MANGANESE RECOVERING FROM ALKALINE SPENT BATTERIES BY AMMONIUM PEROXODISULFATE

Paola Macolino[1)], Adriana Loredana Manciulea[2)], Ida De Michelis[1)*], Muresan Silviu Anton[2)], Petru Ilea[2)], Francesco Veglio[1)]

[1)] *University of L'Aquila, Department of Industrial Engineering, Information and Economic, Italy*
[2)] *Babes – Bolyai University, Faculty of Chemistry and Chemical Engineering, Cluj-Napoca, Romania*

*Corresponding author: e – mail: ida.demichelis@univaq.it, Tel.:+39 0862434221, Department of Industrial Engineering, Information and Economic, University of L'Aquila, Via Monteluco di Roio, 67100, L'Aquila, ITALY

Abstract

The process of manganese removal from spent battery leaching solutions, with ammonium peroxodisulfate, prior to recovery of zinc by electrolysis is presented. The experiments were carried out according to a 2^3 full factorial design considering ammonium peroxodisulfate concentration, temperature and pH as factors investigated. The analysis of variance (ANOVA) was carried out on the precipitation yields of Mn and Zn after 30 min, 1h, 2h and 3h of reaction. Optimal conditions for obtaining Mn as MnO_2 have been 20 % $(NH_4)_2S_2O_8$, 90 °C and pH 6. Data from XRF and AAS during the reaction at different time are presented to analyse the kinetic behaviour of the system. The MnO_2 precipitated and solutions were characterized by XRF and XRD. The solid samples were kept at 800 °C for 1 h to produce chemical manganese dioxide (CMD) and were characterized by cyclic voltammetry for their electrochemical activity. The overall results denoted that chemical oxidation of manganese from spent batteries leaching solutions with ammonium peroxodisulfate is a suitable method for manganese recovery as MnO_2 prior zinc recovery by electrolysis, also to produce of a suitable product (CMD), in other words, it could be used in a process for recycling spent batteries.

Keywords: alkaline spent batteries, CDM, selective precipitation, recovery

1   Introduction

The recycling of spent batteries (SB) is imposed by environmental regulations/legislation [1]. Even though the costs of recycling SB could be quite high, a new perspective might arise as wastes to be considered secondary raw materials. In this case their price would be cheaper than ores.

At present time, most of research work of recovery and recycling of SB is focused on the recovery and recycling of metal and oxides [2-4], due to their economic and environmental impact. The process of recycling helps to eliminate wastes and allows obtaining of new materials with specific properties. By volume and economic value, SB are undoubtedly wastes worth to be recycled for the obtained materials and the conservation of raw materials in the interest of the sustainable development.

Two major approaches have been considered for SB recycling, pyrometallurgical and hydrometallurgical methods [2]. The hydrometallurgical processes are characterised by different pretreatment stages (physical treatment processes of the spent batteries), followed by leaching and separation of different metals by electrolysis, liquid-liquid extraction, or selective precipitation. Usually, Zn is recovered from spent batteries leach solutions by electrolysis, but the excessive manganese concentration can cause problems.

A major area of research is based on the MnO_2 production (using methods as soon chemical, sol – gel, electrodeposition and hydrothermalmethod) and improvement of its electrochemical performance [5-9]. MnO_2 is economic and commercial important with applications in different fields such as battery industry, water treatment plants, steel industry and chemicals [9].

The studies presented in the literature described the obtaining of elemental metals, oxides, alloys, salts from spent batteries. Valuable materials can be re – use or synthetize from leaching solutions of SB. Therefore, manganese oxides were obtained from SB by electrochemical methods which are clean, versatile and effective remediation alternative. A mixture of Mn_2O_3 and Mn_3O_4 with 70 % grade of Mn was obtained from spent alkaline and Zn – C batteries by acid leaching and electro – winning [10]. High current efficiency (90 %) has been obtained in the process of simultaneous recovery of Zn and Mn (as MnO_2 on lead anode) from alkaline SBs [11].

