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”BABEŞ-BOLYAI” UNIVERSITY CLUJ NAPOCA
FACULTY OF CHEMISTRY AND CHEMICAL ENGENERRING
DOCTORAL SCHOOL OF CHEMICAL ENGINEERING

Zinc recovery from spent Zn-MnO$_2$ batteries

PhD Thesis Abstract

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SUMMARY (As in full text)

Part I. Bibliographic study

Part II. Personal contribution

INTRODUCTION

The PhD thesis addresses a current topic, namely zinc recovery from spent batteries using electrochemical methods.

In recent years, more emphasis has been given to recover metals from wastes. The wastes contain a high proportion of recyclable materials that can be (re) used in the production process, which decreases the need to seek untapped mineral resources. An important category of waste represents those containing zinc from waste batteries.

Recycling and reuse of metals from used batteries becomes essential because of the environmental concerns and new regulations. In order to develop a recycling technology is very important to know the detailed structure of each type of electrochemical source (battery, battery) and also to establish the chemical composition.

In this context, the thesis develops a technology to recycle zinc from Zn-MnO_2 spent batteries (ZMSB). The thesis is structured in two parts: the analysis of the results presented in the literature and the personal experimental contributions.

The literature review approaches: general and particular aspects of the recycling process of Zn-MnO_2 battery, the main characteristics of this type of waste, the recovery process of zinc and manganese from spent batteries and also the recycling technologies industrially applied.

Based on existing literature on the subject, were developed electrochemical alternatives for leaching and metals recovery from batteries, designed to streamline the recycling process and complement existing information.

In this context, personal contribution includes:

(i) The chemical characterization of electrode materials obtained in the dismantling step;

(ii) The chemical/electrochemical leaching of electrodic batteries components;

(iii) The separation of Mn^{2+} ions by chemical oxidation with $(NH_4)_2S_2O_8$ and the electrochemical characterization of the obtained MnO_2;

(iv) The zinc electrowinning from solutions resulting from the leaching process of electrodic batteries components;

(v) The development of a flow sheet for the recovery of zinc and manganese, based on the experimental results.

The studies were complex, achieving different evaluation of the parameters involved, in order to improve the recycling process.

The experimental results obtained were exploited in a serie of publications and participation in national and international conferences listed at the end of this thesis.

Keywords: recycling, Zn-MnO2 batteries, electrodeposition, technological flow

4. LEACHING OF BLACK POWDER FROM ZN-MNO$_2$ SPENT BATTERIES

In agreement with the literature, the researches regarding the leaching of black powder (BP) from spent batteries assumed a preliminary stage of dismantling and separation of SB components, followed by the solubilization in acid or alkaline medium.

In this study were used R20 size spent Zn –carbon batteries, collected from waste yard. These cells were manually cut into halves along with their longitudinal axes using a saw blade. The electrodic inactive material, black powder was recovered from inside the SBs, representing about 65 % of total battery weight (Tabel 1).

Tabel 1. *The ZMSB components recovered after the dismantling stage*

Battery components	**g**	**%**
BP	63.3	65.16
Zn anodic remnants (ZAR)	11.9	12.25
Outer casing, plastic, paper, C current collector	20.12	20.71
Handling losses	1.83	1.88
TOTAL	**97.15**	**100**

The analytical methods allowed the determination of the metal content, through the atomic absorption spectroscopy (AAS). For that purpose was used an atomic absorption spectrometer Avanta AAS (GBC Scientific Equipment, Dandenong, Australia). For the AAS analyses, the BP was solubilized using *aqua regia*, during 2 hours, at a solid liquid mixing ratio (S:L) of 1:10. The metals content in black powder were approximately 20 % Zn, 30 % Mn and 0.7 % Fe (percentages calculated in relation to the mass of solid taken for analysis; others miscellaneous parts, graphite and oxygen, represent the difference up to 100 %).

The high quantity of black powder, as well as the metal content underlines the necessity of ZMSB recycling.

The next step of the recycling process is the chemical solubilization of the BP, in two medium: H_2SO_4 and NaOH, for evaluating the metals solubilization degree (SD).

Chemical acid leaching [1, 2] takes into account a subsequent recovery of zinc by electrodeposition; aqueuos mediums are preffered at industrial level and approximately 80 % of the zinc word production uses solutions based on sulphuric acid and zinc sulphate [3, 4].

The acid solubilization takes place according to the following reactions [5]:

$$ZnO+H_2SO_4 \rightarrow ZnSO_4+H_2O \tag{4.1}$$

$$Mn_xO_y+ H_2SO_4 \rightarrow MnSO_4+H_2O \tag{4.2}$$

The solubilization of inferior manganese oxides Mn_xO_y, Mn_2O_3 or Mn_3O_4 is partial due to MnO_2 formation, which is insoluble in H_2SO_4 [6, 7, 8]:

$$Mn_2O_3+H_2SO_4 \rightarrow MnO_2+MnSO_4+H_2O \tag{4.3}$$

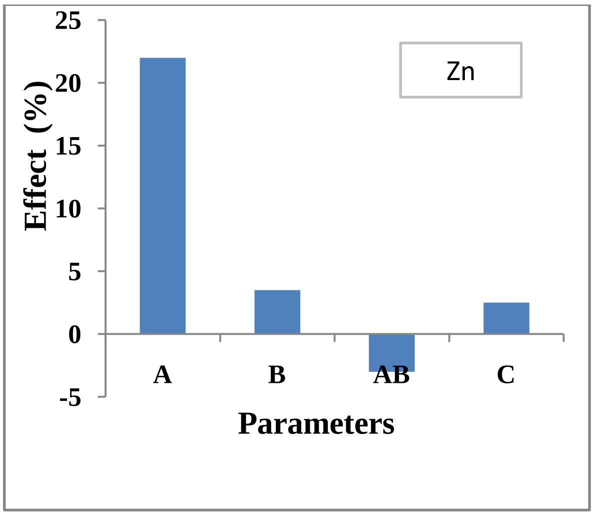
$$Mn_3O_4+2H_2SO_4 \rightarrow MnO_2+2MnSO_4+2H_2O \tag{4.4}$$

