Classification of spent Li-ion batteries based on ICP-OES/X-ray characterization of the cathode materials

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Abstract

Development of lithium-ion batteries (LIBs) during the latest decades resulted in improved performances of the new integrated cathode materials and in their wide applications. This rapid expansion of new materials led to the intensive replacement of the old-fashioned, traditional materials and increased a simultaneous accumulation of both kinds of materials at extremely hazardous electronic waste sites, which additionally increased an urgent need for their recycling. Most importantly, in this way, spent LIBs may further serve as a significant source of valuable metals such as Li and cobalt. However, one of the key problems in LIBs recycling is the absence of a precise battery classification/sorting based on the chemical composition of the used cathode material. In this paper, characterization of the cathode material was performed regarding chemical composition of 40 samples of spent LIBs using inductively coupled plasma - optical emission spectrometry and X-ray diffraction. Preparation of the samples, (pretreatment) included: discharging, dismantling, separation of the main components (cathode, anode and the separator), and detachment of the cathode material from the aluminium foil. The obtained results showed that, in the investigated commercially available LIBs, lithium cobalt oxide was the most frequently used (cathode) material.

Keywords: LIBs sorting; Instrumental analysis; lithium cobalt oxide; recycling

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1. INTRODUCTION

Lithium-ion batteries (LIBs) were principally developed in Japan by the company Asahi Kasei Co in order to respond to the growing need for batteries with better characteristics, whereby the companies Sony Co, Japan (during 1991) and A&T Battery Corp., Japan (during 1992) contributed significantly to their commercialization [1]. In comparison with the other types of similar products, LIBs have a longer service life, low self-discharge efficiency, high specific energy and energy density, wide range of operating temperatures, negligible memory effect and a very high capacity while not requiring almost any maintenance; these properties contributed to consideration of LIBs as the best solution for sustainable transport and smart electronics [2-7]. For instance, the existing expansion of information technologies, and hybrid and electric vehicles (HEV and EV, respectively), resulted in a constant growth of applications of LIBs [8-10]. It is estimated that the global LIB-market will reach USD 93.1 billion by 2025, whereby in 2016, lithium cobalt oxide ($LiCoO_2$), as a dominant product segment, valued USD 7.15 billion [11].

A typical LIB consists of a cathode composed of $LiCoO_2$ adhered to an aluminium (Al) sheet and an anode made of graphite adhered to a copper (Cu) sheet; the other important constituents include the appropriate organic electrolyte, a separator, and a metallic shell. Separation of the electrodes is usually accomplished by a plastic film, which is further covered by a metal casing wrapped in another plastic. The electrodes are soaked in an electrolyte, the composition of which depends on the brand and/or battery model; the most commonly used electrolytes are $LiClO_4$, $LiBF_4$ and $LiPF_6$ [12].

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Due to the high costs and a problematic safety of $LiCoO_2$, development of new cathode materials is in constant progress, including combinations such as $LiNiO_2$, $LiMPO_4$-type olivines (M = Fe, Co, Ni, Mn), $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$, and $LiMn_2O_4$ [13-14]. According to a survey of the battery market, performed in 2012, the most used cathode material was $LiCoO_2$ with the share of 37.20 %, while the shares of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$, $LiNiO_2$ and $LiFePO_4$ were smaller, and accounted for 29.00, 21.40, 7.20 and 5.20 %, respectively [14].

Among the LIB constituents, the oxide layer coating the cathode ($LiCoO_2$) represents the part with the highest recycling potential [15]. Positive environmental aspects of cobalt recovery should be certainly considered due to the risks originating from Co carcinogenicity, mutagenicity and a general toxicity to human health [3]. Lithium, as one of the main components of LIBs, represents a very valuable metal with many industrial applications, but it can cause serious environmental problems, too (prevailingly due to its reactivity with H_2O, N_2, and O_2) [16]. The environmental harms could be also attributed to some other LIB-components such as electrolytes containing toxic organic compounds and LiOH (exhibiting extremely corrosive properties), as well as to the extremely dangerous heavy metals [16,17]. From the environmental point of view, recovery of metals present in spent LIBs is preferable [18]. The recovery of Co is recognized as the most economically reasonable since it is estimated that this metal is twice as expensive as Ni and 15 times as expensive as Cu [3].

