



Simultaneous recovery of Zn and Mn from used batteries in acidic and alkaline mediums: A comparative study



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ABSTRACT

A parallel study of acidic and alkaline leaching for the recovery of Mn and Zn from spent alkaline batteries is outlined. Using H_2SO_4 as solvent and selecting appropriate conditions of temperature and concentration, all residues were dissolved except carbon. The separation and recovery of the two components were performed by electrodeposition with satisfactory results at pH values above 4 (current efficiency above 70% for Zn and Mn) but rather lower efficiencies as the pH decreased. Most of the Zn was selectively dissolved by alkaline leaching using a 6.5 M NaOH solution, and its recovery was examined by means of both electrochemical and chemical processes. The expected formation of pure Zn by electrowinning failed due to the formation of ZnO, the content of which was highly dependent on the electrodeposition time. For short periods, Zn was the main component. For longer periods the electrodeposit consisted of agglomerated microparticles of ZnO with a minor fraction of Zn metal (barely 3% as measured by X-ray diffraction). A chemical reaction of the element with oxygen released at the anode surface might be responsible for its conversion to ZnO. A simple chemical route is described for the first time for the direct conversion of Zn $(OH)_4^{2-}$ solution to nanostructured ZnO by lowering the pH to values around 12 using 2 M HCl solution.

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1. Introduction

The high consumption of primary Zn-MnO₂ batteries is due to their reliability, safety and cheapness, among other reasons. They are used in many daily applications, such as portable radios, toys, flashlights and other modern electronic devices (MP3 players, GPS, laptops, etc.), and more than 300,000 tons of zinc batteries are sold per year (Sayilgan et al., 2009b); an average of six units per person (Freitas and de Pietre, 2004). In fact, more than 80% of all batteries sold are alkaline batteries. Different chemical species are needed for the manufacture of these batteries, the more important of which include Zn and MnO₂ as the electrochemical active materials, KOH as the electrolyte, polymers as separators, carbon as an additive conductor, and stainless steel for the case. The widespread use of these devices has resulted in a rapid increase in the accumulation of spent alkaline batteries, the disposal of which requires resolute management policies that are harmonious with sustainable development.

1.1. Waste management spent batteries

In Europe, the Directive 2006/66/EC regulates the waste management of spent batteries and accumulators, and directs the member states to promote research into environmentally friendly and cost-effective recycling methods for all types of these devices by encouraging the development of new recycling and treatment technologies. Special attention is paid to the heavy metal content, particularly Hg and Cd, by prohibiting the sale of all batteries or accumulators that contain more than 0.0005% of Hg and 0.02% of Cd by weight, regardless of whether or not they are incorporated into appliances. In this directive, the collection of waste batteries is also considered and the annual estimation was 35% in 2014, 40% in 2015, and 45% in subsequent years.

Another directive (2008/98/EC) regulates the disposal of spent batteries for incineration and/or landfilling. Incineration of batteries is a controversial method due to the foreseeable release of heavy metals and organic toxic compounds into the atmosphere. For this reason, environmental legislation continues to be more restrictive on spent batteries management. Landfill disposal, a common waste management in past decades, is now an increasingly expensive procedure due to the high safety controls required. Leaching of metals from spent batteries is the main problem because it can contaminate rivers, effluents and lakes, and the

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multiple prejudicial risks can affect human health, agriculture, ecology, etc.

1.2. Recycling strategies for alkaline batteries

Recycling and further reuse of spent alkaline battery materials is perhaps the most satisfactory choice to mitigate the environmental problems emerging from this popular electrochemical energy source and is more adapted to sustainability models (Sayilgan et al., 2010). A report by the European Portable Battery Association (EPBA) in 2011 stated that among the primary batteries sold in Europe in 2009, about 21% were collected for recycling and the remaining 79% were landfilled or incinerated (Brito et al., 2012). Thus, the recycling and further reuse of metals from spent batteries are becoming essential due to environmental considerations and new regulation (Sayilgan et al., 2010). The main metals in zinc-carbon and alkaline batteries are manganese and zinc. These valuable metals can be recovered (De Michelis et al., 2007) to be reused for battery production as raw materials, or can be used for other purposes (Gallegos et al., 2013).

Another incentive for recycling is that the energy expended during battery production is greater than that for recovery. For example, if we take the zinc used in battery manufacturing, the energy required for recycling and that needed for extraction from primary resources has a ratio of 1:4 (De Michelis et al., 2007). Another important point is the preservation of raw materials in accordance with sustainable development. In the case of manganese, around 270,000 tons of electrochemical manganese dioxide are required to produce an average of 60 billion alkaline batteries, and the demand grows by 10% per year. To satisfy these needs, producers must develop sufficient production capacity (Souza et al., 2001).

