Study on preparation of NiCo ferrite using spent lithium-ion and nickel–metal hydride batteries

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A B S T R A C T

To reduce cost and secondary pollution caused by complicated separation and purification in the recycling of spent batteries, an environmentally friendly process was proposed to treat and recycle a mixture of spent lithium-ion batteries (LIBs) and nickel–metal hydride (Ni–MH) batteries. In this novel process, spent LIBs and NiMH batteries were used as source materials to prepare magnetic nanoparticles of NiCo ferrite by sol–gel combustion. Characterization studies, such as XRD, FESEM and TEM, have been carried out to explore the particle size. The presence of functional group has been identified by Fourier transform infrared spectra. From TG–DSC studies, crystallization occurs at temperatures above 550 °C. The magnetic properties of final nanoparticles were found to be directly influenced by average size of products. The values of $M_s$, $M_r$, and $H_c$ of NiCo ferrite increase with the increasing size of the final products.

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1. Introduction

Secondary batteries, including nickel metal hydride (Ni–MH) batteries and lithium ion batteries (LIBs), are widely used as electrochemical power sources in mobile phones, personal computers, video-cameras, hybrid cars and other modern-day appliances, these batteries have many advantages, such as high energy density, high battery voltage, long charging–discharging cycle, and large temperature range. However, there is a large quantity of spent Ni–MH batteries and LIBs that have been disposed of as waste that must be recycled. Recycling spent batteries is not only important for environmental reasons. This type of residue represents an important secondary source of metals that can be found in very high concentrations, sometimes even higher than those found in natural ores. In addition, some metals are quite expensive, such as cobalt and nickel. According to Mantuano et al. [1], Ni–MH batteries contain 6.1 ± 0.7% (w/w) of cobalt and 49 ± 5% (w/w) of nickel, while LIBs may contain 36 ± 9% (w/w) of cobalt, excluding the plastic and metallic shells. Therefore, recycling of spent LIBs and Ni–MH batteries has become an urgent matter from the viewpoint of environmental protection and resource conservation [2].

An overview of the current techniques including pyrometallurgical process, hydrometallurgical process or the combination of both for the recycling of spent LIBs and Ni–MH batteries, is demonstrated elsewhere [3–12]. The massive energy consumption, high cost, low efficiencies and serious secondary pollution of the traditional techniques make it desirable to find an economic and environmentally-friendly process to treat and recycle spent batteries.

Ferrite nanoparticles exhibit unique chemical, mechanical, structural and magnetic properties and have a variety of promising technological applications in high-density recording devices, color imaging, ferrofluids, high frequency devices and magnetic refrigerators [13,14]. Cobalt ferrite is a well-known hard magnetic material with relatively high coercivity and saturation magnetization. Nickel ferrite is a soft material with low coercivity and saturation magnetization. Many of these (hard and soft magnetic) properties make them very promising candidates for a variety of applications in biomedical, electronic and recording technologies [15–18]. For practical applications in recording devices, sometimes relatively high blocking temperature of the nanoparticles is required of the nanoparticles, but in other applications (biomedical), a relatively low blocking temperature is required. Thus, it is important to tailor the magnetic properties of these materials according to the application’s requirements. This can be accomplished by adjusting the concentrations of soft (e.g. nickel ferrite) and hard (e.g. cobalt ferrite) magnetic phases in these materials [19].

In the present investigation, spent LIBs and Ni–MH batteries are used as source materials to prepare NiCo ferrite by sol–gel combustion. The characterization of prepared NiCo ferrite has been performed by employing various techniques examine the particle size and to explore other parameters of interest.
2. Experimental

2.1. Materials and reagents

Cylindrical, spent LIBs and Ni–MH batteries of different sizes and manufactures were collected for this study. The positive electrodes of spent NiMH batteries were comprised of formed nickel substrate and Ni(OH)₂ active material. The negative electrodes consisted of AB₅-type hydrogen storage alloy powders and iron or copper-mesh substrate. In spent LIBs, LiCoO₂ and carbon powders were pasted on aluminum and copper foil as positive and negative electrodes, respectively. The quantities of the materials in the two batteries were similar to those of similar sized commercial batteries on the market.

Auxiliary reagents including nickel sulfate, cobalt sulfate and ferrous sulfate were analytical grade.

