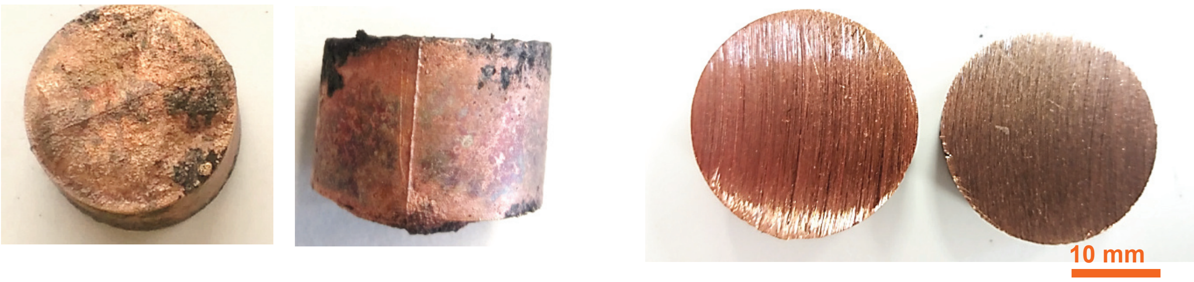

Figure 3 Cu casting with Co and other metals from LIB material

Table 2 OES analysis of pure copper and Cu collector (wt%)

Sample	Point of meas.	Co	Cu	Ni	Al	Si	Mn	Fe	Zn	Pb	C
Cu 1 wire	Upper	0.0000	99.9657	0.0057	0.0000	0.0000	0.0000	0.0000	0.0055	0.0000	0.0014
	Bottom	0.0000	99.9711	0.0050	0.0000	0.0000	0.0000	0.0000	0.0051	0.0000	0.0023
	Average	**0.0000**	**99.9684**	**0.0054**	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0053**	**0.0000**	**0.0019**
	Deviation	0.0000	0.0027	0.0004	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	0.0005
Cu 2 wire	Upper	0.0000	99.9607	0.0035	0.0000	0.0062	0.0000	0.0000	0.0052	0.0000	0.0061
	Bottom	0.0000	99.9648	0.0034	0.0000	0.0032	0.0000	0.0000	0.0058	0.0000	0.0044
	Average	**0.0000**	**99.9628**	**0.0035**	**0.0000**	**0.0047**	**0.0000**	**0.0000**	**0.0055**	**0.0000**	**0.0053**
	Deviation	0.0000	0.0020	0.0001	0.0000	0.0015	0.0000	0.0000	0.0003	0.0000	0.0009
Cu 3 LIB5	Upper	0.1840	99.5013	0.0280	0.0000	0.0054	0.0088	0.0000	0.0000	0.2430	0.0037
	Middle	0.1860	99.4717	0.0270	0.0010	0.0170	0.0084	0.0000	0.0000	0.2390	0.0200
	Bottom	0.1810	99.5292	0.0270	0.0062	0.0000	0.0110	0.0000	0.0000	0.2120	0.0032
	Average	**0.1837**	**99.5007**	**0.0273**	**0.0024**	**0.0075**	**0.0094**	**0.0000**	**0.0000**	**0.2313**	**0.0090**
	Deviation	0.0021	0.0235	0.0005	0.0027	0.0071	0.0011	0.0000	0.0000	0.0138	0.0078
Cu 4 LIB10	Upper	0.6900	98.6752	0.0940	0.0092	0.0000	0.0630	0.0056	0.0130	0.4080	0.0050
	Middle	0.7000	98.6479	0.0950	0.0086	0.0110	0.0640	0.0062	0.0130	0.4030	0.0160
	Bottom	0.7000	98.6615	0.1020	0.0130	0.0000	0.0650	0.0069	0.0140	0.3990	0.0078
	Average	**0.6967**	**98.6615**	**0.0970**	**0.0103**	**0.0037**	**0.0640**	**0.0062**	**0.0133**	**0.4033**	**0.0096**
	Deviation	0.0047	0.0111	0.0036	0.0019	0.0052	0.0008	0.0005	0.0005	0.0037	0.0047
Cu 5 LIB15	Upper	1.1100	97.5955	0.1740	0.0120	0.0220	0.1470	0.0150	0.0270	0.8000	0.0350
	Middle	1.1800	97.5296	0.1880	0.0120	0.0330	0.1420	0.0140	0.0270	0.7900	0.0340
	Bottom	1.0800	97.6534	0.1690	0.0110	0.0300	0.1350	0.0140	0.0290	0.7900	0.0290
	Average	**1.1233**	**97.5928**	**0.1770**	**0.0117**	**0.0283**	**0.1413**	**0.0143**	**0.0277**	**0.7933**	**0.0327**
	Deviation	0.0419	0.0506	0.0080	0.0005	0.0046	0.0049	0.0005	0.0009	0.0047	0.0026