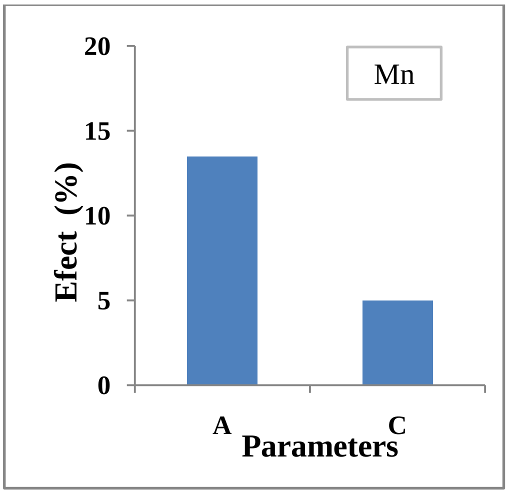
The metal solubilization degrees were investigated as a function of experimental parameters: H_2SO_4 concentration (0.05, 0.5, 1, 2 M), solid liquid mixing ratio (S: L= 1:3; 1:5; 1:10; 1:20; 1:40; 1:60), time (30, 60, 90 and 120 minute) and solubilization temperature (40, 60 and 80 °C). The effects of the parameters on the solubilization degree, as well as the interactions between them are discussed in the following section.

The results obtained in this study indicated the proper experimental conditions to obtain a complete solubilization degree for zinc. Therefore, using a S:L=1:5, one hour solubilization time, in 2 M H_2SO_4 at room temperature, the metal solubilization degrees obtained were: 98 % for zinc, 24 % for manganese and 18 % for iron. Although, the SD for zinc was satisfying, the high quatity of dissolved manganese could create difficulties in the stage of zinc electrochemical recovery.

The experimental results obtained at room temperature were analyzed by ANOVA statistical analyses according with the Yates algorithm [6, 9] to determine the interaction of the studied experimental parameters. The effects with the statistical significance higher than 95 % have been reported.

As figure 1 shows, sulphuric acid concentration had a strong positive effect on the zinc solubilization (22 %). In the same time, the interaction between the acid concentration and the solid liquid mixing ratio had a negative effect on zinc solubilization (-3 %). This last aspect shows that with increasing mixing ratio, the positive effect of H_2SO_4 concentration decreased. This result may be due to a complex set of reactions that occur during BP solubilization.





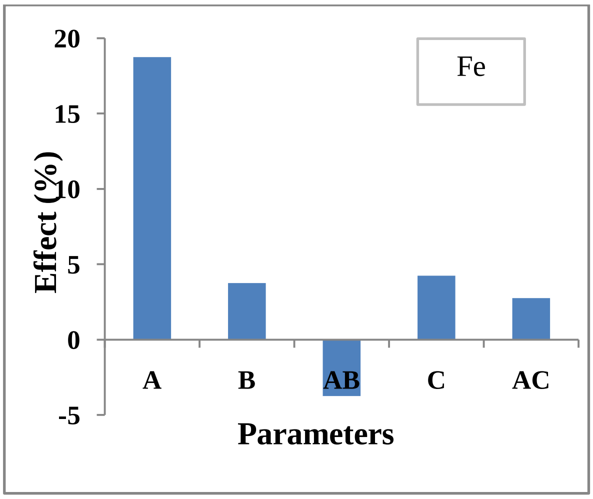


FIGURE 1. *The effect of main parameters on the metals solubilization from BP*

A- Sulphuric acid concentration

B- Solid :liquid mixing ratio

C- Reaction time.

Regarding manganese leaching, there are only two parameters that have positively influenced the process, namely acid concentration (13.5 %) and reaction time (5 %). The positive effect of acid concentration on the solubilization of zinc and manganese was observed also in literature [5, 6].

The iron solubilization was positively influenced by the concentration of H_2SO_4 (18 %), time of leaching (4 %) and the mixing ratio S: L (3 %). The interaction between acid concentration and reaction time has positive effect, while the interaction between acid concentration and mixing ratio had a negative effect on the iron solubilization.

The alkaline leaching was performed under constant stirring, using NaOH. As in the acidic medium were evaluated the effects of NaOH concentration (1 M, 3 M, 6 M) as well as the effect of temperature (25 and 80 °C) on the SD, taking into account the results obtained in the literature [10]. Increasing concentration of NaOH, leads to a selective solubilization of zinc, obtaining a SD of aproximately 60 % Zn. Increasing the reaction temperature does not improve zinc solubility. Due to the low zinc solubilization degrees in alkaline medium, further research use only acid leaching.

The electrochemical experiments were designed to improve the performance of the solubilization process in weak acidic medium. Anodic leaching tests were carried out in 0.5 M and 2 M H_2SO_4. The current intensity values were from 0.2 A to 0.6 A, in order to investigate the degree of extraction of metals from the black powder. The working electrodes used were aluminium plate as a cathode and lead as current collector. Aluminium was used due to low adherence of the deposited zinc, which ca m be removed easily from the cathode [11]. Lead plate was inserted in a nylon bag, which contained the black powder of batteries and then was immersed in the electrolyte solution.

Table 2 shows the comparative results between the chemical extraction (C) and a mixed chemical / electrochemical (MCE) extraction in different concentrations of H_2SO_4. Thereby, for 0.5 M H_2SO_4, by using electrochemical method the Zn solubilization was increased up to more then 90 %.

Table 2. *The degree of extraction for Zn, Mn and Fe by chemical and chemical/electrochemical solubilization in* H_2SO_4*, S: L = 1:10, 1 hour at 25° C.*

Extraction methods	**I(A)**	**H_2SO_4 concentration, M**					
		0.5			**2**		
		Zn	**Mn**	**Fe**	**Zn**	**Mn**	**Fe**
		Solubilization degree, %					
C	-	56	18	8	98	24	18
MCE	0.2	90	3	7	96	27	23
	0.4	91	2	4	98	25	28
	0.6	91	3	5	98	17	20

It can be seen a decrease of the extraction degree for Mn and Fe with increasing the current intensities, due to the oxidative precipitation of manganese and iron as insoluble compounds, mainly MnO_2 and $Fe(OH)_3$. During the anodic solubilization process, the electrolyte solution had pink coloration specific to MnO_4^- ions, which oxidized Mn (II) and Fe (II) to higher valence oxides [1].

Under these circumstances, the subsequent electroextraction of pure Zn is simpler and more efficient than in presence of higher concentrations of Mn and Fe. In the same time, the electrochemical method allowed the recovery of metallic zinc, even if the cathodic current efficiency was not optimal in this stage of research.