The aim of this study is to recover manganese as MnO_2 (CMD) from spent battery leaching liquors obtained from an industrial plant using ammonium peroxodisulfate, without altering the concentration of zinc in solutions that can be recovered by precipitation or electro winning.

2   Experimental materials and methods
2.1 Battery pretreatment
Spent alkaline and zinc – carbon batteries were collected and dismantled in an industrial area located in North of Italy. The black powder (BP) was separated from plastic, paper, metallic scraps and non – metallic scraps and milled by a ball mill. In this study the fine fraction of black powder, less than 2 mm. This powder was washed with water to remove chlorine, ammonium and potassium, in order to reduce the consumption of sulphuric acids in the subsequent leaching step. The acid leaching was performed with $2M$ H_2SO_4, at 60 °C and 3 hrs. Original and leached powder were analysed by X – ray fluorescence. All these treatments were carried out in an industrial scale plant.

2.2 Preparation of MnO_2/CMD
To obtain MnO_2 from spent batteries leaching solutions the following chemical reaction was considered:

$$MnSO_4 + (NH_4)_2S_2O_8 + 2\,H_2O \longrightarrow MnO_2 + (NH_4)_2SO_4 + 2\,H_2SO_4 \tag{1.}$$

The solutions used were of analytical grade: sulphuric acid (Sigma Aldrich) and ammonium peroxodisulfate (Fluka). A 2^3 full factorial design with a replicated central point was developed. The factors investigated were ammonium peroxodisulfate concentration, temperature and initial pH. The experimental conditions of each treatment are reported in **Table 1**.

Tests were numbered according to the Yates' algorithm and the central points (samples 9-11) were carried out to have an independent estimation of the variance of experimental error [12].

Table 1 Experimental conditions of 2^3 full factorial design with central point and the final pH of solutions

| Sample | Treatment | Codified Factor Level | | | Factor Level | | | |
		A (Ammonium peroxodisulfate)	B (Temperature)	C (pH)	A (%)	B (°C)	C (initial pH)	final pH
1	(1)	−	−	−	10	30	4	3.1
2	a	+	−	−	20	30	4	2.6
3	b	−	+	-	10	90	4	1.3
4	ab	+	+	-	20	90	4	1.2
5	c	−	−	+	10	30	6	5.8
6	ac	+	−	+	20	30	6	5.5
7	bc	−	+	+	10	90	6	1.2
8	abc	+	+	+	20	90	6	1.3
9	I	0	0	0	15	60	5	1.7
10	II	0	0	0	15	60	5	1.6
11	III	0	0	0	15	60	5	1.6

The tests were performed in 200 mL flasks introduced in a thermostatically controlled water bath equipped with a mechanical stirrer (Dubnoff, ISCO). For each test, 25 mL of spent battery leaching solution was brought to desirable pH and then the volume of 40 % ammonium peroxodisulfate for the suitable concentration was added, according to the experimental plan. During each test, 1 mL of solution was withdrawn after 15min, 30 min, 1 h, 2 h and 3 h to measure the concentration of Mn and Zn by AAS(AAS, spectrometer SpectrAA 200, Varian), after centrifugation. Each sample was diluted 1:10 with solution of nitric acid (pH 2) to avoid precipitation of metals. The pH was measured at the end of each reaction. The filtered residual solid was washed with 150 mL of solution of nitric acid (pH 2), dried at 105 °C for 24 h and weighted by an analytical balance (Mettler PE 600).

The Yates' algorithm was used to evaluate whether effects and interactions among the investigated factors are significant with the respect to the experimental error.

The solution and powders obtain were analysed by X-ray fluorescence analyses (XRF, Spectro Xepos).

The solids obtained were analyzed by X – ray diffraction analyse (XRD Philips Analytical).