One of the main problems associated with the development of a LIBs recycling process is the inability to identify the exact composition of the cathode material. Practically, the manufacturers of LIBs do not provide details on the individual components and their chemical compositions, which represents a serious obstacle in various investigations related to the spent LIBs. In fact, many large companies already have their own processes and devices for battery sorting developed based on their physical properties. For example, the Philips company, developed a sorting machine based on battery dimensions, mass and electromagnetic properties [19]. In addition, there are some opinions that many other battery characteristics and parameters may be used as sorting criteria in recycling processes, such as the cell capacity, internal resistance, open circuit voltage, self discharge rate *etc.* [20]. These characteristics are typical monitoring parameters in the separation processes of healthy cells from the bad ones in used battery packs or modules [21]. They are chiefly but not exclusively affected by the ingredients, or composition and structure of the battery material. The applied temperature, state of health, state of charge, charge/discharge current rate, etc. may also represent very important influential factors [20]. There are many examples in the scientific literature on sorting based on capacity and internal resistance [22], electrochemical impedance spectroscopy [23], voltage curve [24], dynamic parameters [25], thermal behavior [26], *etc.*

In this paper, possibilities for classification of spent LIBs based on the type of the cathode material were investigated with the main aim to demonstrate that this approach can improve sorting of Li-ion batteries so to be more precise and profound.

2. EXPERIMENTAL

Characterization of the cathode material in the collected samples of battery cells was performed by using inductively coupled plasma - optical emission spectrometry (ICP-OES), as one of the most accurate methods for elemental analysis. In this study, it was applied for detection of metals present in the cathode materials, while their crystal structures were identified by using the X-ray diffraction method. The identification of the cathode materials was performed after a specific pretreatment consisting of: discharging of the spent cells, dismantling, separation of the main cell components (cathode, anode and separator), and removing of the cathode material from the Al-foil.

2. 1. Materials and reagents

In this research, 40 spent LIBs of different manufacturers were taken from about forty laptop computers (produced during last 20 years) and then subjected to a specific pretreatment and finally to ICP-OES/XRD-analyses. In order to determine the total metal concentrations in the cathode material, the acid digestion was performed in aqua regia using 65 % HNO_3 and 36 % HCl (Merck, Darmstadt, Germany), in ratio 1:3. All reagents used in this study were of analytical purity and the solutions were prepared by deionized water.

2. 2. Experimental procedure

2. 2. 1. Pretreatment

After the removal of plastic battery cases, the cells were separated into 22 different types based on their visual characteristics (colour of the plastic cell covering, the ring around the positive contact and the model number). The investigated LIB cells were subsequently numbered from 1 to 22, discharged using a wire with a resistance of 5.5 Ω, and then manually dismantled. Materials inside the cells were separated as a cathode, anode, separator and a metallic shell. In order to separate the cathode material from the Al-foil, heating was performed for 10 min at 580 °C in a muffle furnace (which contributed to the removal of polyvinylidene fluoride (PVDF)), and finally, the material was cooled at room temperature. However, since the vast majority of the cathode materials still remained attached to the separator, this part was further heated to 300 °C. The cathode powder obtained by this particular heating process was further mixed with the cathode powder obtained after heating of the Al-foil; finally, the obtained combined powder was additionally heated for 6 h at 630 °C (to remove organics such as acetylene black (AB) and carbon (C)). Subsequently, 0.5 g of the prepared cathode powder of each cell was dissolved in 20 mL of the prepared mixture of HNO_3 and HCl (1:3); afterwards, 15 mL of each sample was taken and transferred into a 100 mL volumetric flask and filled up with demineralized water. All the samples were filtered, and 1 mL of each solution was taken and transferred into a new volumetric flask and filled up to 25 mL using 1 % HNO_3.

The described steps in the pretreatment of the spent LIBs are shown in Figure 1.

