

Short communication

# Recycling manganese from spent Zn-MnO<sub>2</sub> primary batteries

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## Abstract

The cathode of spent Zn-MnO<sub>2</sub> primary batteries is made up of mainly Mn<sub>3</sub>O<sub>4</sub> and α-MnO<sub>2</sub>. Energy dispersive X-ray analysis of the cathode surface also shows the presence of zinc from the anode and chloride from the electrolyte. Manganese was recovered by precipitation, electrodeposition and anodization. X-ray diffraction measurements confirmed that the Mn<sub>3</sub>O<sub>4</sub> material was recycled by chemical precipitation. The charge efficiency by electrodeposition was 85% at 25.0 mA cm<sup>-2</sup>. In the current density range studied, the potential/current density plots follow a Tafel-like relation. In the anodic process, the material oxidizes at the electrode/solution interface and precipitates to the bottom of the cell. Only a fraction corresponding to 20% of the charge density is deposited onto the electrode. This happens because Mn<sup>2+</sup> oxidizes to Mn<sup>3+</sup>, which then suffers disproportionation. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Manganese; Recycling; Zn-MnO<sub>2</sub> batteries

## 1. Introduction

Primary batteries are used in applications that require a relatively low energy density. Li-ion, metal hydride, and nickel-cadmium batteries have a large specific capacity but at a high cost [1,2]. Since Zn-MnO<sub>2</sub> batteries are inexpensive, they are more commonly used. In Brazil, an average of six batteries are consumed per inhabitant every year [3]. According to a National Environment Council of the Environment Ministry (CONAMA) resolution, this type of battery may be disposed of in home rubbish and waste dumps [4]. Spent Zn-MnO<sub>2</sub> batteries in the domestic garbage have become a serious environmental problem. The presence of batteries in organic waste jeopardizes the quality of the fertilizer produced and prevents its use in agriculture due to the large percentages of toxic metals. The recycling of batteries to recover the metals involves hydrometallurgical or pyrometallurgical processes. The pyrometallurgical process basically consists of selective volatilization of metals at an elevated temperature of around 900 °C followed by vapour condensation. This process would be a possible solution; however, it is extremely hazardous to the environment because some of the metal is released into the atmosphere, and even con-

taminates distant areas. Another means of recycling batteries is the hydrometallurgical process that involves the dissolution of anodes and cathodes in acidic or alkaline solutions. Afterwards, the dissolved metals are recovered by precipitation, extraction or by electrochemical methods. The hydrometallurgical process is highly selective and avoids gaseous emissions and also the energy consumption is lower. Therefore, it is more efficient in the recycling of spent Zn-MnO<sub>2</sub> batteries [5–12]. The object of this paper is recycling the manganese from spent primary Zn-MnO<sub>2</sub> batteries by chemical precipitation, electrodeposition, and anodization. Characterization of the recycled materials was made by X-ray diffraction, scanning electronic microscopy (SEM) and energy dispersive X-ray (EDS).

## 2. Experimental

### 2.1. Cathode disassembly and dissolution

Recycling batteries requires selective collection, disassembly and a sequence of physical and electrochemical transformations. Spent batteries were separated into homogeneous lots during selective collection. In this work used Zn-MnO<sub>2</sub> batteries were Panasonic AA type because the disassembly was easier. The cells with a volume of 500 ml were used in a dissolution process. Cathodes were dissolved using H<sub>2</sub>SO<sub>4</sub> 0.50 mol l<sup>-1</sup> and H<sub>2</sub>O<sub>2</sub>

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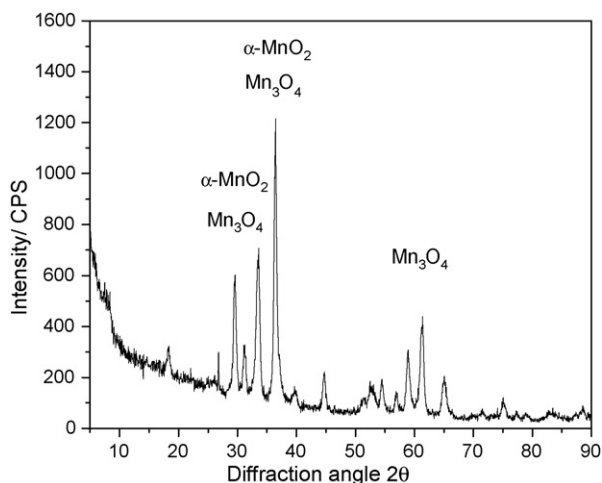


Fig. 1. Typical X-ray diffraction of the positive electrode from the spent Zn-MnO<sub>2</sub> batteries.