The commercial EMD from 3 different battery producers and 4 of the solid samples obtained by chemical oxidation with ammonium peroxodisulfate of the spent batteries leaching solution (the precipitates obtained for sample 4 and sample 8, before and after they were kept in the furnace at 800 °C) were characterised by cyclic voltammetry to assess their electrochemical activity. The three trade batteries Toshiba R6KG Size AA 1.5V (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 cathode active 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 (0.1002 g) as active material with 20 wt. % of graphite (0.0268 g) (Fluka, purum powder; $\leq$ 0.1 mm). The constituents were mixed together with 3 μL 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 and graphite bar as current collector.

A DXC240 computer controlled Bipotentiostat was used for all electrochemical measurements. An electrochemical glass cell (V = 100 mL) equipped with a MnO_2 based working electrode, a saturated Ag/AgCl reference electrode and a platinum wire counter electrode were used.

Cyclic voltammetry (CV) studies were performed between 1 V - (-0.2V) in 1 M Na_2SO_4 electrolyte solution at different scan rates. In order to determine the contribution of graphite to the overall charge capacity of the electrode, a cyclic voltammetry, CV, experiment was performed on a blank electrode containing no MnO_2. The charge storage capacity of this electrode was found to be negligible ($\approx 10^{-4}$ mA*h/cm^2).

The capacity values (mAh/cm^2) were calculated from the area of the cathodic part of CV, corresponding to the different MnO_2 samples [7] and were reported to the electrode disk area.

The stability of the electrode material was achieved by multi – pulse technique for loading and unloading. Galvanostatic charge – discharge experiments were performed in a similar setup cell as described above and consisted in maintaining the charge/discharge current at 0.14 mA/cm^2 for 3 hours. The curves obtained were represented by the potential evolution over time.

3   Results and discussion

The focus of this study was the selective separation of manganese as MnO_2 from solutions, without loss of Zn.

Table 2 reports the characterization of the initial solid and liquid samples obtained from leaching solution of spent batteries in the industrial plant.

Table 2 XRF data of some elements in BP < 2mm and leach liquor solutions

Sample	Zn (%)	Mn (%)	Fe (%)	K (%)	Cl (%)	S (%)
BP <2mm (Solid)	20	33	0.3	4.6	3.5	0.1
Leaching solution (Liquid)	11	7	0.03	0.8	0.1	6

Table 3 and **4** shown the data of the XRF (semi – quantitative composition of element after precipitation of Mn) for the solid samples (precipitates) obtained in different treatments and for the final solutions after the reaction between the spent batteries leaching solutions and ammonium peroxodisulphate.

It can be noticed that most of the manganese content was found in the precipitates obtained after the filtration of solutions resulted in the reaction between the spent batteries leaching solutions and ammonium peroxodisulphate. Most of Zn content remained in solutions. This confirms the fact that Mn was selective precipitated from the solution as MnO_2, based on the chemical reaction (1). Liquid samples collected at different time (15 min, 30 min, 1 h, 2 h and 3 h), during the precipitation process, were also analysed by AAS. **Table 5** and **6** report the Mn and Zn precipitates during the treatments. Also Zn was investigated in order to evaluate the co-precipitation with Mn.

Percentage of precipitation is calculated as indicated in the follow relation:

% Y = Co Vo – Cf (Vo+Vr)/ Co Vo *100   (2.)

