

Recycling Spent Primary Cells for the Synthesis of Spinel ZnMn_2O_4 using Waste Polypropylene as Reductant in a Microwave Oven*

J. R. Dankwah, B. O. Sakyiama, M. Acquah, F. Adjei-Kyeremeh and P. Koshy

Dankwah, J. R., Sakyiama, B. O., Acquah, M., Adjei-Kyeremeh, F. and Koshy, P. (2015), "Recycling Spent Primary Cells for the Synthesis of Spinel ZnMn_2O_4 using Waste Polypropylene as Reductant in a Microwave Oven", *Ghana Mining Journal*, Vol. 15, No. 1, pp. 58 - 63.

Abstract

This work investigates the recycling of spent primary cells for the synthesis of spinel zinc manganese oxide (ZnMn_2O_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 $\text{MnO}_2/\text{Mn}_2\text{O}_3/\text{ZnO}$ /carbon black mixture was 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 pulverised in a mortar using a pestle. The pulverised mass was thoroughly mixed with pulverised 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_2O_4) were isolated after crushing the reduced mass. Analysis (XRD) of the residual reduced mass showed that it consisted of several peaks of ZnMn_2O_4 along with peaks of SiO_2 and uncombined ZnO and Mn_3O_4 .

Keywords: Spinel ZnMn_2O_4 , Primary cells, Zinc-carbon battery, Polypropylene, Microwave oven

1 Introduction

ZnMn_2O_4 belongs to the family of mixed transition-metal oxides (MTMOs) (designated as $\text{A}_x\text{B}_{3-x}\text{O}_4$; 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). Mn doped ZnO 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_2O_4 is a promising functional material and has become the focus of various researches owing to its potential applications. ZnMn_2O_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_2O_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.

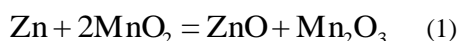
Large amounts of primary cells are discarded annually across the globe. In Ghana, zinc-carbon and alkaline zinc-manganese dioxide batteries have traditionally been the most popular among the rural folk and lately among the low to middle income populace in the urban areas owing to erratic power supply. 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.



Fig. 1 A Typical Zinc-Carbon Battery used in Ghana

During the discharging process, zinc is oxidised and manganese dioxide is reduced with the overall cell reaction shown in Equation (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_2O_4 particles have been prepared earlier by various methods, such as solid-state reaction (Peiteado *et al.*, 2007; Bessekhoud, 2002), sol-gel (Peng and Wu, 2009), co-precipitation method (Bessekhoud and Trari, 2002), and hydrothermal method (Xiao *et al.*, 2009; Zhang *et al.*, 2007). For instance, Bessekhoud and Trari (2002) prepared spinel ZnMn_2O_4 powder by solid-state reaction under high temperature. Zhang *et al.*, (2007) fabricated ZnMn_2O_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_2O_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 $\text{MnO}_2/\text{Mn}_2\text{O}_3/\text{ZnO}/\text{carbon}$ 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_4Cl 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.

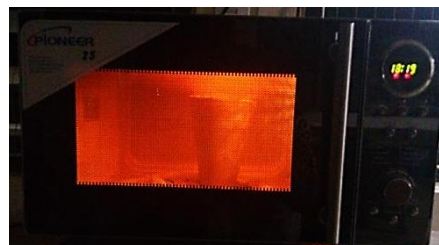


Fig. 2 Calcination Process in Domestic Microwave Oven

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.



Fig. 3 Pulverised Mass obtained from Spent TigerHead Battery

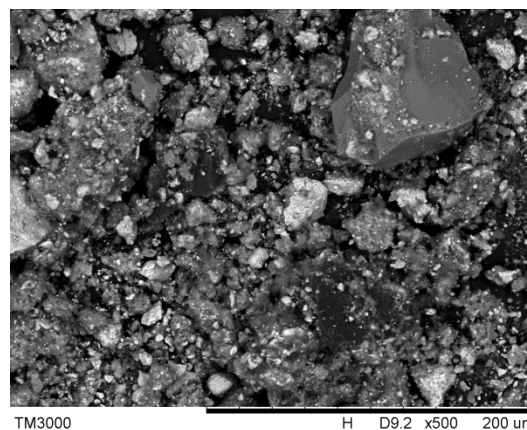


Fig. 4 SEM of Pulverised Mass obtained from Spent TigerHead Battery (×500)

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_3O_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_2O_4 along with peaks of SiO_2 and uncombined ZnO and Mn_3O_4 .

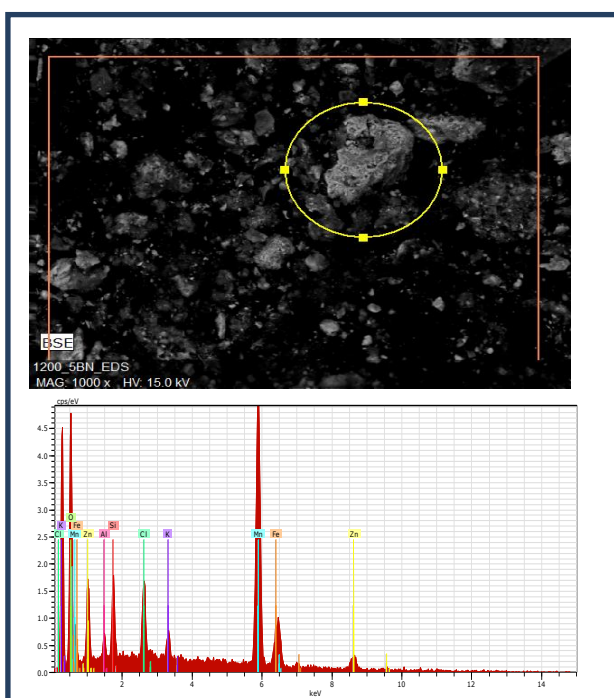


Fig. 5 SEM/EDS of Region 1 of Pulverised Mass obtained from Spent TigerHead Battery

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_2O_4 .

