Recycling spent zinc manganese dioxide batteries through synthesizing Zn–Mn ferrite magnetic materials

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Abstract

A novel process to reclaim spent zinc manganese dioxide batteries (SDBs) through synthesizing Zn–Mn ferrite magnetic materials is present. Firstly, the dismantling, watering, magnetism, baking and griddling steps were consecutively carried out to obtain iron battery shells, zinc grains and manganese compounds using the collected SDBs, and then these separated substances were dissolved with $4 \, mol \, L^{-1} \, H_2SO_4$ to prepare $FeSO_4$, $ZnSO_4$ and $MnSO_4$ reactant solutions. Secondly, Zn–Mn ferrites with stoichiometric ratio of $Mn_{0.26}Zn_{0.24}FeO_2$ were synthesized using chemical co precipitation process with ammonium oxalate precipitator. The XRD results showed that the obtained Zn–Mn ferrites had spinel structure and high purity at the calcining temperatures of 850–1250 °C. With the increase of calcining temperature, the finer crystalline structure could be formed, and their intensity of saturation magnetization reached the highest value at 1150 °C. The magnetization performances of Zn–Mn ferrites prepared from the SDBs were similar to that of from analysis reagents, suggesting the feasibility to synthesize Zn–Mn ferrites with high properties from SDBs.

1. Introduction

More and more zinc manganese dioxide (Zn–Mn) batteries are used in the recent years as the power sources of electric appliances. For instance, more than 15 billion of acidic or alkaline Zn–Mn batteries have been produced annually after 2002 in China. After their lifespan, the same amount of spent Zn–Mn batteries (SDBs) are discarded as wastes. Wherein, some of them are incinerated in municipal incinerator plants together with domestic waste; the others are usually discarded to the nature. Because a mass of zinc and manganese, corrosive electrolyte and toxic mercury additive are involved in SDBs, dealing with the recycling of SDBs has thus become an urgent matter from the viewpoint of environmental preservation, resource saving and waste volume reduction [1,2].

A variety of recycling methods, which are usually summarized as pyrometallurgy and hydrometallurgy, have been explored. Espinosa et al. [3] reviewed the current processes for the recycling of spent batteries. In the proposed recycling methods of SDBs, de Oliveira et al. [4] showed that pyrometallurgy could eliminate Hg contained in Zn–Mn dry batteries, and after Hg decontamination, Zn might be recovered by distillation. Saotome et al. [5] studied recovering selected zinc and electrolyte materials from used alkaline manganese dry batteries by vacuum-aided recycling systems technology. The advantage of pyrometallurgical process is mercury and zinc can be reclaimed completely, but more energy and large-scale recycling are needed. While combined with or based on hydrometallurgy, i.e. the electrolysis [6–8], solvent extraction [9] and other integrated methods [2,3], each substance containing in SDBs could be reclaimed, respectively, although it involved more steps and lots of waste solutions that needed treatment.

Recently, using SDBs as raw material to synthesize Zn–Mn ferrite magnetic materials has also been developed because there are adequate amounts of Mn, Zn and Fe in SDBs. Kanemaru et al. [10] showed that the spent batteries material was cleaned with water after dismantling and griddling, Zn–Mn ferrites was synthesized using the prepared Zn, Mn and Fe oxide. Xi et al. [11] presented their studies on preparing Zn–Mn ferrites by co precipitation method in which the spent Zn–Mn batteries

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were dissolved with 3 mol/L H_2SO_4 + 2.4% H_2O_2. The suitable preparing conditions included removing Hg with Fe powder, preparing precursors at pH 7–7.5 and 50 °C and calcining temperature at 1100–1150 °C. Xia and Li [12] reported an integrated battery recycling (BATINTREC) process. Vacuum metallurgical reprocessing were used to reclaim the mercury in the dry batteries and the cadmium in the Ni–Cd batteries, the ferrite synthesis process reclaims the other heavy metals by synthesizing ferrite in a liquid phase.

