Recycling Spent Primary Cells for the Synthesis of Spinel ZnMn$_2$O$_4$ using Waste Polypropylene as Reductant in a Microwave Oven*

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Abstract

This work investigates the recycling of spent primary cells for the synthesis of spinel zinc manganese oxide (ZnMn$_2$O$_4$) using waste polypropylene as reductant in a domestic microwave oven. Spent zinc-carbon batteries (TigerHead brand) were cut into approximately two equal parts and the MnO$_2$/ZnO/carbon black mixture was carefully removed. The residual mass was thoroughly mixed with polypropylene obtained from a mixture of waste bucket and the cap of the zinc-carbon battery. The mixture was then placed in a fireclay crucible and irradiated in a domestic microwave oven (Pioneer, Model PM-25 L, 2450 MHz, 1000 W) for 20 minutes and reaction products were separated and characterised. Spherical particles of spinel zinc manganese oxide (ZnMn$_2$O$_4$) were isolated after crushing the reduced mass. Analysis (XRD) of the residual reduced mass showed that it consisted of several peaks of ZnMn$_2$O$_4$ along with peaks of SiO$_2$ and uncombined ZnO and MnO.

Keywords: Spinel ZnMn$_2$O$_4$, Primary cells, Zinc-carbon battery, Polypropylene, Microwave oven

1 Introduction

ZnMn$_2$O$_4$ belongs to the family of mixed transition-metal oxides (MTMOs) (designated as $A_xB_yO_z$; $A$, $B$= Co, Ni, Zn, Mn, Fe, etc.) with stoichiometric or even non-stoichiometric compositions, typically in a spinel structure (Xie et al., 2014). In recent years, these mixed transition-metal oxides have attracted a lot of attention, owing to their various properties, among which are photocatalytic (Xu et al., 2009; Ding et al., 2009; Cui et al., 2009; Fierro et al., 2005), electrochemical performance (Tian and Yuan, 2009), magnetic properties (Chen and Sorensen, 1996; Blanco-Gutiérrez et al., 2010), or being used in lithium ion batteries (Yang et al., 2008). Manganese oxide has also aroused lots of interest because it has been documented experimentally as a room-temperature diluted magnetic semiconductor (Dietl et al., 2000). Accordingly, the Mn-Zn-O ternary systems belong to a class of interesting and useful materials based on their electrical and magnetic properties. As one of the important mixed transition-metal oxides with spinel structure, ZnMn$_2$O$_4$ is a promising functional material and has become the focus of various researches owing to its potential applications. ZnMn$_2$O$_4$ could be used for the negative temperature coefficient thermistors on account of their unique electrical properties (Guillemet-Fritsch et al., 2000). Ferraris et al., (2002) studied the catalytic activity of zinc manganite for the reduction of NO by several types of hydrocarbons [Fierro et al., 2005; Barth et al., 2010]. They suggested that ZnMn$_2$O$_4$ was an efficient catalyst for the reduction of NO to N$_2$, and, in all cases, its best selectivity to N$_2$ and CO$_2$ was at almost the maximum conversion temperature.

Large amounts of primary cells are discarded annually across the globe. In Ghana, zinc-carbon and alkaline-zinc-manganese dioxide batteries have traditionally been the most popular among the rural folk and lately among the low to middle income populace in the urban areas owing to erratic power supply. In its construction, the zinc-carbon battery consists of a zinc can that serves as the battery container and anode, a manganese dioxide cathode and an electrolyte consisting of ammonium chloride and/or zinc chloride dissolved in water.

To improve upon conductivity of the cell and retain moisture, the manganese dioxide is mixed with carbon in the form of acetylene black. This mixture is compressed under pressure to form a bobbin that serves as the positive electrode. A carbon rod inserted into the bobbin serves as the current collector for the positive electrode.

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During the discharging process, zinc is oxidised and manganese dioxide is reduced with the overall cell reaction shown in Equation (1).

\[
\text{Zn} + 2\text{MnO}_2 = \text{ZnO} + \text{Mn}_2\text{O}_3
\]  

(1)

Owing to its popularity and short lifespan, spent zinc-carbon and alkaline zinc-manganese dioxide batteries can function effectively as a considerable secondary source of zinc and manganese. Methods used in recovering metal values from spent primary batteries are based primarily on pyrometallurgical (Buri, 1999; Schneider and Schwab, 1999; Krebs, 1999) or hydrometallurgical (Zhang et al., 1999; Reinhard, 1995; Pietrelli, 1999) concepts. However, the pyrometallurgical recovery in a microwave oven using polypropylene as an additional reductant has not been investigated before.