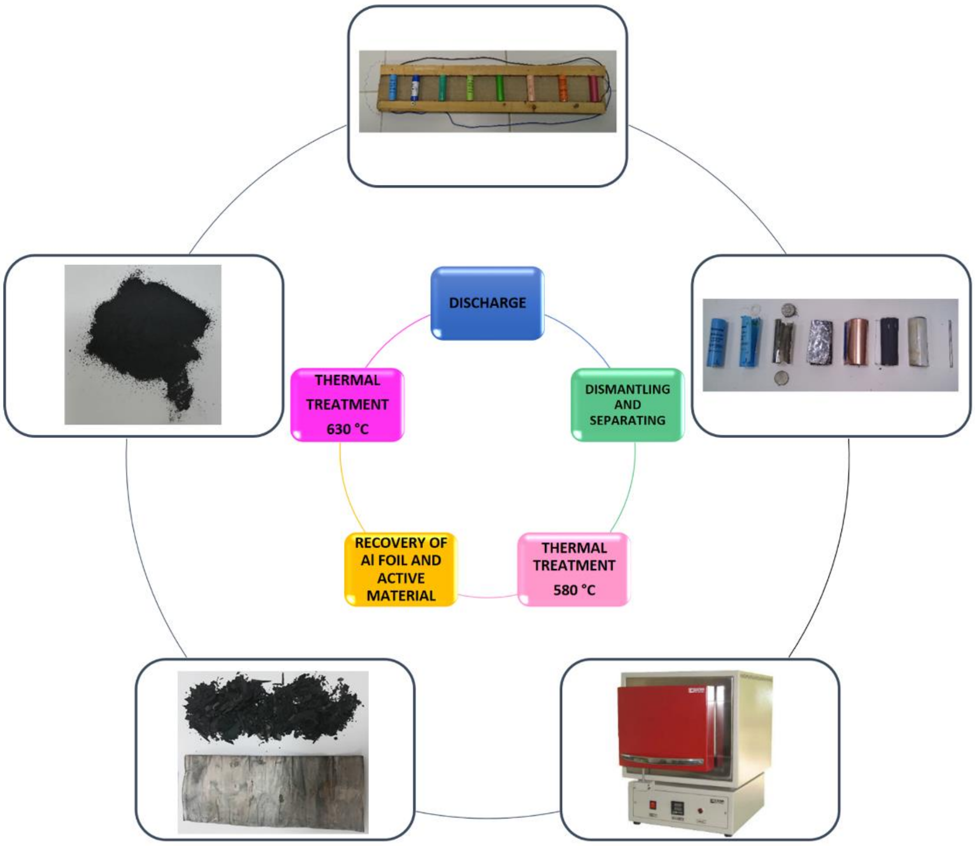


Figure 1. The main steps in the applied pre-treatment procedure

2. 2. 2. Analytical methods

The optimum temperature for calcination of the cathode material from the selected spent LIBs was determined by the thermogravimetric analysis (TGA), using an SDT Q600 apparatus (Oxford, UK). TGA experiments were operated in the temperature range from 70 to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

ICP-OES was applied for determination of the contents of Li, Co, Mn, Ni, Al and Cu, using the instrument PerkinElmer Optima 8300 (PerkinElmer, USA). The operating conditions employed in the ICP-OES analysis were 1300 W RF power, 8 dm^3 min^{-1} plasma flow, 0.5 dm^3 min^{-1} auxiliary flow, 0.75 dm^3 min^{-1} nebulizer flow, 2 cm^3 min^{-1} sample uptake rate. Axial view was used for metals determination, while 2-point background correction and 4 replicates were used to measure the analytical signal. The emission intensities were obtained for the most sensitive lines free of spectral interference. Calibration standards were prepared by diluting a stock multi-elemental standard solution (1000 mg dm^{-3}) in 0.2 % nitric acid. The selected emission lines for the investigated metals were as follows: 610.362 nm for Li, 238.892 nm for Co, 257.610 nm for Mn, 221.648 nm for Ni, 396.153 nm for Al and 327.393 nm for Cu. The obtained results were expressed as mg dm^{-3} (for each metal), as it is given in the Table 1 together with the related mole fractions.