Where: Co= Initial composition

Cf = Final composition
Vo = Initial volume
Vr = Reagents Volume
Y % = Mn or Zn

Table 3 Semi – quantitative composition of solid samples, by XRF, after Mn precipitation

Sample n°	[%] Mn	[%] Zn
1	−	−
2	3,7	16
3	52	1,5
4	62	2,3
5	−	−
6	−	−
7	73	2,7
8	60	2,8
9	40	9
10	70	0,4
11	50	6

Table 4 Semi – quantitative composition of leach liquor, by XRF, after Mn precipitation

Sample n°	[g/l] Mn	[g/l] Zn
1	70	58
2	13	33
3	30	70
4	3	30
5	70	70
6	13	35
7	33	85
8	4	70
9	40	60
10	41	56
11	40	63

The best results were obtained in the treatments 4 and 8, where the Mn precipitation was the highest (~ 90 %) and Zn precipitation was the lowest (25 % for sample 4 and 5 % for sample 8). These results were obtained after 3 hours of reaction at 90 °C. The difference between these two samples was the pH; pH 4 for sample 4 and pH 6 for sample 8. Optimal conditions to obtain MnO_2 are: 20 % $(NH_4)_2S_2O_8$, pH 6, 3 hours of reaction and 90 °C.

The Anova results for Mn extraction yield after at 30 min, 1 h, 2 h and 3 h are presented in **Fig. 1** [12]. As it can be seen, after 30 min of reaction only temperature has a significant positive effect on Mn precipitation (**Fig. 1a**). After 1 h of reaction all three factors: ammonium

Table 5 Mn precipitation yield versus time in the investigated experimental conditions

Sample n° / Time	Mn precipitation yeld (%)				
	15'	30'	60'	120'	180'
1	42	36	31	32	31
2	40	34	34	34	35
3	43	38	42	50	49
4	80	85	92	92	91
5	42	39	39	40	40
6	51	45	43	45	45
7	50	55	52	66	63
8	81	85	89	91	91
9	44	30	35	38	40
10	22	30	35	39	44
11	37	47	37	39	42

Table 6 Zn precipitation yield versus time in the investigated experimental conditions

Sample n° / Time	Zn precipitation yeld (%)				
	15'	30'	60'	120'	180'
1	36	16	34	41	32
2	33	30	61	53	63
3	23	6	27	24	24
4	35	13	14	21	28
5	43	39	33	37	44
6	47	50	61	67	71
7	13	21	38	51	33
8	21	30	28	21	5
9	24	46	28	29	25
10	18	26	80	48	58
11	69	70	79	83	86

peroxodisulfate concentration, temperature and pH have a positive effect on Mn precipitation yield (**Fig. 1b**). Interaction between factor A and B is also positive: increasing the ammonium peroxodisulfate concentration and temperature the precipitation of manganese is higher with respect to the single effect. The other effects although significant from the statistical point of view are not relevant.

Similar significant effects of factors and interaction between them can be noticed after 2 h of reaction (**Fig. 1c**).

There are positive effects on manganese precipitation of all three factors (A, B, C) and the interaction between ammonium peroxodisulfate concentration and temperature (AB) after 3 h of reaction (**Fig. 1d**). The positive effects of ammonium peroxodisulfate concentration, temperature and their interaction have been identified.