Several methods to recover metal from batteries are described in the literature (Xará et al., 2015), but industrial routes generally employ either pyrometallurgical or hydrometallurgical processes. More recently, biological processes that operate under milder conditions are postulated as an attractive option (Kim et al., 2016; Gallegos et al., 2013). Although pyrometallurgical processes are more commonly used (Sayilgan et al., 2010; Belardi et al., 2012), hydrometallurgical processes are gaining relevance due to their smaller environmental footprint, lower cost, and ability to treat materials even with low zinc contents on a small scale. The treatment of such waste for the recovery of zinc is therefore necessary for 'waste to raw material' recycling.

Metals can be leached from their oxides by direct reactions with acid or alkali solutions, or by reactions with either of these solutions in the presence of an oxidizing or reducing agent (Sayilgan et al., 2010). After leaching, further separation methods are required to recover the metals from the leach solutions. Table 1 lists details from the abundant literature reported over the two last decades on the recycling of spent alkaline batteries. Its content deserves several comments. Acid leaching dominates over alkaline leaching. Sulfuric acid is preferred and frequently in combination with a reducing agent, either organic (ascorbic, citric and oxalic acids and glucose) or inorganic (H_2O_2 , SO_2) to convert insoluble Mn (III) and Mn (IV) oxides into soluble Mn (II) salts. In most cases, the recovered product is a mixture of Zn and Mn compounds, either in solution or as solid phases.

In this review, we have found only one report, (Buzatu et al., 2013b), where a simultaneous study under basic and acid leaching conditions is described. Although Freitas and de Pietre (2004) also used both treatments, the unique material recycled was that coming from the anode. The separation of the anodic and cathodic components can be carried out either by chemical or electrochemical procedures. With regards to chemical methods, liquid-liquid extraction is more common but complex steps and the use of special chemicals are required, which are expensive and slow as a

result (Babaa et al., 2009; Deep et al., 2011; Sobianowska-Turek et al., 2016). The application of other chemical methods to separate Zn and Mn components is more limited and also requires different steps and chemicals (Silva et al., 2010; Quintanilha et al., 2014).

Electrodeposition is an alternative method to separate the two active components as Zn and MnO_2 , the pristine forms used for battery manufacture. For this reason, electrodeposition is a more direct tool for achieving the recovery of battery wastes and reusing them in the manufacture of new batteries. Hence, there are a significant number of reports where this separation method is used (Table 1), particularly under acid leaching conditions. By contrast, the study of Zn electrodeposition under alkaline leaching conditions has hardly been studied. Freitas and de Pietre (2004) described Zn electrodeposition from alkaline solution of anode material of spent Zn- MnO_2 batteries. However, with the exception of some data related to current density and charge efficiency, little information was reported on the effect of other parameters, such as zinc concentration, electrodeposition time, or an accurate characterization of the electrodeposited material.

One of the main objectives of this article is to shed additional light on the recovery of the wastes of spent alkaline batteries from alkaline solution, with special attention given to the characterization of recovered products by electrochemical and chemical procedures. At the same time, the recovery of these wastes is also carried out under acidic conditions, in order to compare the advantages and/or disadvantages of both mediums. The results of this study, together with the already existing literature summarized in Table 1, provide guidelines for the significant and unquestionable interest in facilitating the steps required in the separation of different electrode components from spent alkaline batteries.

2. Experimental

2.1. Battery dismantling and powder preparation

Spent alkaline batteries from different manufacturers were manually dismantled. Dismantled by-products, including plastic films, ferrous scraps and paper pieces, were discarded. The powders, which were approximately 40–64% of the total weight of the dismantled batteries, were dried for 24 h at 105 °C. The powder samples were crushed using a mortar and washed with distilled water at a 1:10 g/mL solid/liquid ratio by mixing at 200 rpm, at 80 °C, for 2 h. The aim of washing (neutral leaching) was to remove salts, including potassium and chloride, from the powders. This step was conducted in a 1 L batch reactor equipped with a water jacket. The washed powder was dried for up to 24 h at 105 °C until the moisture was removed and a constant weight was achieved. All leaching tests were carried out with the same batch of this washed and dried powder fraction.

2.2. Characterization of battery powders

The X-ray diffraction data (2θ range: 15–80°) of studied samples were collected at room temperature in step scanning mode using a Bruker D8 Advance powder diffractometer with a curved germanium primary monochromator and Lynx eye XE detector. The X-ray patterns were recorded with $CuK_{\alpha 1}$ radiation using a step of 0.019° (2θ) and counting time of 38.4 s per step. Rietveld quantitative phase analysis was carried out using the Topas-Academic software package by Bruker. The starting structural models for ZnO and Zn were Code ID 2107059 and 9012435, respectively.

Quantitative analysis was also carried out using X-ray fluorescence (XRF) (Thermo Fisher Scientific) and atomic absorption spectroscopy (AAS) (SpectrAA 200 spectrometer, Varian) in order to accurately evaluate the manganese and zinc contents. Images were

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