30% (v/v) solutions. The optimized conditions obtained were 8.40 g of cathode per 100.0 ml of H<sub>2</sub>SO<sub>4</sub> 0.50 mol l<sup>-1</sup> and 1.0 ml of H<sub>2</sub>O<sub>2</sub> 30% (v/v) solutions. The hydrogen peroxide avoids the oxidation of the Mn<sup>2+</sup> for the oxygen dissolved in the dissolution solution. Cathode dissolution took 3 h under constant magnetic stirring speed of 800 rpm at 298 K. The suspension was filtered after manganese oxide dissolution. Graphite was separated after filtration and dried at 50 °C for 91 h. The graphite mass remained constant under these conditions. Plastic electrodes for electrolytic cells were obtained using the graphite recovered from the spent Zn-MnO<sub>2</sub> batteries. Graphite was added to a solution of polyvinyl alcohol 20 (w/v) at 50 °C. The plastic electrode was prepared by pasting and pressing the paste under a carbon steel grid.

α-MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> phases constitute the discharged electrodes in agreement with the measures of X-ray diffraction (Fig. 1). The composition of the discharged electrodes of the batteries Zn-MnO<sub>2</sub> depends on the discharge rate and of the procedure used in the recycling process. Adsorbed chloride on the electrode surface was present, however, as sludge (Fig. 2). Therefore, the chloride anions exercised a small influence in the process of dissolution of the positive electrodes of the Zn-MnO<sub>2</sub> batteries. The cathode dissolution reaction is:

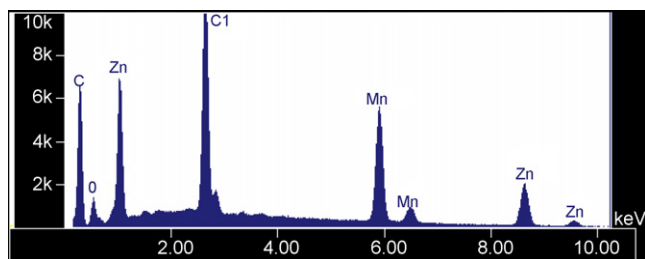
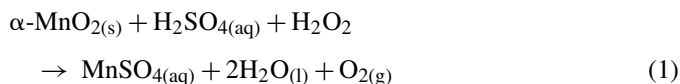
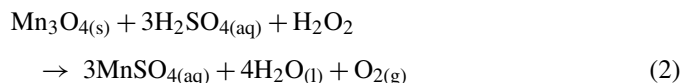


Fig. 2. Typical energy dispersive X-ray of the positive electrode from the spent Zn-MnO<sub>2</sub> batteries.



The solution pH went from 0.515 to 0.744 during anode dissolution. The conductivity and viscosity of the leaching solution were equal to 69.2 mS cm<sup>-1</sup> and 1.15 cP, respectively. The ionic manganese concentration was determined by the colorimetric method and was 0.5 mol l<sup>-1</sup> [13]. The study on the cathode leaching of positive electrodes from spent Zn-MnO<sub>2</sub> batteries is not an objective in this work.

## 2.2. Synthesis of manganese oxide

In order to precipitate the ionic manganese, an aliquot of the dissolution solution was diluted to one tenth of its concentration. A LiOH solution (1.00 mol l<sup>-1</sup>) was used as the precipitating agent to verify ionic lithium incorporation in the manganese oxide. This material is used as positive electrodes in ion lithium batteries. There is no ionic lithium incorporated in the manganese oxide according to X-ray diffraction. The LiOH solutions was added dropwise to an aliquot of 50.0 ml under magnetic stirring of 800 rpm. LiOH 1.00 mol l<sup>-1</sup> was added until pH was equal to 10. Turbidity and conductivity were measured after the addition of the LiOH solution. In the leaching of the positives electrodes we used hydrogen peroxide to avoid the oxidation of the Mn<sup>2+</sup>. Therefore, in the leaching solution there is dissolved oxygen from the decomposition reaction of the hydrogen peroxide and from the atmosphere. The separation between the precipitate and the solution was done by filtration. In the next stage, the precipitate was dried at 50 °C during 72 h. The manganese oxide mass remained constant under these conditions. Finally, the precipitate was pulverised and the powder was passed through a 37 mesh sieve.