The positive effect of pH could be related to the precipitation of Mn^{2+} and the possible reaction of Mn^{2+} with dissolved oxygen as indicated in reactions (2) and (3).
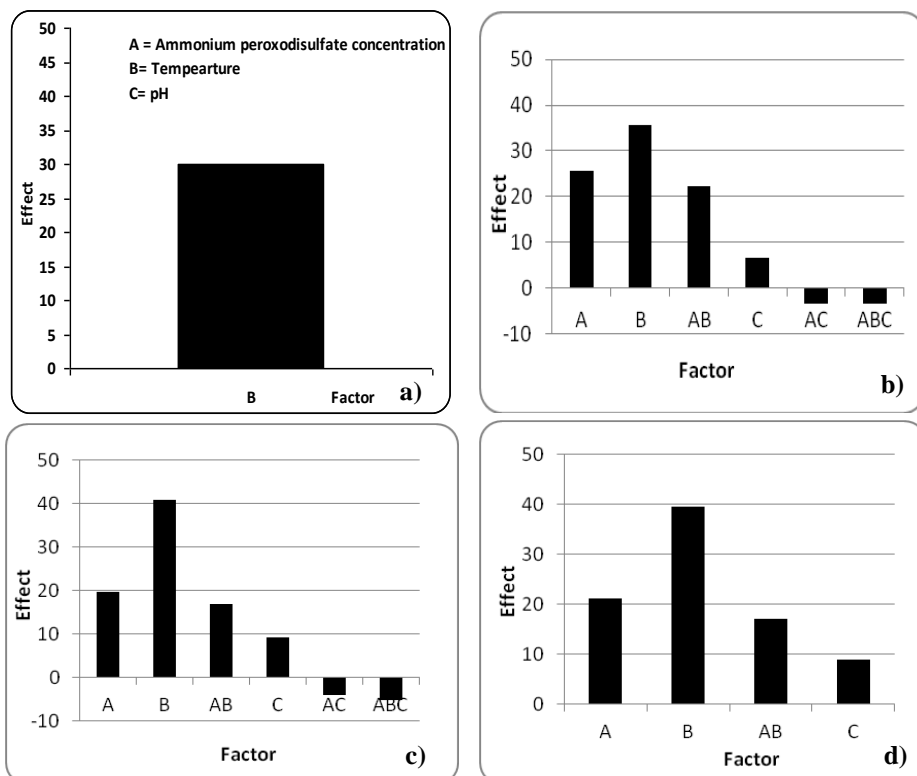
Fig. 1 Effect of most significant factors (> 95 %) and their interactions on Mn precipitation
yield at a) 30 min; b) 1 h; c) 2 h; d) 3 h

$$Mn^{2+} + 2\,OH \leftrightarrow Mn(OH)_2 + (NH_4)_2SO_4 + 2\,H_2SO_4 \qquad (2.)$$

$$Mn(OH)_2 + \tfrac{1}{2}\,O_2 \longrightarrow MnO_2 + H_2O \qquad (3.)$$

Therefore, the Mn precipitation is positively influenced by increasing of pH.

To conclude, all the investigated factors have strong positive effects on the Mn precipitation process. At the same time Zn precipitation is not significant affected by any factor or their interaction, after 3 h of reaction (data not shown here).

The XRD performed on the most significant solid sample obtained during Mn precipitation is shown in **Fig. 2**. As it can be seen, the ammonia manganese oxide is the main component of the precipitates obtained.

3.1 Electrochemical characterization

Electrochemical activity of manganese oxides can be assessed by voltammetry which can provide additional information for material characterization from the shape, the number and the position of the different peak resembling the redox processes [9].

The samples obtained from chemical oxidation, and used in these experiments, were the precipitates obtained for sample 4 (S1) and 8 (S2) and kept in the furnace at 800 °C (see Table 1).
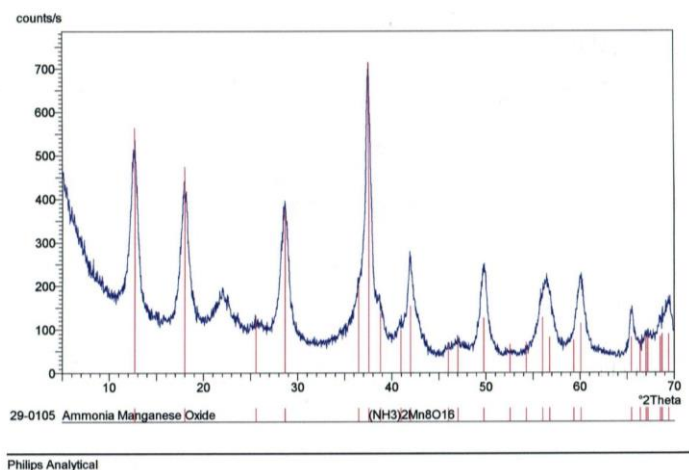
**Fig. 2** XRD of the precipitate obtained during test number 4