5. LEACHING OF ZN ANODIC REMNANTS [12,13,14]

The zinc anodic remnants could be recycled by pyrometallurgical treatments (in 10 % NH_4Cl, 10 % KCl and 10 % NaCl) at temperatures above 600 K, the obtained material being further subjected to a hydrometallurgical process [15]. During this research, we propose the direct solubilization in acidic medium. In this case, the experiments assumed the chemical, respectively the electrochemical solubilization in H_2SO_4.

Chemical leaching of zinc anodic remnants (ZAR) was achieved using different concentrations of H_2SO_4 (1.5, 2.0 respectiv 4 M) and mixing ratios (1:10, 1:20, 1:50).

In 20 hours, the chemical process ensures a complete dissolution of Zn anodic remnants in 2 M H_2SO_4, regardless of the mixing ratios. In 1.5 M H_2SO_4 a total dissolution was achieved only in 48 hours at mixing ratios higher then 1:10. The increase in H_2SO_4 concentration leads to a decrease in zinc dissolution, due to the passivation process. Given the relatively long dissolution time, an electrochemical process was developed, allowing also the zinc cathodic recovery.

The electrochemical alternative was performed using different concentrations of H_2SO_4 (0.5 and 2.0 M), respectively different concentration of Zn^{2+} in the electrolyte (10-40 g/L). The investigated anodic current densities were 217, 434, 652, 870, respectively 1087 A/m^2.

The obtained results highlighted that the solubilization process is slow and the current density did not accelerated the process. When the current density increased up to 1087 A/m^2, the solubilization degree droped from 45 % to 34 %, and the cathodic current yield (CCE) decreased from 75 to 50 % in 0.5 M H_2SO_4. Considering these results, the anodic current density of 217 A/m^2 was considered adequated for the ZAR electrodissolution process.

The effect of zinc concentration on current efficiencies and power consumptions were investigated under the following conditions: current density of 217 A/m^2, four zinc concentrations (2, 10, 20 and 40 g/L) in 0.5 M H_2SO_4. The results illustrate that high cathodic current efficiencies (93-98 %) were obtained with increasing the zinc concentrations and also the specific power consumptions (~ 0.4 kWh/kg Zn) were much lower than in conventional zinc electrowinning (3 – 4.3 kWh/kg Zn) [16, 17]. In the mentioned concentration range, the SD had little fluctuation.

At high acid concentration (2 M) takes place a massive hydrogen production, generating low cathodic current efficiency (~50 %) and an excessive consumption of the zinc anode, increasing the solubilization degree 73 %.

Electrochemical recovery of zinc anodic remnants allows shortening the dissolution time of these wastes and increasing the solubilization degree with low specific energy consumption. At the same time, the recovery of pure metallic zinc was achieved with high current efficiency and lower energy consumption than in conventional cases.

6. ZN ELECTROEXTRACTION FROM SYNTHETIC SOLUTIONS

A fundamental and an applied study of Zn electrodeposition process was developed in order to know in detail the features of this process.

The fundamental study of zinc electroextraction from synthetic solutions was performed by cyclic voltammetry at different concentrations of Zn^{2+} (10 - 20 g/L), Mn^{2+} (0.1-0.5 g/L), respectively Fe^{2+} (0.005 g/L-0.04 g/L). The electrolyte solution was maintained at pH=4 by alkalinization with 1 M NaOH.

The applied study, involving the influence of current density and pH on zinc electrodeposition process, was performed in galvanostatic mode, on aluminum support. The acidity was adjusted with sulfuric acid to pH=2 or 4 as appropriate. The cathodic current densities tested (100-350 A/m^2) were specific to zinc electrohidrometallurgy [18,11, 19].

The study of Zn electrodeposition from synthetic solutions in presence of Fe^{2+} and Mn^{2+} ions was performed in 0.5 M H_2SO_4. The metal ions concentration used (5 g/L Zn^{2+}, 0.1 g/L Fe^{2+} and 1 g/L Mn^{2+}) were chosen according to the results of the BP leaching in 0.5 M H_2SO_4. The current densities tested were between 100 and 1000 A/m^2.

The results obtained the cyclic voltammetry study, showed the adverse effects of Fe^{2+} and Mn^{2+} ions on Zn electrodeposition among them including: shifting reduction potential towards more negative values and decreasing the amount of deposited Zn with increasing concentration of Fe^{2+} in electrolyte solution [20] (see figures 2-5).

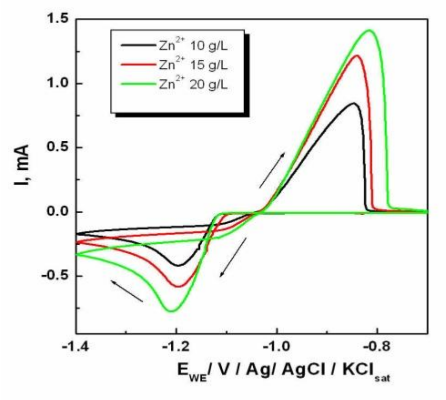


FIGURE 2. *The influence of Zn^{2+} concentration on the electrodeposition process.*

Experimental conditions: electrolyte solutions Zn^{2+} (10 g/L; 15 g/L; 20 g/L) at pH=4; scanning rate, 50 mVs^{-1}; start potential, -0.5 V vs. Ag/AgCl/KCl$_{sat}$.

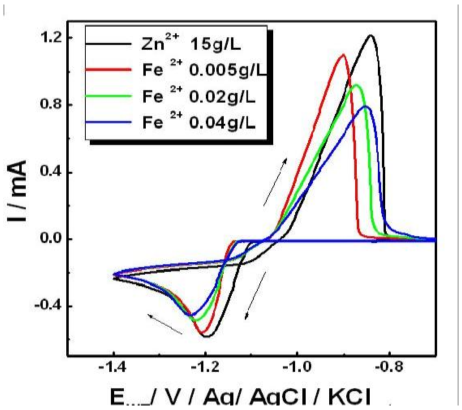


FIGURE 3. *The influence of Fe^{2+} concentration on the Zn electrodeposition process.*

Experimental conditions: electrolyte solutions Zn^{2+} (15 g/L) and Fe^{2+} (0.005 g/L; 0.02 g/L; 0.04 g/L) at pH=4; scanning rate, 50 mVs^{-1}; start potential, -0.5 V vs. Ag/AgCl/KCl$_{sat}$.

