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Potential market value of electrolyte condensate recovered from LIBs mechanical treatment

Potencjalna wartość rynkowa kondensatu elektrolitycznego odzyskanego z obróbki mechanicznej LIBs

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Key words: *recycling of LIBs; waste electrolyte condensate; chemical composition of electrolyte condensate; recovery of raw materials*

Abstract
Due to the present and future regulatory and economic effectiveness requirements of spent LIB's recycling process, the recovery of each component of the batteries should be carefully considered. However, most of the presented to date research and development results have been focused on the selective recovery of pure e.g. nickel, cobalt and lithium salts or hydroxides obtained from the waste of Li-ion batteries and accumulators. In the present paper, preliminary effectiveness assessment of recycling process of spent LIB's organic electrolyte components is presented. The analysis is based on new experimental data of the actual chemical quantitative and qualitative composition of the electrolyte condensate. On the basis of gas chromatography method coupled with mass spectrometry (GC-MS), it can be concluded that the average recovery of electrolyte condensate from a ton of used and/or waste lithium-ion cells from electric cars is about 12.5%, which is quite important part of LIB's mass to be recycled. Estimated market value of the electrolyte condensate obtained during mechanical processing of (waste) electric cars cells is approximately 3 480.5 USD/ton. The value of the recovered cells electrolyte components have been estimated with assumption that the organic compounds may be separated in the recycling processes.

Słowa kluczowe: *recykling LIBs; odpadowy kondensat elektrolitów; skład chemiczny kondensatu elektrolitycznego; odzysk surowców*

Streszczenie
Ze względu na obecne i przyszłe wymagania regulacje prawne i ekonomiczne dotyczące procesu recyklingu zużytych LIB's, należy dokładnie rozważyć odzyskiwanie każdego elementu zużytych i/lub oodpadowych ogniw Li-ion. Jednak większość dotychczas przedstawionych wyników prac badawczo-rozwojowych koncentrowała się na selektywnym odzysku czystych substratów m.in. soli lub wodorotlenków niklu, kobaltu i litu otrzymywanych z odpadów baterii i akumulatorów litowo-jonowych. W artykule przedstawiono wstępną ocenę efektywności procesu recyklingu zużytych składników elektrolitów organicznych z ogniw litowo-jonowych. Analiza wyników oparta została na podstawie nowych danych doświadczalnych dotyczących rzeczywistego składu chemicznego ilościowego i jakościowego kondensatu elektrolitycznego. Na podstawie metody chromatografii gazowej sprzężonej ze spektrometrią mas (GC-MS) można stwierdzić, że średni odzysk kondensatu elektrolitycznego z tony zużytych i/lub odpadowych ogniw litowo-jonowych z samochodów elektrycznych wynosi około 12,5%, co jest dość ważną częścią masy ogniw poddanych recyklingowi. Szacunkowa wartość rynkowa kondensatu elektrolitycznego uzyskiwanego podczas mechanicznej obróbki zużytych i/lub odpadowych ogniw samochodów elektrycznych wynosi 3 480,5 USD/tonę. Wartość odzyskanych składników elektrolitów z ogniw została oszacowana przy założeniu, że związki organiczne mogą zostać oddzielone w procesach recyklingu.

1. Introduction

The development of the technology for recycling of various types and different chemistries of lithium-ion cells (Li-ion, LIBs) is a challenge at both the research and development as well as the industrial implementation stages. Most of the presented to date research and development results have been focused on the selective recovery of pure nickel, cobalt, lithium, manganese and copper metals products obtained from the waste of Li-ion batteries and accumulators [3]. Recently, a few studies have been published, dealing with the subject of preceding to the basic LIBs processing pyrometallurgical and/or hydrometallurgical technologies. For example, such important aspects as safe transport and waste flammability of Li-ion batteries and accumulators, discharge of cells with or without recovery before mechanical treatment [2], management of the battery mass after recovery of valuable components, management of chemically complex technological waste solutions containing large amounts of undesirable components, both inorganic and organic, as well as fluorine, whose chemical form and the concentration should be considered for cell recycling process [1]. Nevertheless, there are only very limited number of studies of the proper management of recovered LIBs cells electrolyte, which is the secondary raw material obtained from the mechanical processing of lithium-ion batteries. Consequently, a more comprehensive analysis concerning the market value of recycled LIBs electrolyte components is required. Such analysis was presented in the paper *Is it worthwhile to recover lithium-ion battery electrolyte during lithium-ion battery recycling?*, which was published in Resources, Conservation and Recycling in February 2023 [5]. In the present paper, more valuable information on the actual chemical, the quantitative and qualitative composition of the condensate is further presented and discussed.

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Tab. 1. Lithium-ion battery electrolyte cond. components and recycling potential.

Tab. 1. Komponenty kondensatu elektrolitycznego akumulatorów litowo-jonowych i potencjał recyklingu.