Zn–Mn ferrites are widely used in many magnetic applications such as in transformers and recording heads due to their high magnetic permeability and low magnetic losses. It is considered that this process is more predominant for it reduces the recycling cost. However, it is noted that although the primary substances of SDBs, i.e. manganese, zinc and iron, are the required three elements to synthesize Zn–Mn ferrites, their composition ratio in the collected SDBs is uncertain and deviates from that of the desirable ferrite. So, the constituent of Zn–Mn ferrite would be restricted and changeful when the collected SDBs are directly used as precursors. The reactant contents have to be adjusted largely with pure reagents when a stoichiometric composition resultant is expected, and this adjustment is uncertain due to the changeability of SDBs collected in the consumer market. In addition, the synthesizing process also affects the performances of Zn–Mn ferrites [13]. In this paper, a novel process for the synthesis of Mn–Zn ferrite magnetic materials with chemical co precipitation by using SDBs as raw reactant and the performances of Zn–Mn ferrites synthesized with the stoichiometric ratio of $Mn_{0.26}Zn_{0.24}FeO_2$ are present.

2. Experimental

2.1. Materials

Spent AA size Zn–Mn batteries used in this work were kindly provided by the environmental sanitation team of our dis-trict. These batteries involved the mass trademarks consumed in china, the acidic and the alkaline Zn–Mn batteries had half each. Prior to the reclamation process, a small quantity of nickel cadmium batteries, nickel metal hydride batteries and lithium ion batteries mixed in SDBs was removed.

2.2. Analysis methods

The contents of various metallic elements in the dissolution solutions and subsequent resultants were determined using atomic absorption spectrophotometer (model AA320, China). The pH value of the aqueous solution was measured with a pH/mV meter (Model DF-801, China). The morphology of the precursor compounds of Zn–Mn ferrites was characterized using scanning electron microscopy (Model JSM-T300, JEOL, Japan). The ferrites were identified from X-ray diffraction (Model D/MAX2200VPC, Rigaku, Japan). The magnetic parameters were determined using the magnetic property measurement system (Model MPMS XL-7, Quantum Design, America).

3. Results and discussion

3.1. The preparation of $FeSO_4$, $MnSO_4$ and $ZnSO_4$ using SDBs

During the pretreatment process, three reactants, whose main compositions are $FeSO_4$, $MnSO_4$ and $ZnSO_4$, were prepared, and the impurity elements for the synthesis of Zn–Mn ferrites were removed as well. The flow chart for the pretreatment of SDBs is shown in Fig. 1. The SDBs were firstly dismantled using an especially designed dismantling machine whose working mechanism will be illustrated in our other paper. Fig. 2 shows the digital image of the dismantled substances. It can be seen that the inner substances of SDBs are appeared after the dismantling of battery shells, which is very usable to the next separating treatment. The dismantled substances were poured into a glass
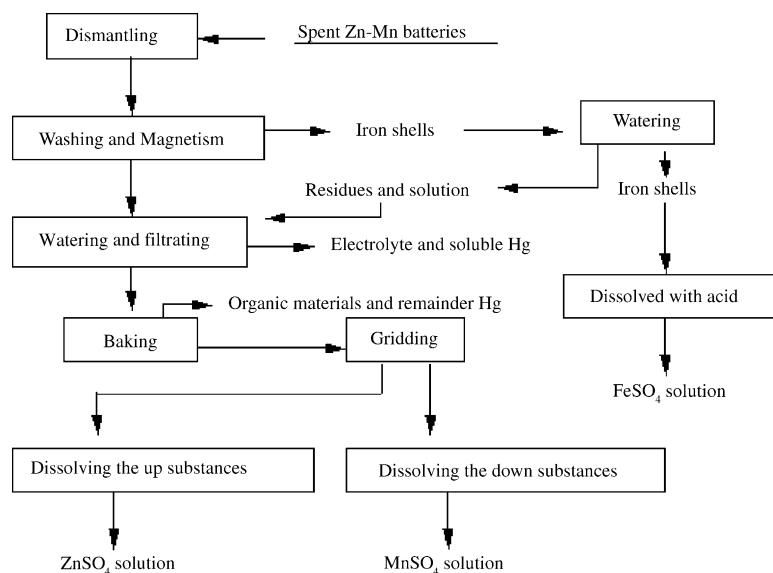

Fig. 1. The flow chart for the preparation of $FeSO_4$, $MnSO_4$ and $ZnSO_4$ reactants from SDBs.

Fig. 2. The digital image of the dismantled substances.