Crystal structures of the present cathode materials were identified by using an X-ray diffractometer (XRD Rigaku MiniFlex 600, Novara, Italy) equipped with a Cu X-ray source (40 kV/15 mA operation for X-ray generation). The operating conditions employed for the XRD analysis were: angular range 3-90°, step size of 0.02°, scanning speed of 10° / min. The subsequent identification of minerals was performed by using the PDXL 2 Version 2.4.2.0. Software, and the obtained diffractograms were compared with the patterns in the database ICDD (PDF-2 Release 2015 RDB). The detection limit for the XRD analysis was ~1 %.

3. RESULTS AND DISCUSSION

3. 1. TGA results

The results of the performed TGA are shown in Figure 2. Three main weight-loss regions were observed at 70−140 °C, 140−570 °C, and 570−630 °C, whereas the fourth region at 630−700 °C was characterized by a weight gain. The first weight-loss region (ca. 0.5061 wt %), *i.e*. between 70 and 140 °C, could be attributed to the loss of bound water [27]. However, the study of Veluchamy *et al.* [28] indicated that the weight loss in the region around 100 °C may be attributed to evaporation of the electrolyte. The second weight-loss region, *i.e*. between 140 and 570 °C (ca. 3.233 wt %), probably corresponded to the decomposition of $LixCoO_2$ into $LiCoO_2$, Co_3O_4 and O_2 [28], followed by pyrolysis of PVDF. The third weight-loss region, *i.e*. between 570 and 630 °C (ca. 0.7828 wt %) could be explained by a loss of carbon black [29]. The fourth region, *i.e*. between 630 and 700 °C, was characterized by a weight gain, which could be a result of the heterogeneity of the system. For example, there is a possibility for development of some specific reactions of traces of Al in the prepared cathode powder (remained from the Al-foil) with some of the components in the system.

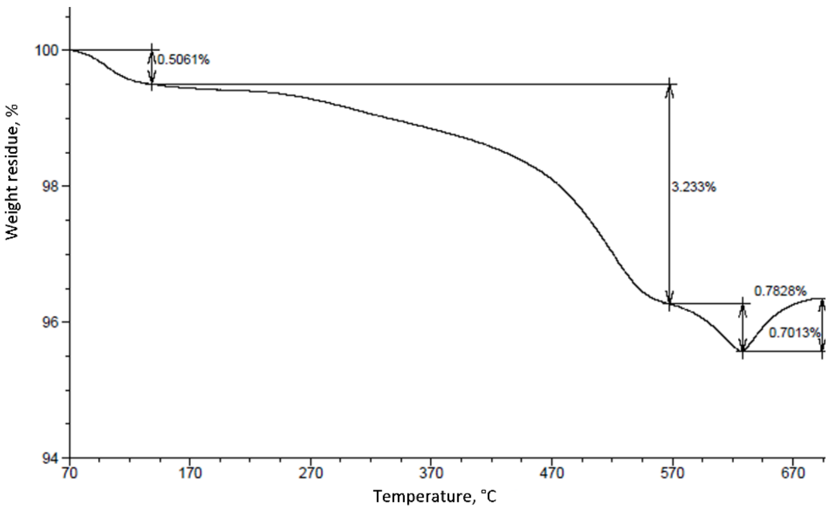


Figure 2. TG curves of the spent cathode materials

Based on the obtained results, it can be suggested that the temperature program of the thermal treatment of spent LIBs should be raised up to a minimum of 550 °C and below the melting point of Al (660 °C). Also, given that a maximal removal of the active cathode materials from Al-foils happens after the multi-stage heating treatment, it is clear that, in this way, the cathode material can be easily peeled off from the foil (with only a minimal loss); Al-foils can be further recycled, too.

3. 2. Chemical composition and characterization of the investigated cathode materials

Chemical composition of the cathode material for each individual cell is shown in Table 1. It can be supposed that the detected concentrations of Al and Cu represent the impurities remained after the pretreatment of the cells.