The electrochemical reversibility (ER) is one of the predominant factors influencing the power capabilities of electrochemical system. To evaluate ER of the sample the potential window of CV was changed in the following three domains: (a) from 1 to -0.2 V; (b) from 0.8 to 0 V; (c) from 0.6 to 0.2 V (**Fig. 3**). The symmetric $i - E$ responses were observed indicating that the sample exhibited an electrochemical reversibility in the mentioned potential ranges and sweep – rate.
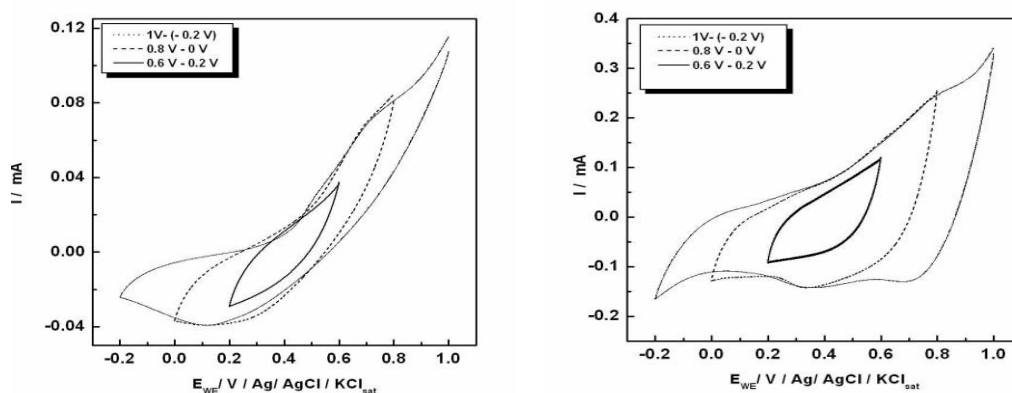
Fig. 3 Cyclic voltammograms of S1 and S2 over different potential ranges, in 1M Na_2SO_4, 5mV/s

The effect of scan rate is presented in **Fig. 4**. As the scan rate increases, the CV profile deviates from the ideal capacitive behaviour. This is mainly because the redox reactions depend on the insertion – deinsertion of the alkali ion or protons from the electrolyte as explained by [13]. At slower scan rates, the diffusion of ions from the electrolyte can gain access to almost all available pores on the electrode surface, leading to a complete insertion reaction.
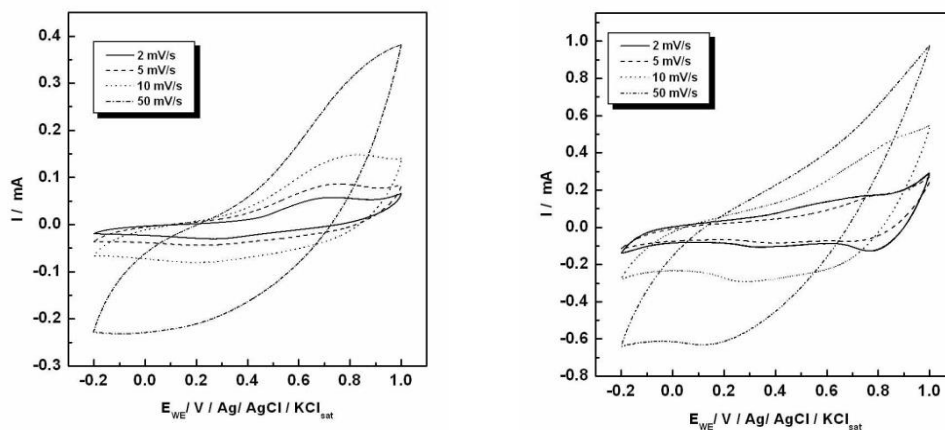
Fig. 4 Cyclic voltammograms of S1 (left) and S2 (right) for different sweep rate, in 1M Na$_2$SO$_4$