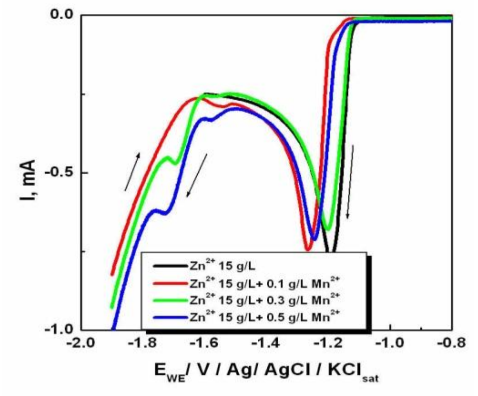


FIGURE 4. *The influence of Mn^{2+} concentration on the Zn electrodeposition process.*

Experimental conditions: electrolyte solutions Zn^{2+} (15 g/L) and Mn^{2+} (0.1 g/L; 0.3 g/L; 0.5 g/L) at pH=4; scanning rate, 50 mVs^{-1}; start potential, -0.5 V vs. Ag/AgCl/KCl$_{sat}$.

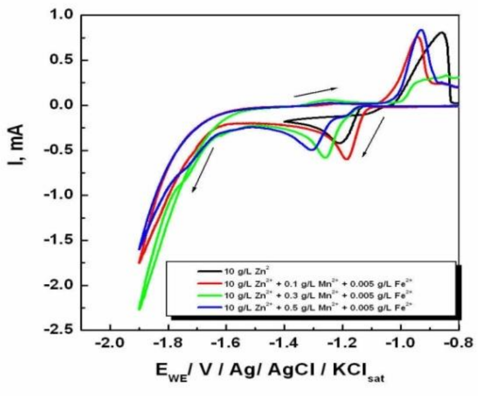


FIGURE 5. *The influence of Mn^{2+} and Fe^{2+} concentrations on the Zn electrodeposition process.*

Experimental conditions: electrolyte solutions, Zn^{2+} (10 g/L), Mn^{2+} (0.1 g/L; 0.3 g/L; 0.5 g/L) şi Fe^{2+} (0.005 g/L) at pH=4; scanning rate, 50 mVs^{-1}; start potential, -0.5 V vs. Ag/AgCl/KCl$_{sat}$.

The results obtained in the applied study (see figure 6) showed that the effect of acidity is very important in the electrodeposition of zinc, leading to a drastic decrease in the CCE, up to 40 % in 2 M H_2SO_4. Previous studies [11,21,22] demonstrated an inhibition of zinc electrodeposition process in highly acidic solutions due to H_2 absorption. Therefore, increasing the pH increases the cathodic current efficiency (93 %, pH=4).

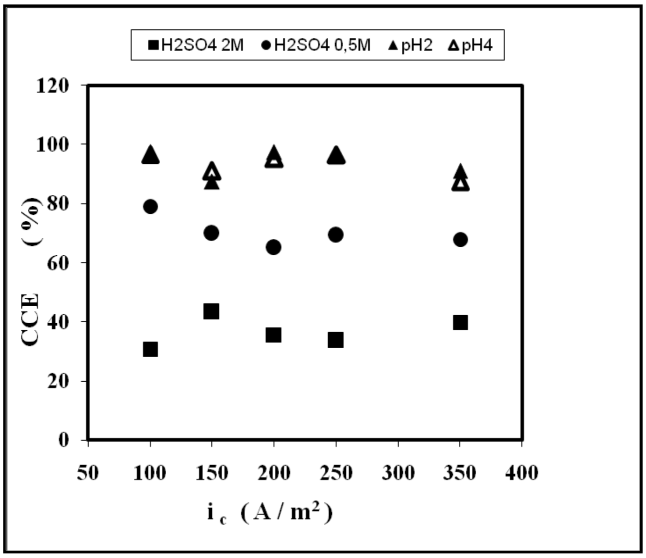


FIGURE 6. *The influence of current density and electrolyte composition on Zn electrodeposition process in electrolit solution that contain* 5 g/L Zn^{2+}.

The influence of the current density on the cathodic current efficiency is not significant in the range studies, as shown in figure 6.

The electrodeposition tests regarding zinc recovery from synthetic solutions similar with the real ones highlighted the difficulty of zinc recovery with high CCE, in presence of Fe^{2+} and Mn^{2+} ions. Depending on the applied current density, CCE is low (22 – 48 %); increasing the current density leads to a decrease of the cathodic current efficiency. This is due to the electrochemical short-circuiting which can occur in a non-divided cell; Fe^{2+} and Mn^{2+} ions are oxidized at the anode and then reduced at the cathode.

Given the low yields in the presence of Mn^{2+} ions for improving the CCE is necessary to separate them from the electrolyte solution, by chemical or electrochemical methods. Chemical/electrochemical separation of Mn^{2+} and electrochemical characterization of the material obtained are discussed in the next chapter.

7. Zn ELECTROEXTRACTION FROM SOLUTIONS RESULTING FROM ACID LEACHING OF THE ELECTRODIC COMPONENTS

The chemical separation of Mn^{2+} from solutions resulted in the acid leaching step of BP was achieved using ammnoniun persulfate. The chemical oxidation with $(NH_4)_2S_2O_8$ allowed obtaining a high precipitation degree of manganese (PGM), as MnO_2, without affecting the zinc content in the solution. The X-ray spectra of the solid samples obtained showed a structure corresponding to the formula: $(NH_3)_2(Mn_xO_y)$.The best results of MnO_2 synthesis were obtained at pH=4, respectively at pH=6 when PGM was highest (~ 90 %), and in case of zinc were obtained the lowest precipitation degrees (28 % for pH=4 and 5 % for pH=6). The best experimental conditions of MnO_2 synthesis were 3 hours, temperature 90 °C, and 20 % $(NH_4)_2S_2O_8$ concentration.

The solubilization and precipitation of manganese dioxide were made by our collaborators from the University of L'Aquila, Italy and the electrochemical characterization of the synthesized MnO_2 was performed at the Babes-Bolyai University. The results of these studies are presented in the paper [23].

Electrochemical activity of the MnO_2 obtained by chemical oxidation with $(NH_4)_2S_2O_8$ was assessed by cyclic voltammetry (CV) studies. To compare the performance of the synthesized MnO_2, parallel measurements were made using a commercial electrochemical manganese dioxide (EMD) from 3 different battery producers. The three trade batteries Toshiba R6KG Size AA 1.5 V (MnO_2 Toshiba), GP Heavy Duty 1604E6 Size F22 9V (MnO_2 GP), Chrome Heavy Duty BR03 Size AAA 1.5V (MnO_2 Chrome) were dismantled, the electrodic inactive material recovered, crushed, washed with water to dissolve the $ZnCl_2$ electrolyte and then dried at room temperature for 48 hours.