Table 1. Chemical composition of the cathode materials in the investigated LIBs represented on the basis of the detected metal concentrations and the calculated mole fractions

Model	Sample	Concentrations, mg dm^{-3} (Mole fractions)					
		Li	Co	Mn	Ni	Al	Cu
1.	ILIFJT7	6.14539 (0.54162)	43.18573 (0.44828)	/	/	0.44400 (0.01007)	/
2.	IFOH2	6.11016 (0.53724)	43.73847 (0.45294)	/	/	0.43076 (0.00975)	/
3.	MICFK56	6.05325 (0.54586)	41.62086 (0.44205)	/	/	0.51827 (0.01202)	/
4.	GKCFHH2	6.13368 (0.52737)	44.47048 (0.45033)	/	/	1.00606 (0.02226)	/
5.	CGR18650 CF	9.34490 (0.34584)	45.76804 (0.19949)	51.92102 (0.24276)	47.56082 (0.20815)	0.39309 (0.00374)	0.39188 (0.00158)
6.	CGR18650 HG	7.47528 (0.59232)	42.79500 (0.39938)	/	/	0.40960 (0.00835)	/
7.	LGDS218650	5.32102 (0.55194)	36.13915 (0.44151)	/	/	0.23631 (0.00630)	0.00826 (0.00009)
8.	NA	/	0.79081 (0.06702)	4.13711 (0.37615)	5.81042 (0.49449)	0.40220 (0.07369)	0.13314 (0.01036)
9.	SF US18650GR	14.67983 (0.58642)	86.42932 (0.40664)	/	/	0.66849 (0.00687)	/
10.	US18650GR	4.23471 (0.58720)	25.11291 (0.41013)	/	/	0.06859 (0.00244)	/
11.	US17670GR	6.67607 (0.58036)	40.91639 (0.41892)	/	/	0.02496 (0.00056)	/
12.	ICR18650-22F	8.47835 (0.34014)	25.57337 (0.12083)	45.66662 (0.23147)	64.80665 (0.30747)	/	0.55766 (0.00244)
13.	ICR18650-22H	8.49949 (0.34942)	24.81588 (0.12015)	43.81556 (0.22758)	61.99779 (0.30141)	0.13457 (0.00142)	0.67035 (0.00300)
14.	CGR18650A	6.29586 (0.57818)	38.95222 (0.42131)	/	/	0.00777 (0.00018)	/
15.	ICR18650-22E	7.01165 (0.55341)	47.88525 (0.44514)	/	/	0.05759 (0.00117)	0.15729 (0.00135)
16.	ICR18650-22B	6.02955 (0.57985)	37.01184 (0.41921)	/	/	0.02496 (0.00062)	/
17.	LGR18650P	6.65093 (0.57162)	42.27406 (0.42792)	/	/	/	/
18.	LGDS318650	8.54289 (0.33973)	23.84106 (0.11166)	45.17901 (0.22699)	68.36522 (0.32151)	/	0.23359 (0.00101)
19.	CGR17670A	6.02609 (0.57151)	38.25157 (0.42727)	/	/	0.03088 (0.00075)	/
20.	CGR18650C	4.83715 (0.57951)	29.74010 (0.41964)	/	/	0.00914 (0.00028)	/
21.	ICR18650-20B	6.95475 (0.55456)	47.07101 (0.44207)	/	/	0.146278 (0.00295)	1.93049 (0.01654)
22.	ICR18650-20	5.73206 (0.56734)	36.93702 (0.43059)	/	/	0.06277 (0.00160)	/

NA – not available; / – below detection limit

Based on the calculated mole fractions of metals in the investigated cathode materials, it can be concluded that a great majority of the analysed materials consisted of $LiCoO_2$ while the cathode material in the samples 5, 12, 13 and 18 was $LiNiMnCoO_2$; the absence of Li was noted in the cell marked as the sample 8. These results were further confirmed by the XRD analysis, *i.e.* during determination of crystal structures of the prepared samples. Three characteristic examples of the obtained XRD patterns (practically - for the three above described cases) are presented in Figures 3-5.