Successive cyclic voltammograms recorded at a scan rate of 5 mV/s for both MnO2 samples, in a potential range, are shown in **Fig. 5**.
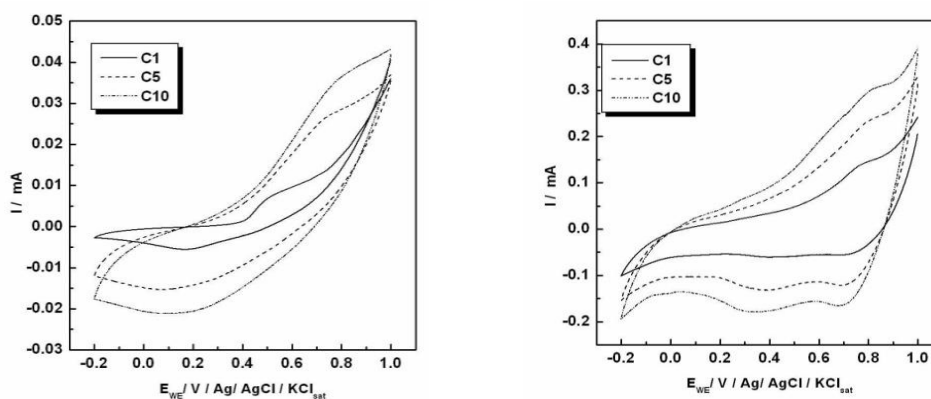

Fig. 5 Voltammetric cycles (1st cycle, 5th cycle and 10th cycle) for S1 (left) and S2 (right) solid samples obtained by chemical oxidation of spent battery leching solution with ammonium peroxodisulphate

For S1 sample, at cathodic polarization a tiny reduction peak comes up at 0.1 V, and an oxidation peak appears at 0.47 V. With increasing number of scanning times, the redox peaks disappear gradually. For S2 sample, the reduction peak appears around 0.3 V, with an oxidation peak at 0.8 V. The CV evolution by repeated cycles indicated an increase in electrode capacity S2 stronger than the in case of electrode S1. The shape of the cycle is strongly dependent on the number of cycle. For S2, form of the curves is preserved, only registering an increase of current with increasing number of cycles. This can be attributed to maintaining the amount of electroactive material on the electrode surface confirming the explication given by Pagnanelli et al. [9].

Capacity values (mAh/cm^2) have been evaluated using a similar method as Pagnanelli et al. [9]. The specific values calculated from the first cycle for each material were 0.03 mAh /cm^2 for S1, 0.6 mAh /cm^2 for S2, showing a higher performance of the S2 material in comparison with the commercial ones.

Dynamic trends of capacity were also calculated for the following cycles and reported in **Fig. 6**. The cycling capability of the S2 was studied galvanostatically at a constant current of 0.14 mA/cm^2 and between 0 and 1 V. Typical charge – discharge curves for the S2 sample is shown in **Fig. 7**.

The charge and discharge curves are basically symmetric and present a good stability in time.
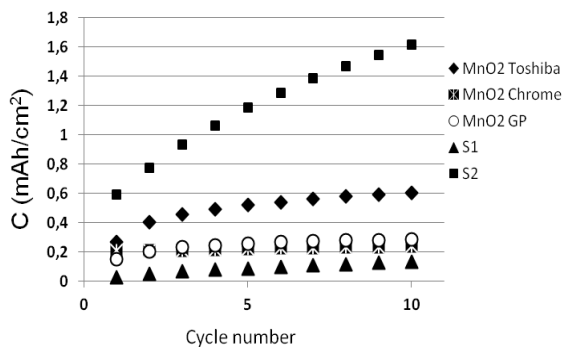
Fig. 6 Capacity of EMD and CMDs calculated for the different voltammetric cycles
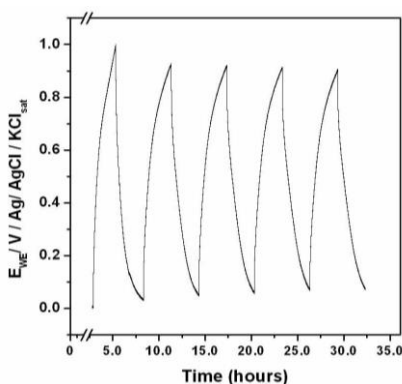
Fig. 7 Cyclic capability of the S2 between 0.9 V and 0 V at constant current of 0.14 mA/cm^2