## 2.3. Electrochemical cell

In the electrodeposition process, the working electrode was made of steel 1020. These electrodes were prepared from a rectangular sheet with a geometric area of 0.20 cm<sup>2</sup>. The auxiliary electrode was made with a platinum sheet with a geometric area of 3.75 cm<sup>2</sup>. The reference electrode was Ag/AgCl/NaCl-saturated. Before each electrochemical experiment, the working electrode was abraded with 600 grit sandpaper and then rinsed with distilled water. The galvanostatic experiments were performed with a regulated power supply built in the laboratory. The working and the auxiliary electrodes were connected to the voltage meter and linked to a microcomputer by an RS232 interface. The electrolyte solutions were prepared with p.a. reagents and pure water. The solutions were changed after each experiment. All electrochemical experiments were performed at 298 K. A working graphite electrode was used in the anodization process. The charge density was kept constant (90.0 C cm<sup>-2</sup>) and the current density was varied during electrochemical deposition.

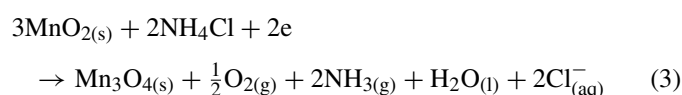
## 2.4. Characterization techniques

The cathode structure was identified by X-ray diffraction, scanning electron microscopy, and energy dispersive X-ray. The diffractograms were taken in a ROTAFLEX RIGAKU RV-20013 with radiation Cu K $\alpha$  = 1.5405 and a nickel filter. The micrographs were obtained in a JEOL JSM model 840A and microanalysis was performed in JEOL JXA model 8900RL equipped with an X-ray dispersive energy detector. Microanalysis was carried out by dispersive energy spectrometry. This technique analyzes the X-rays generated on the sample surface by the interaction of the X-ray beam with the characteristic electron beam of the elements of the material studied. The samples were cold-mounted onto bakelite and carbon-coated for microanalysis. The concentration of ionic manganese was measured by UV-vis spectroscopy by using the Cary model.

## 3. Results and discussions

### 3.1. Characterization of manganese electrodes of spent Zn-MnO<sub>2</sub> batteries

The first step of the electrode discharge reaction is the reduction of the active material, MnO<sub>2</sub>, to Mn<sub>3</sub>O<sub>4</sub> (Eq. (3)). These reactions yield a mixture of MnO<sub>2</sub> and Mn<sub>3</sub>O<sub>4</sub> as showed in Fig. 1. The mechanism proposed is in agreement with the diffractograms spectra of the cathode after discharge [14,15]. Therefore, the composition of positives electrodes from Zn-MnO<sub>2</sub> batteries depends on the discharge rate.



X-ray diffraction analysis does not show the presence of contaminants on positive electrodes clearly. Therefore, the EDS spectrum was analyzed. The X-ray diffraction measures characterize the volume phase of the electrode. The EDS analysis (Fig. 2) of the cathode surface shows the presence of zinc from the anode, chloride from the electrolyte, and oxygen present in the form of manganese oxides. This confirms that the zinc is present in the surface and not in the phase volume of the positive electrode material. Fig. 3 shows the results of scanning electron microscopy. The micrographs show that the electrode is formed by crystal aggregates (Fig. 3A). Fig. 3B and C shows enlargements of the central part of Fig. 3A. Fig. 3B and C shows that the aggregates are formed by micropores, which allow the diffusion of the electrolyte to inner regions of the electrode, and microparticles, which assure a high specific area.

### 3.2. Chemical recovery and characterization of the recycled material

The pH and conductivity measurements showed the variation of the concentration of the dissolution solution with reagent addition. The turbidity plot characterizes the moment of precipitate formation. These measurements are easy to implement and