ZnMn$_2$O$_4$ particles have been prepared earlier by various methods, such as solid-state reaction (Peiteado et al., 2007; Bessekhouad, 2002), sol-gel (Peng and Wu, 2009), co-precipitation method (Bessekhouad and Trari, 2002), and hydrothermal method (Xiao et al., 2009; Zhang et al., 2007). For instance, Bessekhouad and Trari (2002) prepared spinel ZnMn$_2$O$_4$ powder by solid-state reaction under high temperature. Zhang et al., (2007) fabricated ZnMn$_2$O$_4$ nanoparticles by a hydrothermal method that lasted for 48 hr.

Accordingly, in this work the recycling of spent zinc-carbon batteries for the synthesis of ZnMn$_2$O$_4$ using waste polypropylene as a reductant is investigated in a domestic microwave oven.

2 Materials and Methods Used

Spent zinc-carbon batteries (TigerHead brand) were cut into approximately two equal parts and the MnO$_2$/Mn$_2$O$_3$/ZnO/carbon black mixture carefully removed. The residual casing was dismantled and scrap iron, plastic and paper separated. The removed mixture was soaked in water for 24 hours after which it was filtered and the residue air-dried for 24 hours and then pulverised in a mortar using a pestle. The essence of the soaking was to remove soluble NH$_4$Cl in order to prevent high temperature corrosion and subsequent dioxin formation with the polymer. The pulverised mass was thoroughly mixed with pulverised polypropylene obtained from waste buckets and the cap of the zinc-carbon battery. The mixture was then placed in a fireclay crucible and irradiated in a domestic microwave oven (Pioneer, Model PM-25 L, 2450 MHz and 1000 W) for 20 minutes and reaction products were separated and characterised by XRD, SEM and SEM/EDS.

3 Results and Discussion

The appearance of the pulverised mass obtained from the spent batteries is shown in Fig. 3 whilst the morphology is illustrated in the SEM shown in Fig. 4. The morphology displays irregularly shaped particles.
The SEM/EDS of two regions are displayed in Figs 5 and 6. The main elements displayed are consistent with the components of a modern TigerHead battery showing the absence of mercury in fulfilment of the requirements of global environmental restrictions.

The product obtained after heating a composite pellet of pulverised mass + the reductant PP is shown in Fig.7 and the resulting morphology is shown by the SEM in Fig. 8. Fig. 7 reveals a dense mass of sintered product surrounded by brown calcined/reduced Mn$_3$O$_4$ along with some silica.

An XRD of the product of heating composite pellet of battery mass with postconsumer PP (Fig. 9) revealed several peaks of ZnMn$_2$O$_4$ along with peaks of SiO$_2$ and uncombined ZnO and Mn$_3$O$_4$.

Part of the sintered mass was crushed with a hammer; several spherical particles rolled out as shown in Fig. 10, majority of which were micro-sized. For use as catalyst, for example, large surface areas provided by nanoscale or at least micro-scale spherical particles are preferable.

The spherical particles were subjected to SEM and XRD analyses as illustrated in Figs 11 and 12, respectively.

The morphology of the particles in the SEM of Fig. 11 reveals a dense continuous mass. The XRD in Fig. 12 indicates that the spherical particles are spinel zinc manganese oxide, with all the peaks corresponding to ZnMn$_2$O$_4$.
4 Conclusions

A laboratory investigation has been conducted on the recycling of spent primary cells for the synthesis of spinel \( \text{ZnMn}_2\text{O}_4 \) using waste polypropylene as reductant in a domestic microwave oven. From the investigation it was observed that:

Spent TigerHead batteries contain appropriate mixtures of \( \text{MnO}_2 \), \( \text{Mn}_3\text{O}_4 \) and \( \text{ZnO} \) needed for the synthesis of spinel \( \text{ZnMn}_2\text{O}_4 \) when heated with appropriate amounts of carbonaceous materials.

Spherical particles of \( \text{ZnMn}_2\text{O}_4 \) were isolated from the bulk mass after heating with postconsumer PP. XRD analyses revealed distinct peaks corresponding to spinel \( \text{ZnMn}_2\text{O}_4 \).

Synthesis of spinel \( \text{ZnMn}_2\text{O}_4 \) provides yet another avenue for recycling postconsumer plastics and spent primary cells.

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References


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