4   Conclusion

Chemical oxidation of leaching spent batteries solutions with ammonium peroxodisulfate yielded to CMD with high extraction degree, without affecting the Zn content in the solutions.

The factors investigated by ANOVA were ammonium peroxodisulfate concentration, temperature and pH. The statistical analysis shown that ammonium peroxodisulfate concentration and temperature had a great positive significant (> 95 %) influence on the product obtained (CMD). Highest Mn precipitation (aprox. 90 %) was achieved after 3 h of reaction.

X – ray spectra of the solid samples with the highest amount of Mn have shown that the CMD composition is mainly ammonia manganese oxide. The conditions of precipitation seem to influence the properties of product (CMD).

Electrochemical measurements denoted that CMD obtained at pH 6, 90 °C, 20 % (NH4)2S2O8 and 3 h present high electrochemical activity when the precipitates are kept at 800 °C for 1 h. The electric capacity of this sample shown a high performance in comparison with the commercial samples.

The results reported in this work denoted that CMD obtained could have industrial and commercial applications, due to similar properties with commercial EMD sample. This lead up to further experiments for optimizing the process conditions and improving the product yields.

References

[1] EU Directive, 91/157/EEC, 1991 [online]. Available at <http://eur-lex.europa.eu/ LexUriServ/LexUriServ.do?uri =OJ:L:1991:078:0038:0041:EN:PDF>.

[2] A. M. Bernardes, D. C. R. Espinosa, J. A. S. Tenório: Journal of Power Sources, Vol. 130, 2004, p. 291-298

[3] I. De Michelis, F. Ferella, E. Karakaya, F. Beolchini, F. Veglio: Journal of Power Sources Vol. 172, 2007, p. 975-983

[4] E. Sayilgan; Kukrer, T.; Civelekoglu, G.; Ferella, F.; Akcil, A.; Veglio, F.; Kitis, M.. Hydrometallurgy, Vol. 97, 2009, p. 158-166

[5] H. Adelkhani, M. Ghaemi, M.: Journal of Alloys and Compounds, Vol. 493, 2010, p. 175-178

[6] M. Ghaemi, A. Gholami, R. B. Moghaddam: Electrochimica Acta, Vol. 53, 2008, p. 3250-3256

[7] H. Kawaoka, M. Hibino, H. Zhou, I. Honma: Journal of Power Sources, Vol. 125, 2004, p. 85-89

[8] V. G. Kumar, K. B. Kim: Ultrasonics Sonochemistry, Vol. 13, 2006, p. 549-556

[9] F. Pagnanelli, C. Sambenedetto, G. Furlani, F. Veglio, L. Toro: Journal of Power Sources, Vol. 166, 2007, p. 567-577

[10] F. Ferella, I. De Michelis, F. Veglio: Journal of Power Sources, Vol. 183, 2008, p. 805-811

[11] C. C. B. M de Souza, J. A. S. Tenório: Journal of Power Sources, Vol. 136, 2004, p. 191-196

[12] D. C. Montgomery: *Design and Analysis of Experiments*, fifth ed., John Wiley & Sons, New York, 2000

[13] V. Subramanian, H. Zhu, R. Vajtai, P. M. Ajayan, W. Bingqing: Journal of Physical Chemistry B, Vol. 109, 2005, p. 20207-20214

Acknowledgements