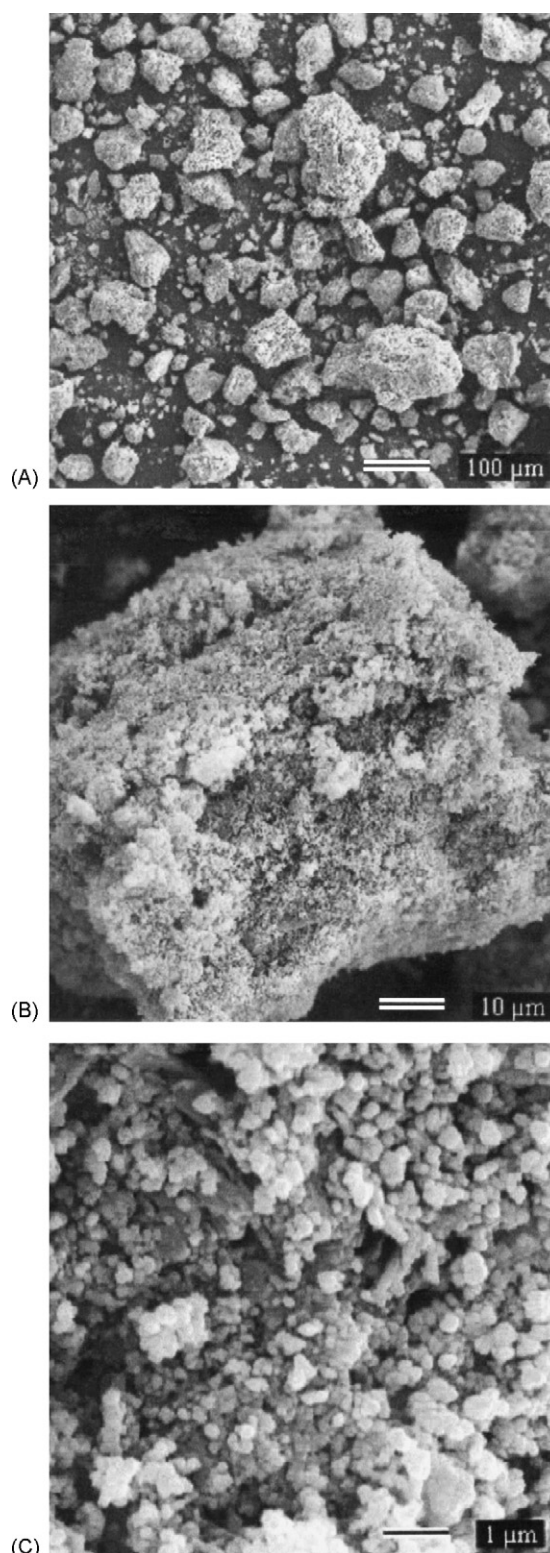


Fig. 3. Typical scanning electron microscopy (SEM) of the positive electrode from the spent Zn-MnO<sub>2</sub> batteries, (A) 100 $\times$ , (B) 1000 $\times$ , and (C) 20,000 $\times$ .

low cost. As shown in Fig. 4, an increase in pH and a decrease in conductivity were observed with the addition of the alkaline solution. After the neutralization reaction (addition of 2.0 ml LiOH), white manganese hydroxide was formed at pH between 7.0 and 8.0. Manganese hydroxide did not dissolve when the pH

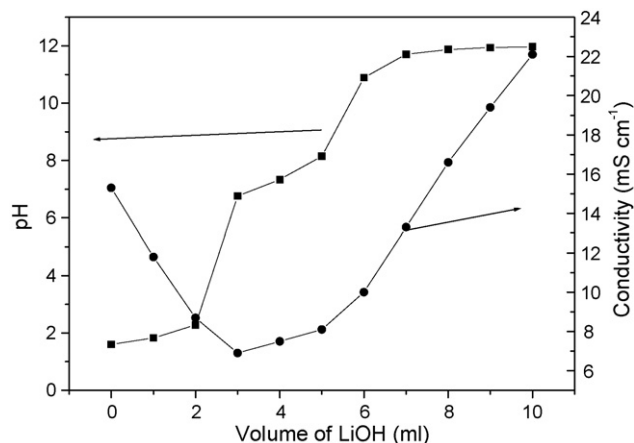
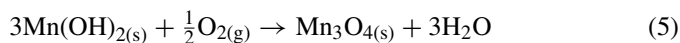
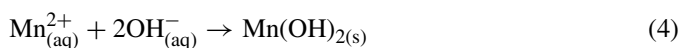


Fig. 4. pH and conductivity in function of the volume of the  $1.00 \text{ mol l}^{-1}$  of LiOH,  $T=298 \text{ K}$ .