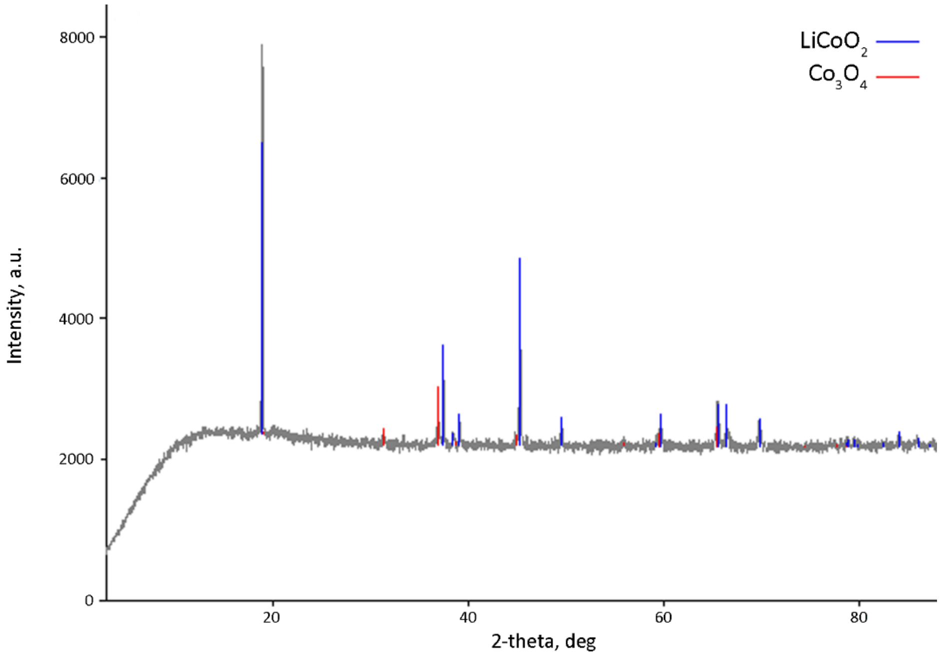


Figure 3. XRD pattern of the cathode material in the sample 1

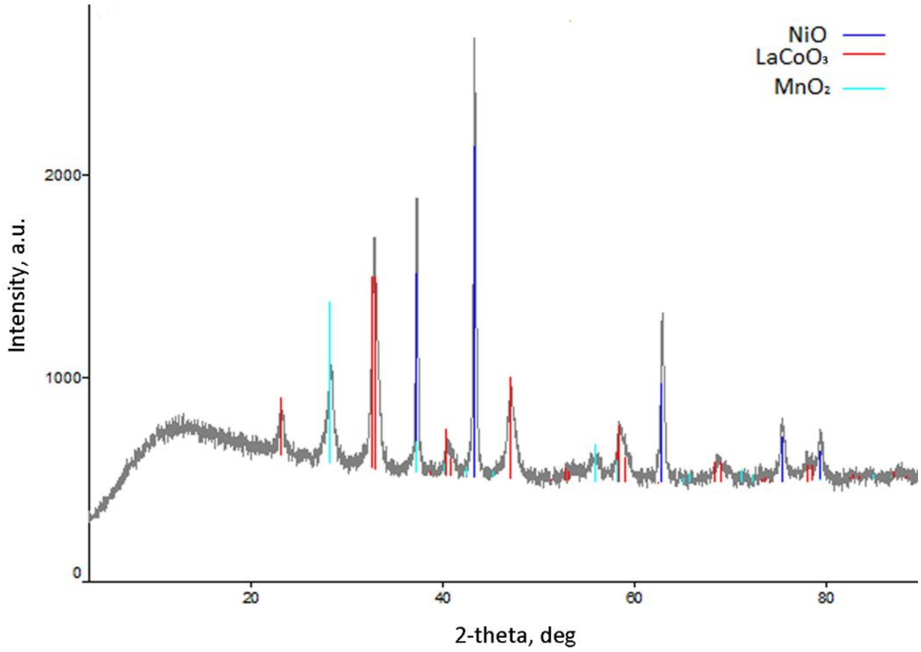


Figure 4. XRD pattern of the cathode material in the sample 8

XRD pattern in the first example in Figure 3 (sample 1) clearly indicated that Li and Co were present as $LiCoO_2$, as well as that Co was also present in the form of Co_3O_4 (it was possibly generated during the battery operation or decomposition and transformation of heated $LiCoO_2$) [30-33]. The XRD pattern presented in Figure 4 showed that the cathode material in the sample 8 contained $LaCoO_3$, which confirmed the absence of Li in this sample. Finally, the XRD pattern determined for the sample 13 indicated $LiNiMnCoO_2$ as the only crystal phase (Fig. 5). The absence of carbon peaks denoted that most carbon residues were destroyed by burning during calcination [32,34].