The MnO_2 electrodes were prepared by mixing 80 wt % of MnO_2 powder as active material with 20 wt% of graphite (Fluka, purum powder; ≤ 0.1 mm). The constituents, having a mass of 0.12 g, were mixed together with 3µL of paraffin oil (Fluka, analytical grade) to obtain a homogeneous black paste. The paste thus obtained was immersed into a homemade disk electrode (disk area of 0.071 cm^2), with glass walls. The electric contact was insured by a graphite bar, with the role of current collector.

The electrode capacity was evaluated based on the quantity of cathodic current registered in the CV by the integration of the cathodic curve made in relation to time. The capacity values of the material were reported to the electrode disk area. The electrochemical measurements indicated that the synthesized MnO_2 presents electrochemical performance if applying a heating treatment at 800 °C for 1 hour, to remove the NH_3 embedded in the samples.

As shown in figure 7, the sample P4, afferent to the MnO_2 synthesezed at pH=4, exhibits lower capacity values to the commercial samples. In exchange, the electrochemical performances of the sample obtained at pH=6, P6, are higher towards the commercial ones. A possible explanation for the significant differences in electrochemical behavior of the two samples is the Zn content, which in P4 is much higher, 28 % versus 5 % in P6.

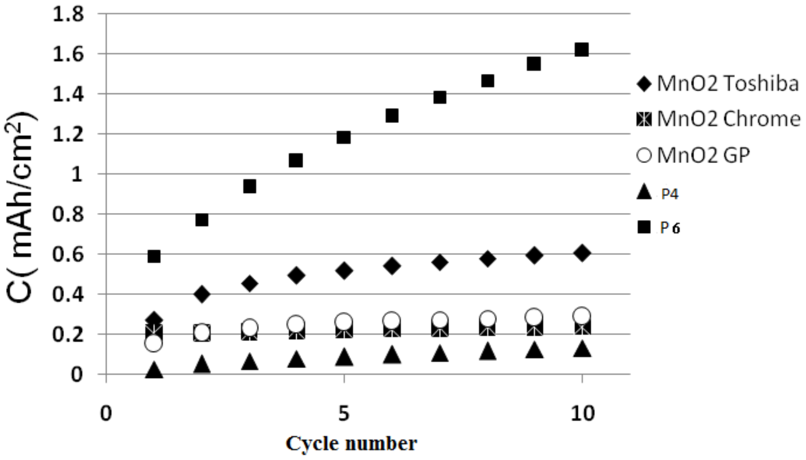


FIGURE 7. *The capacity of EMD and CMD calculated for the different voltammetric cycles.*

Zn electroextraction in a divided cell is focused on the recovery of zinc and MnO_2 from solutions resulting from the solubilization of electrodic materials of Zn-MnO_2 spent batteries, in an anion-exchange membrane electrolysis reactor.

The parameters investigated were: the current density, Zn^{2+} concentration in catholyte solution and concentration ratio of Zn^{2+} and Mn^{2+}. Thus, the current densities tested were in the range: 50-500 A/m^2 for the anodic process and 100-500 A/m^2 for the cathodic one. The catholyte consisted in the solution resulting from the acid leaching of ZAR, respectively from solutions resulting from BP acid leaching, before and after manganese dioxide recovery. In order to assess the influence of Zn: Mn concentration ratios on zinc electrodeposition, different amounts of ZAR were used.

Regarding the cathodic process, in the range of current densities studied, the CCE for Zn electrodeposition from the solutions obtained after the chemical dissolution of ZAR is little influenced by the increasing of current density (~71 %). In exchange, the anodic current efficiency has a strong tendency to increase with increasing the current density, leading to a maximum of 45 % at 500 A/m^2.

The chemical acid solubilization of ZAR ensured an increase of Zn^{2+} concentration in the solution, leading to high current efficiencies for zinc electrowinning, even in presence of Mn^{2+} and Fe^{2+} ions. While Zn: Mn concentration ratios were over 10:1 zinc electrowinning took place with cathodic current efficiency higher than 90 %. At the same time, increasing the concentration of Zn^{2+} in solution, leads to a change in the morphology of the deposits obtained. In diluted solutions, the deposit is compact and homogeneous; with a predominant tendency to form clusters (see figure 8 a-b). Increasing the concentration to about 125 g/L Zn^{2+}, the structure of Zn deposit is changed in the form of needles, whose size increases with increasing the concentration (Figure 8 c-d).

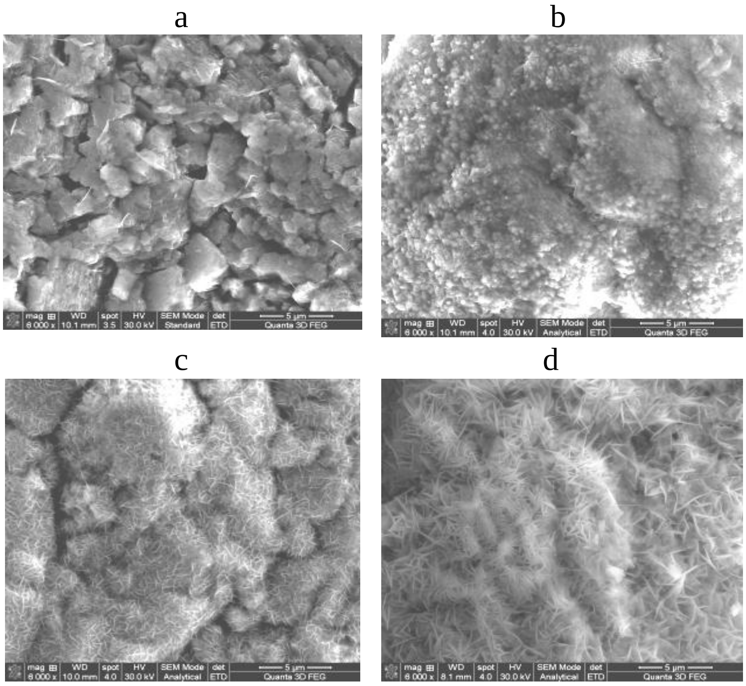


FIGURE 8. *SEM images of Zn deposits obtained at 500 A·m^{-2} from solutions with different concentrations of Zn^{2+} and Mn^{2+}*

(a) 50 g/L Zn^{2+}, 6 g/L Mn^{2+}
(b) 90 g/L Zn^{2+}, 8 g/L Mn^{2+}
(c) 125g/L Zn^{2+}, 8 g/L Mn^{2+}
(d) 143 g/L Zn^{2+}, 12 g/L Mn^{2+}
x 6000.