Elements	Zn^{2+}	Mn^{2+}	Fe^{2+}	Cu^{2+}	Ni^{2+}	Co^{2+}
$FeSO_4$	0.054	1.08	19.21	0.0032	0.0047	0.00029
$ZnSO_4$	25.13	4.85	1.09	0.040	0.024	0.0032
$MnSO_4$	14.13	22.39	1.52	0.075	0.087	0.0072

steel container, and the washing treatment with water was carried out to separate the electrolyte and the soluble mercury from the dismantled substances. It was indicated that the corrosive electrolyte with the added water and the soluble mercury could be washed out to the washing solution, only about 2% electrolyte still remained in the residues after the washing treatment. At the same time, with the help of sharp mechanical stirring at the end of washing treatment, iron battery shells could also be separated from the residues using the magnetic method. The little powder left on iron battery shells was watered out and then put into the remainder residues. To wash 1 kg the dismantled substances, about 0.15×10^{-3} m^3 water was required. In order to improve the economy and eliminate the possibility of repeated contamination, the washing solution would be treated with a special process to reclaim mercury and the mixed salts of K, Na and Zn.

As shown in Fig. 1, $FeSO_4$ comes from the reaction of the recovered iron battery shells with H_2SO_4 solution. These iron battery shells usually have a nickel-plated coating to increase their corrosion resistance. Nickel is an impurity in the synthesis of Zn–Mn ferrite; so, it must be separated on the preparation course of $FeSO_4$. The results showed that $FeSO_4$ solution could be obtained by using H_2SO_4 solution with suitable concentration. The higher concentration of H_2SO_4 solution (>5 mol L^{-1}) was advantageous to the dissolution of iron battery shells, while passivity easily occurred at lower reaction temperature. Over 90% of iron was dissolved with 4 mol L^{-1} H_2SO_4 within a day at room temperature, and the most of nickel-plated coating was left. Although a longer reaction time was needed, the $FeSO_4$ solution with acceptable Ni^{2+} content and known concentration could be obtained. Thus, the separation of nickel impurity from $FeSO_4$ solution would be neglected, and nickel can be recovered from the filtrating residues that enriched nickel coating.

After the separation of iron battery shells and electrolyte, the residues were baked to vaporize the remainder mercury and the organic materials, i.e. separator, plastics and label, in an especially designed furnace at an optimized temperature. In the mean time, the metal zinc was melted as zinc grains, and high valence

manganese compounds were reduced to acid-dissolvable compounds. The results showed that it was unfavorable for the incineration of organic materials, the evaporation of remainder mercury and the reduction of manganese dioxide at the lower baking temperatures, while zinc would be vaporized at the too high temperatures. Considering all the related factors, a baking temperature of 780–800 °C for 2 h was used. It was demonstrated that the remainder mercury and the organic materials in residues was almost completely volatilized. A little of zinc was also vaporized together with mercury into the smoke gas, zinc and mercury could be reclaimed through a recovery chamber, the other exhaust gas was innocuously flowed through a special filtration device.

After the baking treatment, the remainder residues were taken out from the furnace, and the block substances were separated using a jounce sieve with 1 mm aperture. The block substances consisted mainly of zinc grains, which came from the melted zinc battery shells, copper electric cap and electric needle. The remainder consisted mainly of zinc and manganese oxides. The up and down sieving substances were dissolved with 4 mol L^{-1} H_2SO_4 at room temperature to prepare $ZnSO_4$ and $MnSO_4$ solution, respectively. The indiscerptible manganese compounds, carbon materials and copper would be filtrated out and recovered. Table 1 gives the contents of element contained in $FeSO_4$, $ZnSO_4$ and $MnSO_4$ solution.

3.2. Synthesis and performances of Zn–Mn ferrites

Zn–Mn ferrite magnetic materials with a composition of $Mn_{0.26}Zn_{0.24}FeO_2$ were synthesized using the obtained $FeSO_4$, $ZnSO_4$ and $MnSO_4$ solution as reactants, and chemical co-deposition process was used. Two kinds of precipitators, i.e. ammonium oxalate and ammonia solution, were applied to prepare the precursor of Zn–Mn ferrites.

In accordance with the required stoichiometric ratio, three reactants were mixed in the reactor. The analysis reagent reactants were used to adjust the deviation with the expected ratio. Then, the precipitator $(NH_4)_2C_2O_4$ with 0.35 mol L^{-1} was added with stirring at 60 °C, its molar amount was 1.2 times of the stoichiometric ratio of precipitate. Ammonia solution was used to adjust the pH value of reaction solution in the range of 3.5–4.0. The yellow precipitates were filtered after aging for 3 h at the reaction temperature, then washed and dried at 100 °C. The obtained yellow deposit was used as the precursor to calcine Zn–Mn ferrite in the next step.