was higher than 8.0 because it is insoluble in alkaline solution. When manganese hydroxide started to precipitate, the turbidity of the mixture increased, as shown in Fig. 5.  $\text{Mn}_3\text{O}_4$  forms a chemical precipitate after the manganese hydroxide is aged, according to X-ray diffraction measurements, and as shown in Fig. 6. The diffraction peak enlargement was due to the small size of the crystallites. Based on the conductivity, turbidity, pH and X-ray diffraction measurements, a two-step mechanism is proposed. In the first step, manganese hydroxide precipitates. Then, manganese hydroxide oxidizes at a later stage because of the oxygen dissolved in the solution. The reactions were:



Total reaction:

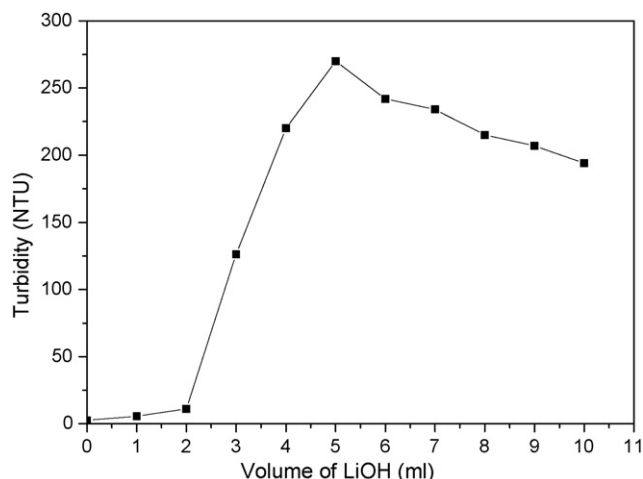
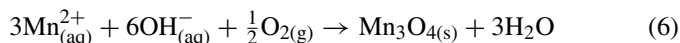


Fig. 5. Turbidity in function of the volume of the  $1.00 \text{ mol l}^{-1}$  of LiOH,  $T=298 \text{ K}$ .

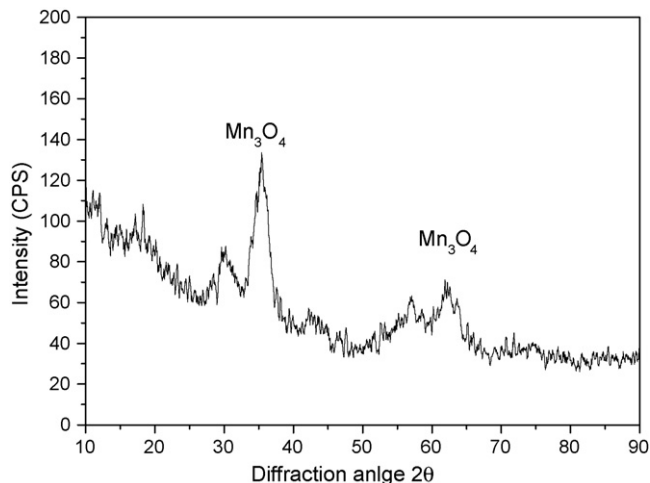


Fig. 6. Typical X-ray diffraction of the recycled manganese from the spent Zn-MnO<sub>2</sub> batteries.

### 3.3. Electrochemical recycling

Electrodeposition can be controlled by either activation or diffusion. However, it was observed that the processes were not mutually exclusive and they depended on the deposition morphology [16–19]. In the activation-controlled process, the reacting species ( $\text{Mn}^{2+}$ ) is in the reaction zone and strongly interacts with the metal atoms as well as with the water molecules adsorbed onto the electrode surface. These interactions result in distortions of the solvation layers of the reacting species and its energetic excitement. In turn, this excitement leads to the appearance of molecular orbitals in the reagent species with energy equal to that of the metal orbitals, which makes the electrochemical reaction possible. The electron transfer occurs by a tunneling effect, without involvement of the activation energy. The electrode/solution interface has an intense electric field. Since the electrochemical reaction involves electrically charged elements and the reaction zone is located within the electric field domain,