To identify existing compounds in MnO_2 deposits, the obtained samples were subjected to XPS analysis. Mn 2p and O 1s spectra (see figure 9) were used to assess the oxidation state of manganese in the samples electrochemically obtained. So, as figure 9 ilustrates, the samples contain Mn^{3+} and Mn^{4+} ions. This means that the Mn^{3+} intermediary is partially oxidized to MnO_2, the rest remaining embedded in the deposit. For the Mn^{3+}

component, the maximum energy binding value for Mn $2p_{3/2}$, is about 642 eV. Together with the O 1s spectrum deconvolution, is specific to Mn_2O_3 compound [24]. The O1s peak has a maximum at 529.7 eV with a distinct shoulder on the high energy branch which distinguishes between the two oxidation states of manganese. This characteristic is typical for MnO_2 [25]. Thereby, it can be concluded that MnO_2 is the main component.

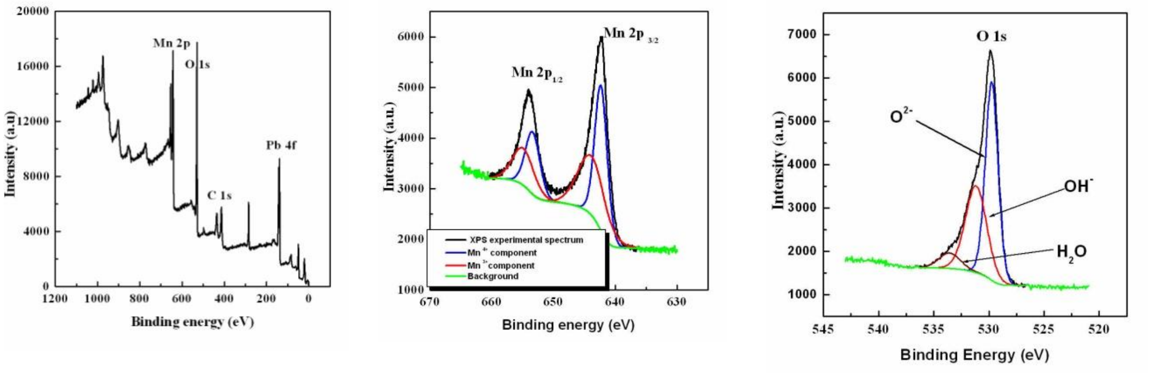


FIGURE 9. *XPS spectra characteristic for the MnO_2 deposit.*

The maximum current yields obtained for Zn and MnO_2 recovery were 98 % for zinc and 45 % for manganese dioxide at a current density of 500 A/m^2 [26]. Anodic current efficiency was strongly influenced by the presence of Fe^{2+} ions, which oxidizes the MnO_2 deposit, consuming it. In this case, it’s neccesary a separation of Fe^{2+} ions from the electrolyte solution or a more rigorous control of electrochemical parameters so that the secondary reactions are blocked.

8. PROPOSED TEHNOLOGICAL FLOW FOR BATTERY RECYCLING

After the preliminary stages of dismantling and separation of material components, are obtained the electrodic materials (anodic zinc remnants and black powder) and the secondary waste (metal outer case, paper, plastic and graphite bars).

Secondary waste resulting from recycling SB, go into different categories of collection and processing, in order to exploit as shown below.

Plastic waste resulting from the SB dismantling consists of thin films that cover the battery, providing electrical insulation of electrodic contacts. Development of the infrastructure of plastic recycling must be consistent with market requirements so it can cover the costs of collecting, processing and transportation. The manufacturing costs of the products made from recycled plastic are lower than those made from raw materials. Whether it's a relatively small quatity, recycling these secondary wastes has to be taken into account, considering that plastic degradation takes over 600 years; the technology for plastic recycling includes methods of grinding, washing, drying and granulating.

The paper present in ZMBS structure is impregnated with electrolyte solution. After dissolving the electrolyte in water, paper can be recycled by cellulose and paper manufacturers.

The current collector, consisting in graphite bars, can be recycled after washing to remove any trace of BP and of the crystallized electrolyte. Recycling the graphite waste is of interest in the conditions of the increased price on world market. So given that 85 % of coal mines in Australia, the world's leading exporter of coal, were affected by floods in 2010, it is expected a masive increase in coal prices including graphite.

The ZMSB outer casing is about 12 % from the total weight of the battery and is made of steel, which can be returned to the industry.

Based on the experimental results, the proposed technological process for Zn recovery includes four important steps: (i) the BP solubilization, respectively ZAR solubilization in 2 M H_2SO_4 (ii) the electrochemical recovery of Zn in the cathodic compartment, respectively of MnO_2 in the anodic compartment (iii) increasing Zn^{2+} concentration by crossing the resulting solution after MnO_2 recovery over a new batch of ZAR, followed by the Zn recovery in the cathodic compartment; (iv) increasing Mn^{2+} concentration by crossing the resulting solution after Zn recovery in the second step over a new batch of BP, followed by Mn recovery in the anodic compartment. The detailed technological flow is shown in Figure 24.

The mass balance (Table 13) performed according to the proposed technological flow, for processing 2 tones of spent batteries, highlights the recovery per hour of about 26 kg metallic Zn and approximately 18 kg MnO_2.