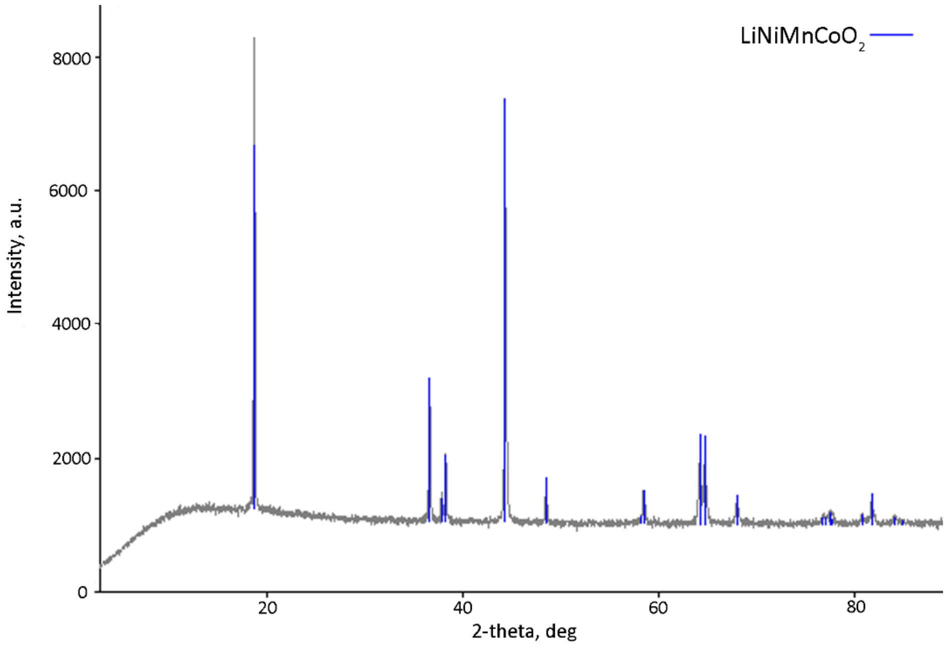
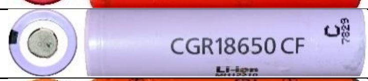
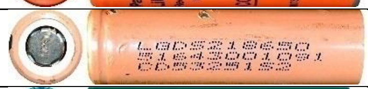
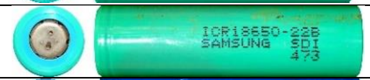
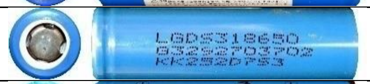
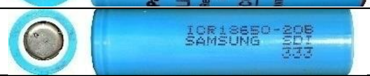
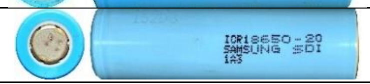


Figure 5. XRD pattern of the cathode material in the sample 13

Based on the obtained results of ICP-OES and XRD analyses, the investigated LIBs were classified and presented in Table 2. In short, of 40 samples of the spent LIBs, 22 cell types were firstly separated on the basis of visual identification. After the performed analytical methods, classification was as follows: the cathode material identified in 17 samples of the investigated cells was $LiCoO_2$, in 4 cells it was $LiNiCoMnO_2$ and one cell contained $LaCoO_3$.

Table 2. Classification of the investigated spent Li-ion batteries

Sample	Model	Cathode material type	Color (Wrap)	Color (Ring)	LIBs cell
1.	ILIFJT7	$LiCoO_2$		Red	
2.	IFOH2	$LiCoO_2$		Blue	
3.	MICFK56	$LiCoO_2$		Green	
4.	GKCFHH2	$LiCoO_2$		White	
5.	CGR18650 CF	$LiNiMnCoO_2$		White	
6.	CGR18650 HG	$LiCoO_2$		Black	
7.	LGDS218650	$LiCoO_2$		White	
8.	Not available	$LaCoO_3$		White	
9.	SF US18650GR	$LiCoO_2$		Black	