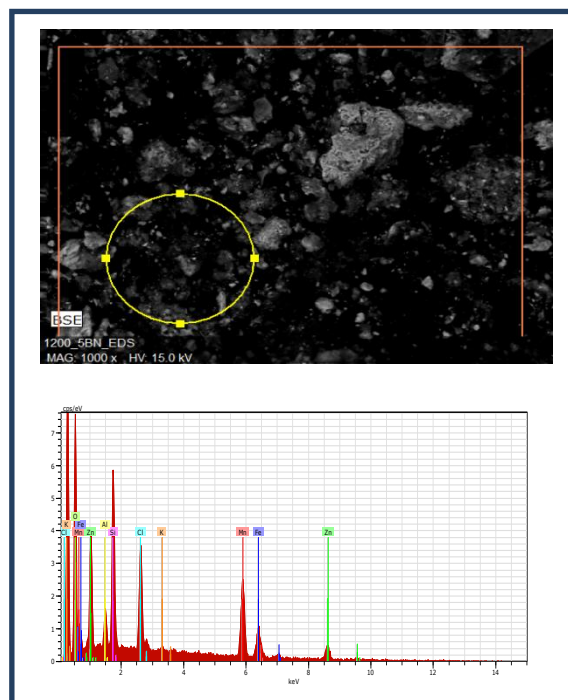


Fig. 6 SEM/EDS of Region 2 of Pulverised Mass obtained from Spent TigerHead Battery

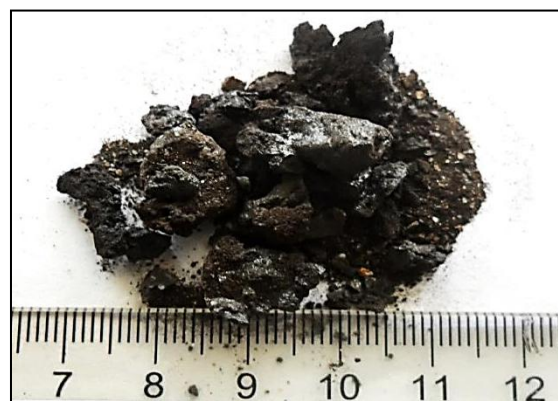


Fig. 7 Reaction Product obtained after heating Composite Pellet of Battery Mass with Postconsumer PP

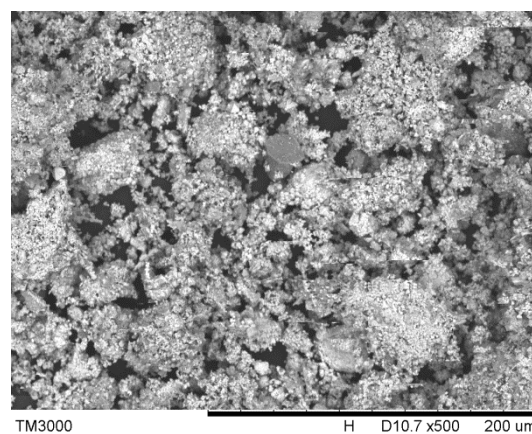


Fig. 8 SEM of Reaction Product obtained after heating Composite Pellet of Battery Mass with Postconsumer PP

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Authors



Dr James R. Dankwah had his Ph.D. from the School of Materials Science and Engineering, UNSW, Australia in 2012. He is currently a Senior Lecturer and Head of Minerals Engineering Department at UMaT-Tarkwa. His current research areas include iron and steel making, high-temperature metallurgical processes, and utilisation of waste polymers in metal extraction processes. He has over 30 refereed journal and conference papers.



Ben O. Sakyiama is final year undergraduate student at the Minerals Engineering Department, University of Mines and Technology, Tarkwa, Ghana. He is currently working on the recycling of spent primary cells and the recovery of valuable metals and compounds using postconsumer plastics and biomass as reductants.



Maxwell Acquah had his BSc. Degree in Minerals Engineering from the University of Mines and Technology, Tarkwa, Ghana, in August, 2014. He worked on the recycling of spent primary cells and the recovery of valuable metals and compounds using postconsumer plastics and biomass as reductants.



Frank Adjei-Kyeremeh had his BSc. Degree in Minerals Engineering from the University of Mines and Technology, Tarkwa, Ghana, in August, 2014. He worked on the pre-reduction of higher manganese oxides in the Ferromanganese Process, utilising postconsumer plastics and biomass as reductants.



Dr. Pramod Koshy completed his Ph.D. from the School of Materials Science and Engineering, UNSW, Australia in 2009. He is currently a Senior Research Associate at the School. His main areas of research include photocatalytic materials, high-temperature metal/ceramic interfaces, and utilization of waste materials. He has over

40 refereed journal papers, one international patent, and over 10 conference proceeding papers.