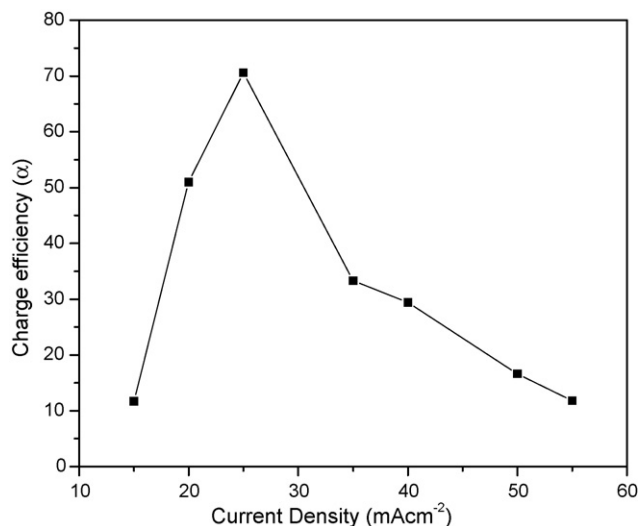


Fig. 7. Charge efficiency vs. current density for ionic manganese electrodeposition from leaching solution, without stirring,  $T=298 \text{ K}$ ,  $q=90.0 \text{ C cm}^{-2}$ .

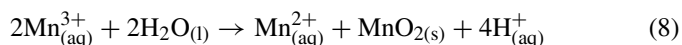
the activation energy depends on the magnitude of the electric potential. Manganese ion electrodeposition and hydrogen are released depending on the electric field, that is, on the applied current density. Therefore, several current densities were used to deposit manganese (with constant charge density  $90.0 \text{ C cm}^{-2}$ ). This procedure was necessary to identify the current density for the best charge efficiency.

Fig. 7 shows the charge efficiency as a function of current density. Charge efficiency was the highest at  $25.0 \text{ mA cm}^{-2}$ . For current densities either lower or higher than  $25.0 \text{ mA cm}^{-2}$ , hydrogen evolution by either acid or water reduction predominated.

Typical chronopotentiograms are shown in Fig. 8. The typical chronopotentiograms for different current densities show

potential oscillations. These oscillations appear as a result of the irregular growth of metallic manganese [19].

Manganese can also be recovered by anodization. In the anodic process, the material oxidizes at the electrode/solution interface and precipitates at the bottom of the cell as a black sediment. Only a fraction corresponding to 20% of the charge density deposits on the electrode. This occurs because  $\text{Mn}^{2+}$  oxidizes to  $\text{Mn}^{3+}$ , which then suffers disproportionation, as demonstrated by Eqs. (7) and (8).



#### 4. Conclusions

The material on the cathode after the discharge of the spent battery is a mixture of  $\alpha\text{-MnO}_2$  and  $\text{Mn}_3\text{O}_4$ . EDS analysis of the cathode surface shows the presence of zinc from the anode and chloride from the electrolyte. The micrographs show that the electrode is formed by crystal aggregates. X-ray diffraction measurements show that the material recycled by chemical precipitation is  $\text{Mn}_3\text{O}_4$ . Manganese was recovered by electrodeposition and anodization. The electrodeposition was a maximum for a current density of  $25.0 \text{ mA cm}^{-2}$ . The release of hydrogen by acid or water reduction became the main reaction at current densities either lower or higher than  $25.0 \text{ mA cm}^{-2}$ . In the current density range studied, the charge transfer reaction at the electrode/solution interface determined the speed of the electrochemical process. Manganese can also be recovered by anodization. In the anodic process, the material oxidizes at the electrode/solution interface and deposits to the bottom of the cell. Only a fraction, corresponding to 20% of the charge density, deposited on the electrode.

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#### References

- [1] M.F. Almedida, S.M. Xará, J. Delgado, C.A. Costa, *Waste Manag.* 26 (2006) 466.
- [2] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, *J. Power Sources* 130 (2004) 291.
- [3] Associação Brasileira da Indústria Eletro-Eletrônica (ABINEE), [abinee.org.br](http://abinee.org.br).
- [4] Conselho Nacional Do Meio Ambiente (CONAMA), Resolution no. 257, June 30, 1999, *Diário Oficial da União (DOU)*, Brazil, July 22, 1999.
- [5] M.W. Paschke, A. Valdecantos, E.F. Redente, *Environ. Pollut.* 135 (2005) 313.
- [6] S. Fröhlich, D. Sewing, *J. Power Sources* 57 (1995) 27.
- [7] G. Xi, Y. Li, Y. Liu, *Mater. Lett.* 58 (2004) 1164.
- [8] M. Bartolozzi, G. Braccini, P.F. Marconi, S. Bonvini, *J. Power Sources* 48 (1994) 389.
- [9] A.L. Salgado, A.M.O. Veloso, D.D. Pereira, G.S. Gontijo, A. Salum, M.B. Mansur, *J. Power Sources* 115 (2003) 367.
- [10] L.R.S. Veloso, L.E.O.C. Rodrigues, D.A. Ferreira, F.S. Magalhães, M.B. Mansur, *J. Power Sources* 152 (2005) 295.