Electrolyte cond. Component	Weight in Electrolyte cond.	Price (USD/ton)	Potential Recovery (kg/ton electrolyte cond.)	Potential Recovery (kg/ton electrolyte cond.)
Ethyl Methyl Carbonate	57.13%	5000 [2]	571.3	571.3
Dimethyl Carbonate	36.30%	1326 [1]	363.0	363.0
Cyclohexylbenzen	2.95%	3000 [3]	29.5	29.5
Diethyl Carbonate	2.48%	1100 [4]	24.8	24.8
Propyl Propionate	0.86%	2640 [2]	8.6	8.6
Propionic Acid	0.28%	1500 [1]	2.8	2.8

[1] Source: chemanalyst.com

[2] Source: molbase.com

[3] Source: lookchem.com

[4] Source: made-in-china.com

2. Materials and methods

Wide range of research and development (R&D) studies as well as the first industrial deployment (FID) of innovative technologies of Li-ion batteries and spent autocatalysts recycling with the recovery of strategic metals have been carried out at Elemental Strategic Metals (ESM). These R&D and FID activities enabled the optimization of multi-stage industrial process consisting of such stages as mechanical treatment of waste batteries from electric cars (module car) leading to the recovery of a battery mass with the best physical and chemical parameters for further treatment to recover secondary raw materials using chemical and metallurgy methods. One of the important by-products of the LIBs recycling process was the electrolyte condensate. The following main components of the electrolyte have been determined by ESM in the obtained condensates: formic acid (CH_2O_2, CAS: 64-18-6), benzene (C_6H_6, CAS: 71-43-2), diethyl carbonate (DEC, $C_5H_{10}O$, CAS: 105-58-8), dimethyl carbonate (DMC, $C_3H_6O_3$, CAS: 616-38-6), acetic acid ($C_2H_4O_2$, CAS: 64-19-7), ethyl methyl carbonate (EMC, $C_4H_8O_3$, CAS: 623-53-0), ethyl propionate ($C_5H_{10}O_2$, CAS: 105-37-3), fluorobenzene (C_6H_5F, CAS: 462-06-6), 2-methyl-1,3-dioxolane ($C_4H_8O_2$, CAS: 497-26-7), propanoic acid ($C_3H_6O_2$, CAS: 79-09-4), methyl propionate ($C_4H_8O_2$, CAS: 554-12-1), propylene carbonate, ($C_4H_6O_3$, CAS: 108-32-7), propyl propionate ($C_6H_{12}O_2$, CAS: 106-36-5), cyclohexylbenzene ($C_{12}H_{16}$, CAS: 827-52-160), methyl propionate ($C_4H_8O_2$, CAS: 554-12-1), fluorobenzene (C_6H_5F, CAS: 462-06-6), methyl trimethylacetate ($C_6H_{12}O_2$, CAS: 598-98-1), ethylene carbonate ($C_3H_4O_3$, CAS: 96-49-1), acetic acid ($C_2H_4O_2$, CAS: 64-19-7). It should be noted that the chemical compositions presented above differ from the following primary electrolytes compositions presented in the publications of Vanderburgt et al. [5], Zachmann et al. [6] and Sobianowska-Turek et al. [4]: ethyl methyl carbonate (EMC, $C_4H_8O_3$, CAS: 623-53-0), dimethyl carbonate (DMC, $C_3H_6O_3$, CAS: 616-38-6), lithium hexafluorophosphate (LiPF6, CAS: 21324-40-3), vinylene carbonate ($C_3H_2O_3$, CAS: 872-36-6), propylene carbonate ($C_4H_6O_3$, CAS: 108-32-7), fluorobenzene (C_6H_5F, CAS: 462-06-6)), lithium difluorophosphate (LiF_2PO_2, CAS: 24389-25-1), lithium bis(fluorosulfonyl)imide ($F_2LiNO_4S_2$, CAS: 171611-11-3), 1,3-propanesultone ($C_3H_6O_3S$, CAS: 1120-71-4) , tetravinylsilane ($C_8H_{12}Si$, CAS: 1112-55-6), 1,3,2-dioxathiolane-2-2dioxide ($C_2H_4O_4S$, CAS: 1072-53-3). The difference in compositions may be explained by the electrolyte components degradation under the influence of physical and chemical factors applied during the mechanical treatment of recycled cells [3].

3. Results and discussion

Analyzing our results of electrolytes condensates chemical compositions obtained in an accredited analytical laboratory by gas chromatography method coupled with mass spectrometry (GC-MS), it can be assumed that the average recovery of electrolyte condensate from a ton of used and/or waste lithium-ion cells from electric cars is about 12.5%. Chemical analysis of the electrolyte condensate obtained during drying of the material after LIBs mechanical treatment, indicates the following main components presented in Table 1: 36.30% dimethyl carbonate, 57.13% ethyl methyl carbonate, 0.28% propionic acid, 2.48% diethyl carbonate, 0.86 % propyl propionate, 2.95 % cyclohexylbenzene. Quantitative and qualitative chemical analysis results of a mixture of organic solvents performed by mass spectrometry coupled with inductively coupled plasma (ICP-MS) showed the presence of lithium at the level of 5.88 ppm, cobalt 0.14 ppm, nickel 2.73 ppm, copper 0.03 ppm and fluorine 0.61 mg/g.

4. Conclusions

Based on the presented above results it was possible to estimate the market value of the electrolyte condensate obtained during mechanical processing of (waste) electric cars cells at the level of approximately 3 480.5 USD/ton of electrolyte condensate. The market value of the presented condensate was calculated based on the current prices of individual components, which are presented on publicly available web sources. The value of the recovered cells electrolyte components have been estimated with assumption that listed compounds may be separated in further processes. Moreover, in our opinion, presented here data may be a valuable source of information allowing further analysis enabling the development of the effective purification and recovery processes for the components that are a potential source of secondary raw materials for use in various industries. As mentioned by Latini et al. [3] it is possible to recover battery grade electrolyte using well known separation technologies, e.g. distillation and not only thermal disposal. Research on the processing of electrolyte condensate, run by Elemental Strategic Metals Sp. z o. o., will make a significant contribution to closing the recycling loop of LIBs batteries.

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Data Availability

The specific sources of the data shown in Table 1 have been web archived from the footnoted websites and the archival links will be made available upon request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. ■

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