In the other reactor, the precipitator ammonia solution was substituted for ammonium oxalate to prepare the precursor. The pH value and temperature of reaction solution adjusted to 8–9
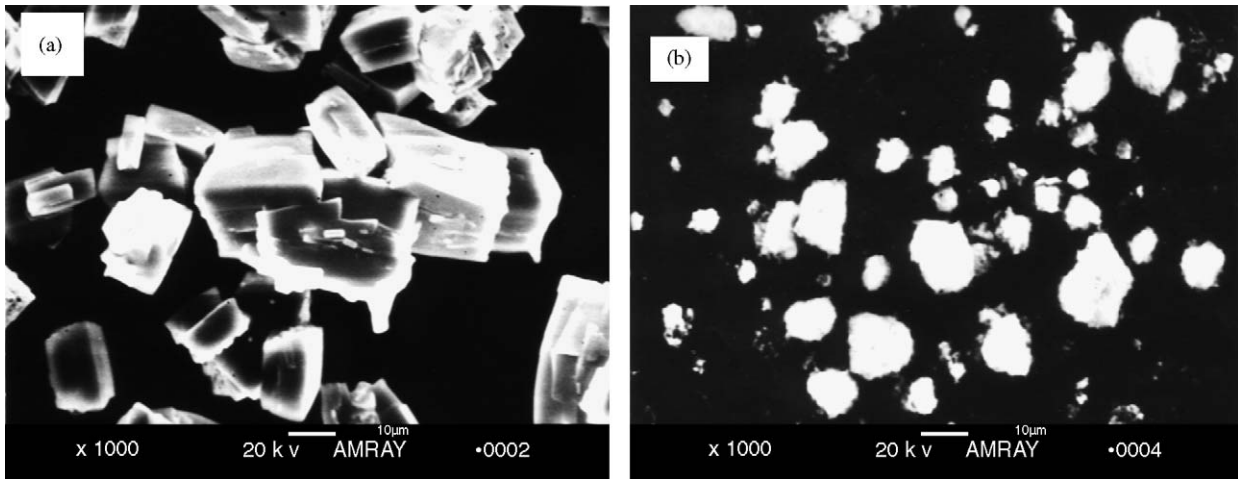
Fig. 3. SEM photographs of precursors prepared with ammonium oxalate (a) and ammonia (b) precipitators.

and 90 °C, respectively. Other preparing parameter was kept the same. In addition, in order to evaluate the effects of impurities contained in the reactants to the final product, other precursor was also prepared using the analysis reagents following the same steps.

From the appearance of the obtained precursors, no difference was found between the SDBs and the analysis reagent reactants. However, it was indicated that better crystal grains with a diameter range of 1–20 μm were formed using ammonium oxalate as precipitator, while smaller crystal grains were formed using ammonia as precipitator. Fig. 3 shows the grain morphologies prepared using ammonium oxalate and ammonia precipitator, respectively. In addition, the next step demonstrates that Zn–Mn ferrite with a higher pile-up density and stable magnetic properties could be obtained by using ammonium oxalate as precipitator. When ammonia solution was used as precipitator, a complex reaction process was involved and the amorphous resultants were always obtained which resulted in a lower pile-up density and the formation of other phases in the spinel Zn–Mn ferrites. So, ammonium oxalate precipitator was finally applied in the followed experiments.

The precursors were pressed as tablets and then pre-calcined in the tube stove in argon atmosphere at 800 °C for 3 h. The pre-calcined solids were ground and then pressed as tablets and calcined to obtain Zn–Mn ferrites. The X-ray diffraction (XRD) patterns of the Zn–Mn ferrite samples calcined at different temperatures are shown in Fig. 4. XRD patterns of the ferrite samples showed the typical spinel phase peaks, almost no other phase peaks, i.e. α-Fe_2O_3 and other reactants or resultants, appeared when the calcining temperatures of 850–1250 were used, indicating a homogeneous microstructure for the synthesized samples could be obtained. It is shown that the solid reaction was completed for the used chemical codeposition method. The mean crystallite sizes were estimated from XRD line width of the (3 1 1) peak using the Scherer equation as follows:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D is the mean crystallite size, K and β the ration constant and the half width of the relevant diffraction peak, respectively, λ the X-ray wavelength and θ is the angle of diffraction. The mean crystallite sizes estimated from the (3 1 1) peak were approximately ~38 nm with the calcining temperature of 850–1150 °C, while the mean crystallite sizes decreased to ~30 nm.