Sample	Model	Cathode material type	Color (Wrap)	Color (Ring)	LIBs cell
10.	US18650GR	$LiCoO_2$		Black	
11.	US17670GR	$LiCoO_2$		Black	
12.	ICR18650-22F	$LiNiMnCoO_2$		White	
13.	ICR18650-22H	$LiNiMnCoO_2$		White	
14.	CGR18650A	$LiCoO_2$		White	
15.	ICR18650-22E	$LiCoO_2$		White	
16.	ICR18650-22B	$LiCoO_2$		Blue	
17.	LGR18650P	$LiCoO_2$		White	
18.	LGDS318650	$LiNiMnCoO_2$		White	
19.	CGR17670A	$LiCoO_2$		White	
20.	CGR18650C	$LiCoO_2$		White	
21.	ICR18650-20B	$LiCoO_2$		White	
22.	ICR18650-20	$LiCoO_2$		White	

Obviously, a dominant cathode material in the investigated batteries was $LiCoO_2$ which was firstly demonstrated as a cathode in a LIB by Goodenough and Mizushima way back in 1979 [35]. The results of this study support the presumption that $LiCoO_2$ is still constantly and dominantly used in LIBs. Namely, although many new generations of layered cathodes were introduced during the latest years, it seems that the properties of $LiCoO_2$ (such as the high-voltage plateau, high energy density, excellent cycling performance and a simple synthesis) were decisive factors for the convincing domination of this compound in the electronic market [36].

4. CONCLUSION

In this paper, a procedure for LIBs sorting based on determination of chemical composition of the cathode materials was tested using methods such as ICP-OES and X-ray analyses. The investigated spent LIBs were subjected to a specific pretreatment comprising the following steps: discharging, dismantling, separation of the main components (cathode, anode and the separator), and detachment of the cathode material from the Al-foil. Although the method for the sample preparation was rather aggressive, it provided a fine outcome as an appropriate basis for the selected analytical methods, which further provided highly precise and accurate results. Namely, the results of ICP-OES and X-ray analyses showed that a great majority of the investigated cathodes consisted of $LiCoO_2$ indicating that this material is still dominantly present in commercial LIBs. At the same time, the results of this study represent a solid basis for all researchers interested in the precise identification of cathode materials and, they may represent a useful contribution to various investigations focusing on the improvements of recovery procedures of valuable metals.

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SAŽETAK

Klasifikacija istrošenih Li-jonskih baterija na osnovu *ICP-OES/XRD* karakterizacije katodnih materijala

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Razvoj litijum-jonskih baterija (LIB) tokom poslednjih decenija rezultirao je poboljšanim performansama novih integrisanih katodnih materijala i njihovom širokom primenom. Ova brza ekspanzija novih materijala dovela je do intezivne zamene starijih, tradicionalnih materijala i istovremeno povećala akumulaciju obe vrste materijala na izuzetno opasnim mestima odlaganja elektronskog otpada, što je dodatno uvećalo potrebu njihove hitne reciklaže. Ono što je najvažnije, na taj način, istrošene LIB mogu dalje da posluže kao značajan izvor dragocenih metala, kao što su litijum i kobalt. Međutim, jedan od ključnih problema u reciklaži LIB jeste odsustvo precizne klasifikacije/sortiranja baterija na osnovu hemijskog sastava korišćenog katodnog materijala. U ovom radu, karakterizacija katodnih materijala urađena je na osnovu hemijskog sastava 40 uzoraka iz istrošenih LIB korišćenjem optičke emisione spektrometrije sa indukovano kuplovanom plazmom i rendgenske difrakcione analize. Priprema uzoraka (prethodna obrada/predtretman) je uključivala: pražnjenje, rastavljanje, razdvajanje glavnih komponenti (katoda, anoda i separator) i odvajanje katodnog materijala od aluminijumske folije. Dobijeni rezultati pokazali su da je u ispitivanim komercijalnim LIB, litijum-kobalt oksid bio najčešće korišćen (katodni) materijal.

Ključne reči: LIBs sortiranje; instrumentalna analiza; litijum-kobalt oksid; reciklaža