Table 1. *Mass balance for the processing 2 tones of SB's, after 2 hour operation time of the electrochemical reactors*

Input materials		**Output materials**	
Component	**Mass (kg)**	**Component**	**Mass (kg)**
ZnO	364	$MnO_{2,\text{ battery}}$	528
Mn_xO_y	594	Fe	18
Fe	22	Graphite	370
Graphite	370	H_2SO_4	716.9
Zn anodic remnants	246	H_2O	5493
H_2SO_4	1508	Zn deposited	52.1
H_2O	5417	MnO_2 deposited	36.8
		H_2	6.32
		O_2	8
		$ZnSO_4$	1199
		$MnSO_4$	78
		$Fe_2(SO_4)_3$	14
		Losses	0.88
TOTAL	**8521**	**TOTAL**	**8521**

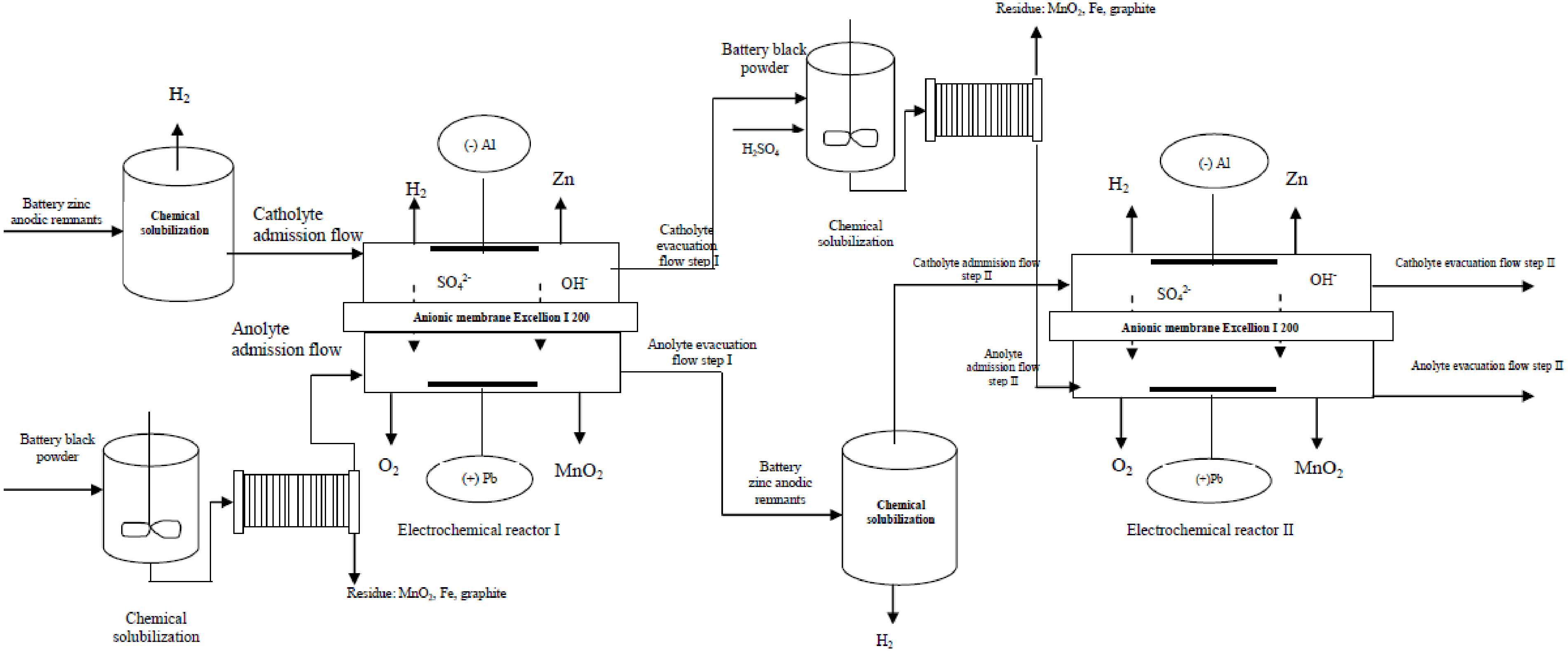


FIGURE 10. *The proposed technological flow for the recycling process of Zn-MnO_2 used batteries.*

General conclusions

In this thesis were performed researches aimed at developing a process for recovering zinc from Zn- MnO_2 spent batteries.

Spent Zn – MnO_2 batteries, collected from waste yard and used during this study were R20 size. These cells were manually cut into halves along with their longitudinal axes using a saw blade. The electrodic inactive material, black powder (BP) and Zn anodic remnants (ZAR) were recovered from inside the SBs, representing about 65 %, respectively 13 % of total battery weight. The BP contains a mixture of manganese oxides (44 % Mn_xO_y), ZnO (27 %), graphite (27.5 %) and traces of iron, resulted in the dismantling step. ZAR contains approximately 98 % zinc and 2 % lead.

The research was oriented in 2 directions: (i) solubilization of electrodic components of SB's and (ii) electrochemical recovery of metallic zinc and partially of MnO_2.

The general conclusions of these researches are:

1. *Solubilization of black powder and zinc anodic remnants*

The solubilization step was achieved both chemically and electrochemically.

The chemical solubilization of BP was accomplished in NaOH and H_2SO_4 medium, in order to determine the extraction degrees of the metals. In alkaline medium, was achieved the selective soublization of zinc, but the degree of extraction attained was low (60 %), hence further research use only acid leaching. By means of acid solubilization, the degrees of extractions registered were: 98 % for ZnO, 24 % Mn_xO_y and 18 % Fe, when using 2 M H_2SO_4, 1:5 solid liquid ratio and 1 hour reaction time.

The electrochemical solubilization was performed in order to improve the performance of chemical solubilization in weak acid medium. The tests were carried out in 0.5 M H_2SO_4, at intensity values between 0.2 A and 0.6 A. In this manner, Zn extraction degree improved with 44 % towards the results obtained during chemical solubilization. In the same time, increasing the current density was observed a decrease with 60 %, respectively with 70 % of the manganese and iron concentrations, as a result of oxidative precipitation.

Complete chemical solubilization of ZAR was performed in 2 M H_2SO_4, aqueous solutions, during 20 hours reaction time, regardless of the solid liquid ratio used. Low acid concentrations had ensured the complet solubilization of ZAR only at high solid liquid ratios. Using high H_2SO_4 concentrations (4 M) determines the zinc passivation, blocking the further solubilization of the waste. In the same time, the electrochemical process attained a degree of extraction of 73 %, with a current yield of 50 % for the Zn electrodeposition process, after only 4 hours of electrolysis.

2. Zinc electrowinning from synthetic solutions

The characteristics of zinc electrowinning process were highlighted through a fundamental study of cyclic voltammetry and an applied study of zinc electrowinning from solutions similar with those resulted after the chemical solubilization of the electrodic materials.

The fundamental study of cyclic voltammetry revealed adverse effects that the Mn^{2+} and Fe^{2+} ions have upon Zn electrodeposition, among them including: shifting reduction potential towards more negative values and decreasing current yield from about 88 % to about 20 % with increasing the concentration of Mn^{2+} and Fe^{2+} in the electrolyte solution. Also, by increasing the concentration of Zn^{2+} was reduced the harmful effect on the cathodic current efficiency, according to section 6.1.