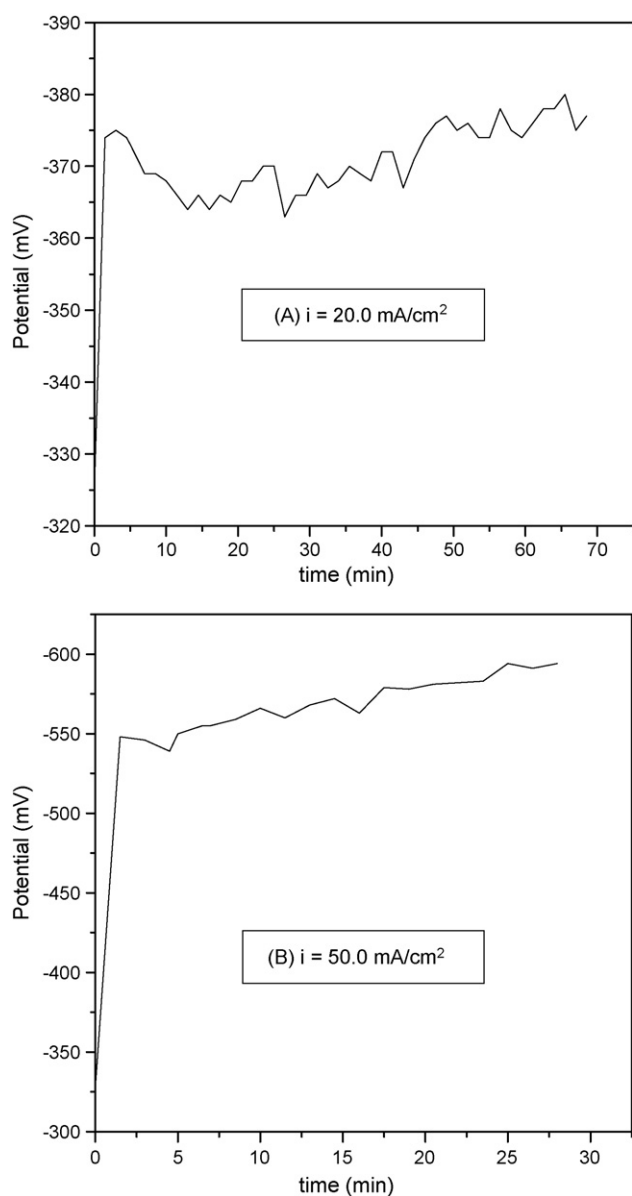


Fig. 8. Chronopotentiometric plot for ionic manganese electrodeposition from leaching solution, without stirring; (A)  $i = 20.0 \text{ mA cm}^{-2}$  and (B)  $i = 50.0 \text{ mA cm}^{-2}$ ,  $q = 90.0 \text{ C cm}^{-2}$ ,  $T = 298 \text{ K}$ .

- [11] C.C.B.M. Souza, D.C. Oliveira, J.A.S. Tenório, *J. Power Sources* 103 (2001) 120.
- [12] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenório, *J. Power Sources* 124 (2003) 586–592.
- [13] J. Basset, R.C. Denney, G.H. Jeffery, J. Mendham, in: A. Spínola (Translator), *Vogel's Textbook of Quantitative Inorganic Analysis*, fourth ed., Guanabara Dois, Rio de Janeiro, 1981, pp. 541–556.
- [14] Joint Committee on Power Diffraction Standards (JCPDS), Card No. 44-0141.
- [15] Joint Committee on Power Diffraction Standards (JCPDS), Card No. 24-0734.
- [16] M.B.J.G. Freitas, A. Rozário, R.K. Silva e Silva, *J. Power Sources* 158 (2006) 754.
- [17] M.B.J.G. Freitas, S.F. Rosalém, *J. Power Sources* 139 (2005) 366–370.
- [18] M.B.J.G. Freitas, M.K. de Pietre, *J. Power Sources* 128 (2004) 343.
- [19] M.B.J.G. Freitas, M.K. de Pietre, *J. Power Sources* 143 (2005) 270.