

End-of-life Zn–MnO₂ batteries: electrode materials characterization

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Physical and chemical characterization of several sizes and shapes of alkaline and saline spent Zn–MnO₂ batteries was carried out, aiming at contributing for a better definition of the applicable recycling processes. The characterization essays included the mass balance of the components, cathode and anode elemental analysis, the identification of zinc and manganese bearing phases and the morphology analysis of the electrode particles. The electrode materials correspond to 64–79% of the total weigh of the batteries, with the cathodes having clearly the highest contribution (usually more than 50%). The steel components, mainly from the cases, are also important (17–30%). Elemental analysis showed that the electrodes are highly concentrated in zinc (from 48–87% in anodes) and manganese (from 35–50% in cathodes). X-Ray powder diffraction allowed for identifying several phases in the electrodes, namely zinc oxide, in the anodes of all the types of saline and alkaline batteries tested, while zinc hydroxide chloride and ammine zinc chloride only appear in some types of saline batteries. The manganese found in the cathode materials is present as two main phases, MnO·Mn₂O₃ and ZnO·Mn₂O₃, the latter corroborating that zinc migration from anode to cathode occurs during the batteries lifespan. A unreacted MnO₂ phase was also found presenting a low crystalline level. Leaching trials with diluted HCl solutions of alkaline and saline battery samples showed that all zinc species are reactive attaining easily over than 90% leaching yields, and about 30% of manganese, present as Mn(II/III) forms. The MnO₂ phase is less reactive and requires higher temperatures to achieve a more efficient solubilization.

Keywords: Spent Zn–MnO₂ batteries; recycling; electrode materials; characterization; leaching.

1. Introduction

Zn–MnO₂ batteries are primary (non-rechargeable) cells that are widely used in portable domestic appliances. These batteries present several geometries (Table 1), and can also be classified according with their chemistry in alkaline or saline (zinc–carbon) types. The term ‘saline’ battery is due to the chemical composition of the electrolyte, a salt of either ammonium or zinc chloride. The anode is usually zinc foil and the cathode is a mixture of manganese dioxide with pulverized carbon, which is used to retain moisture and improve the battery’s conductivity [1,2].

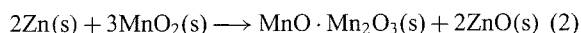
The functional mechanism of a saline battery is based on the following simplified overall reaction,



where zinc is oxidized and manganese dioxide reduced. However, the chemical processes that occur in these cells are more complex and depend on several factors such as: electrolyte concentration, cell geometry, velocity and temperature of discharge, diffusion velocity, and type of manganese dioxide used [1]. In fact, a number of other reactions and intermediate states can occur, producing other different species. In the anodic reaction, zinc can be oxidized

to zinc ammine chloride or hydroxyl chloride complexes (depending on the composition of the electrolyte), while Mn(IV) can be previously reduced to Mn(III), e.g. MnOOH or Mn₂O₃, being further probably reduced to Mn(II/III) species such as Mn₃O₄.

In alkaline-type batteries, the electrolyte is an alkaline solution of potassium hydroxide mixed with manganese dioxide in order to minimize the polarization effect. The cathode consists of manganese dioxide and a zinc metallic paste is used as the anodic material [1,2]. The functional mechanism of an alkaline battery on continuous discharge is based on the following simplified overall reaction,



but depending on manganese reduction degree as well as water content, hydrated species such as MnOOH and Zn(OH)₂ can also be produced. The general Equation (1) can also occur in alkaline-type batteries. In the initial discharge conditions, the excess of alkalinity lead to the formation of zincate (Zn(OH)₄²⁻) in the anode which further precipitates as zinc oxide hydrate and even additionally dehydrate to ZnO. The reduction in cathode occurs frequently through a Mn(III) state, as MnOOH, being further reduced to Mn(II/III) state as Mn₃O₄.

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