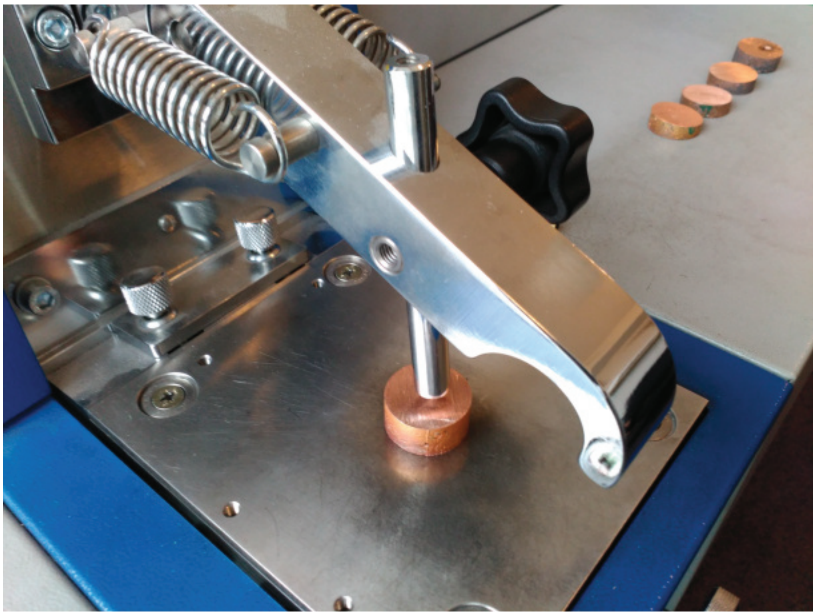

Figure 4 Measurement of Cu castings - OES method

Content of Sn and Cd is low, the values are in the order of thousandths of wt%. The contents of these metals are not listed in the table. Cobalt passed to the Cu collector depending on the LIB mass input fraction. It was found that after smelting the castings contained up to 1.12 wt% Co for the highest LIB mass. The carbon content was also determined by the OES method.

The LIB mass after re-melting was again analysed by ED-XRF method. The composition of the residual LIB mass after melting exhibits some depletion of Co, Ni, Al and Mn metals, but a certain amount of these metals still remains in the LIB mass.

3. CONCLUSIONS

A LIB mass was used for the experiment, which was annealed at 500 °C to constant mass. The contents of the selected metals were determined in the initial state and after annealing. The metal content after annealing in the LIB electrode material increased and the cobalt content was approx. 45 wt%. The annealed mass and pure copper were melted by vacuum induction melting in an Ar atmosphere. The melt was centrifugally cast into a graphite mould. The castings thus prepared were machined and cut in several points. The places of cuts were dry ground and they were used to determine the metal content in the castings. The cobalt content was determined also in the mass that remained after melting. It was found that after smelting the casting contained up to 1.12 wt% of Co for the highest percentage of LIB mass. The cobalt content in the mass after melting was by several percents lower than the input feedstock, but in spite of that, its content was high. The melting process can be further improved.

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