The intensities of magnetic parameters calcined at different temperature are present in Table 2. It is indicated that the calcining temperature affected the magnetic properties of ferrites largely. With the increase of the calcining temperature, the specific saturation magnetization of the ferrites increased to the highest of 78.83 emu g^{-1}, while B_m and at H_c decreased to the lowest at the temperature of 1150 °C. The notable changes of magnetic parameters at 1250 °C are attentively attributed to the volatility of zinc element, and also related with the visible change in the mean crystallite size. So, in practice, the Zn–Mn ferrites should be synthesized under 1250 °C to avoid the volatility of Zn element.
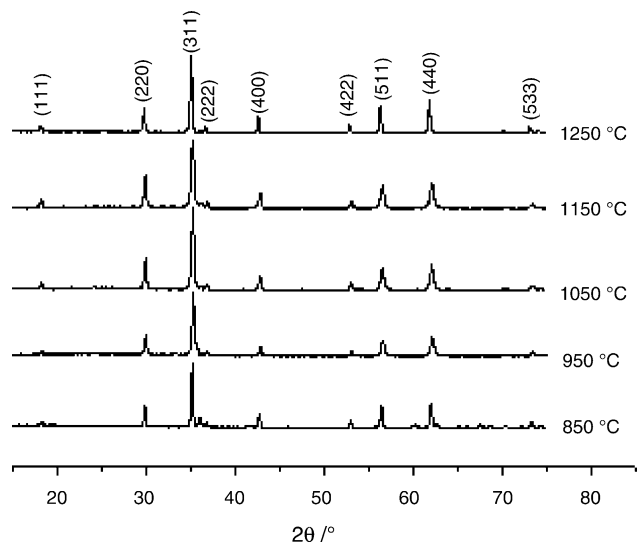

Fig. 4. XRD patterns of ferrite powder calcined at different temperature for 3 h.

Table 2
The magnetic parameters of Zn–Mn ferrites calcined at different temperature

Temperature °C	With SDBs					With pure reagents				
	850	950	1050	1150	1250	850	950	1050	1150	1250
B_s (emu g^{-1})	45.06	57.65	66.95	78.83	15.4	43.94	50.53	77.63	78.78	25.47
B_m (emu g^{-1})	2.15	0.58	0.56	0.075	0.15	1.27	0.26	1.10	1.46	0.37
H_c (Oe)	10	9	6.5	0.008	4	18	7	10	14.5	12

Note: B_s is intensity of saturation magnetization; B_m is intensity of surplus saturation magnetization; H_c is coercive force.

In general, the similar magnetic properties were obtained when the analysis reagents were used as reactants, suggesting the feasibility of the synthesis Zn–Mn ferrites from SDBs. In addition, the reactants of $FeSO_4$, $MnSO_4$ and $ZnSO_4$ were prepared independently in this given process, which also indicates the possibility of synthesizing Zn–Mn ferrites with an expected stoichiometric ratio of Zn, Mn and Fe atoms according to the demands of magnetic properties.

4. Conclusions

According to the components of SDBs, a novel recycling process of SDBs involving the preparation of reactants and the synthesis of Zn–Mn ferrites is proposed and optimized.

In the course of preparing reactants $FeSO_4$, $MnSO_4$, and $ZnSO_4$ solution from SDBs, the dismantling, watering, baking and dissolving steps were needed. The SDBs could be dismantled with an especially designed machine, then the dismantling substances were watered and the iron battery shells were separated with magnetic method to obtain residues. After the baking and griddling treatment for the residues to separate zinc and manganese roughly, the reactants of $FeSO_4$, $MnSO_4$, and $ZnSO_4$ solution could be obtained using H_2SO_4 as dissolving agent.

Using the recovered $FeSO_4$, $MnSO_4$, and $ZnSO_4$ as reactants, Zn–Mn ferrite magnetic materials with the composition of $Mn_{0.26}Zn_{0.24}FeO_2$ were synthesized. The products were characterized as high pure spinel Zn–Mn ferrites with the calcining temperature of 850–1250 °C. With the increase of the calcining temperature to 1150 °C, the saturation magnetization of Zn–Mn ferrites increased to the highest at 78.83 emu g^{-1}. It is shown that the magnetization performances of Zn–Mn ferrites synthesized from spent batteries were similar to that of from analysis reagents. In addition, the given recycling process was environmentally acceptable and had a relatively low energy demand, indicating the feasibility to synthesize Zn–Mn ferrites with high properties from SDBs.

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