In presence of Mn^{2+} and Fe^{2+} ions, depending on the current density applied, the cathodic current efficiency was low (22 - 48 %), the increase of current density provoking the CCE decrease. The low cathodic current efficiency in presence of Mn^{2+} ions underlined the necesity of manganese separation from the electrolyte solution or the usage of a divided electrochemical reactor.

3. The separation of Mn^{2+} from the electrolyte solution

The chemical separation of manganese from acid leaching solutions of BP was realized by chemical oxidation with ammonium persulfate. The results obtained show a high degree for Mn precipitation (approximately 90 %) as MnO_2, without affecting the content of zinc in the solution. The optimum conditions for MnO_2 precipitation were: 20 % $(NH_4)_2S_2O_8$, pH =6, reaction time of 3 hours and temperature of 90 °C.

Electrochemical activity of manganese oxides was assessed by cyclic voltammetry (CV) studies, in order to investigate the electrochemical properties and to assess the possibily of using the material as cathodic material. Thus, the electrochemical characterization of the synthetized material involved studies evaluating the capacity and the electrochemical reversibility, respectively the stability over time. To compare the performance of synthesized manganese dioxide were made parallel measurements using MnO_2 derived from dismantling 3 charged batteries from the three battery manufactures.

The MnO_2 chemically obtained presents an electrochemical activity, when subjected to a heating treatment at 800 °C for 1 hour. The reason for this behaviour was the presence of NH_3 in MnO_2 structure, being neccesary its removal by heating treatment. Electrochemical characterization reported in this study shows that chemical MnO_2 obtained at pH=6, has electrochemical capacity values (~ 1.6 mAh/cm^2) superior to the commercial MnO_2 samples (~ 0.6 mAh/cm^2). Thus, it can be used successfully in industrial and commercial applications due to its electrochemical properties.

4. *Zinc electrowinning from the solutions resulted in the solubilization step*

The maximum current yields obtained for Zn and Mn recovery were 98 % for zinc and 45 % for manganese at a current density of 500 A/m^2. It was also established that while Zn^{2+} and Mn^{2+} concentration ratio was over 10:1, zinc electrowinning was achieved with high current efficiency (>90 %). Mantaining this ratio was possible by the solubilization of zinc anodic remnants. Anodic current efficiency was modest, being strongly influenced by the acidity levels of the solution.

5. *The proposed technological flow for recycling Zn from used batteries*

Based on the experimental results (chapter 8), the proposed technological process for Zn recovery includes four important steps: (i) the BP solubilization, respectively ZAR solubilization in 2 M H_2SO_4 (ii) the electrochemical recovery of Zn in the cathodic compartment, respectively of MnO_2 in the anodic compartment (iii) increasing Zn^{2+} concentration by crossing the resulting solution after MnO_2 recovery over a new batch of ZAR, followed by the Zn recovery in the cathodic compartment; (iv) increasing Mn^{2+} concentration by crossing the resulting solution after Zn recovery in the second step over a new batch of BP, followed by MnO_2 recovery in the anodic compartment.

The mass balance performed according to the proposed technological flow, for processing 2 tonnes of spent batteries, highlights the recovery per hour of about 26 kg metallic Zn and approximately 18 kg MnO_2. The resulting solutions from this technological process should be recycled in the electrochemical reactors. Secondary waste (paper, plastic, steel, graphite) resulting from the recycling process can be redirected to the specific industry.

The scientific activity of the PhD Student

Participation at conferences related to the thesis topic

1. **M.Anton**, F. Imre-Lucaci, S. Dorneanu, P.Ilea, *Zinc recovery from spent batteries I. Researches regarding dissolution and electrowinning of Zn from spent Zn-*MnO_2 *batteries*, National Conference with international participation "Corrossion and anticcorosive protection, 16 -18 September 2010, Cluj-Napoca, Romania
2. **M. Anton**, S-A. Dorneanu, P. Ilea , *The recovery of metals from spent alkaline Zn-*MnO_2 *batteries*, International Conference of Physical Chemistry "Romphyschem", 2 - 4 June 2010, Bucharest, Romania
3. **M. Anton**, A. Manciulea, P. Ilea, *The study of zinc solubilisation process from the active mass of Zn/*$ZnCl_2$ */*MnO_2 *used batteries,* International Conference "Journee d'Electrochimie, 4-8 July 2011, Grenoble, France
4. A. Manciulea, **M. Anton,** R. Racz, P. Ilea., *Zn recovery from spent batteries II. Zinc electrowinning process from Zn anode scraps of spent Zn-*$ZnCl_2$*-*MnO_2 *batteries,* 17th Romanian International Conference on Chemistry and Chemical Engineering, 7-10 September 2011, Sinaia, Romania
5. **M. Anton**, A. Manciulea, U. Schmidt, A. Bund, P. Ilea, *The electrochemical dissolution of zinc anodic remnants from Zn-*MnO_2 *waste batteries,* Third Regional Symposium on Electrochemistry: South- East Europe, 13-17 May 2012, Bucharest, Romania
6. **M. Anton**, U.Schmidt, A. Bund, A. L. Manciulea, P.Ilea, *The Electrochemical Recovery of Zinc from Zn-*MnO_2 *Waste Batteries,* 63rd Annual Meeting of the International Society of Electrochemistry, 19-24 August 2012, Prague, Czech Republic.

Publication

1. **M. Anton**, A. Manciulea, P. Ilea, *Comparative study of solubilization for Recycling metals from spent batteries*, Studia UBB Chemia LVI 4 (2011) 223 – 233
2. M. Anton, A. Manciulea, U. Schmidt, A. Bund, P. Ilea, *Hydrometallurgical flow for zinc recovery from Zn-MnO waste batteries I. Zinc solubilization from anodic remnants*, Studia UBB Chemia (2012), Accepted manuscript
3. P. Macolino, A.L. Manciulea, **M.S. Anton**, P. Ilea, F. Veglio, *Recovering Mn from leaching solutions of alkaline spent batteries with ammonium peroxodisulfate,* Journal of Power Sources, In progress
4. **M. Anton,** A.Manciulea, O. Ponta, P. Ilea, *Electrodeposition of Zn and* MnO_2 *from solutions obtained in the leaching steps of the electrodic materials of Zn-*MnO_2 *batteries,* In progress

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