2.2. Pretreatment of LIBs and Ni–MH batteries

Spent LIBs and NiMH batteries were dismantled manually. The plastic cases of the batteries were first removed using a small knife and a screwdriver. To remove the metallic shell, the battery was immersed in liquid nitrogen for 4 min and fixed in a lathe. This cryogenic method was adopted for safety precautions. The metallic shell was then cut using a saw. The ends of the metallic shell were removed first and a longitudinal cut was made to access the internal battery materials, which were removed using pliers. The anode and cathode were manually uncurled, separated and dried for 24 h at 80 °C. All experimental steps were performed while wearing glasses, gloves, and gas masks to ensure safety.

2.3. Leaching

A batch of 100 g mixed powders from electrode materials was dissolved in 3 mol/L sulfuric acid solution containing 2.5 wt.% hydrogen peroxide at a solid-to-liquid (S/L) ratio of 1:15 while stirring for 4 h. After complete dissolution, insoluble residue was filtered and washed with hot water.

2.4. Separation of other valuable metals

The pHₐ/₂ values (defined as the pH at which 50% metal extraction occurs) of di(2-ethylhexyl)phosphoric acid (P204) for Re³⁺, Fe³⁺, Zn²⁺ and Mn²⁺ in sulfuric acid are below 2.5 [20–24], whereas the pHₐ/₂ values of Co²⁺ and Ni²⁺ are 3.6 and 3.9, respectively [25]. After a single-stage metal ions extraction in the actual leach liquor with 20% P204 at an O:A ratio of 1:1, approximately 92.3% Re, 87.6% Fe and 98.2% Zn could be removed at pH = 2.5, while the removal of Mn was 62.1%. Hence, a multi-stage counter-current operation was needed to remove manganese thoroughly. After carrying out a four-stage counter-current extraction at pH 2.5, the concentration of rare earth metals, Mn, Zn and Fe in the raffinate decreased to below 0.01 g/L, and only about 2.7% Co and 0.1% Ni were co-extracted into the organic phase. Therefore, the separation of impurities and rare earth metals from cobalt and nickel can be realized by solvent extraction with P204.

2.5. Sample preparation

The separation of impurities and rare earth metals had precipitated 97% of the remaining RE³⁺, Fe³⁺, Zn²⁺ and Mn²⁺, meaning that the quantities of these elements were reduced to very low concentrations. Thus, a solution containing mostly Co²⁺ and Ni²⁺ was obtained. To prepare ferrite, suitable amounts of analytical grade nickel sulfate, cobalt sulfate and ferrous sulfate were added to adjust the concentration of Ni, Co and Fe. A 1:1 M ratio of citric acid to metal ions was added to the solution. During this addition, the
solution was continuously stirred using a magnetic agitator, and the temperature was held at 50 °C. Upon complete dissolution of citric acid, a certain amount of ammonia solution is added drop-wise to yield a brown solution. The temperature was raised to 80 °C and held until the solution transitioned to a brown–red sol. The pH of the sol was maintained between 7 and 8. Subsequently, the sol was placed into a dish and dried in an oven at 100 °C for 2 h to yield dried gels. The gels were ground into powder and heated at 800 °C for 3 h. The resulting black, loose powder obtained by combustion of the dried gels is nanocrystalline ferrites. The experimental procedure is shown in Fig. 1.

3. Results and discussion

3.1. Main metal contents of spent LIBs and NiMH batteries

The solution obtained after acid leaching was examined by atomic absorption spectrophotometry (AAS), and the composition of the mixed powders was found to contain 31.6% Co and 44% Ni. The quantity of the useful metals summed up to 75.6% of the total weight. Disposal of these metals would cause serious environmental pollution and represent tremendous waste. Hence, spent batteries are treated as an important secondary resource, and novel means for utilizing these spent batteries would be significant.

3.2. Preparation of NiCo ferrite samples

The leach liquor was used as a starting solution for the preparation of ferrite powder after adjusting the molar ratio of Ni(II):Co(II):Fe(II) to 1:1:4, as described in the experimental procedure. Thermal analysis measurements (TG, DTG and DSC) of the dried gel powder was carried out in dynamic air atmosphere (20 mL min⁻¹) under non-isothermal linear regimes. A STA 449C analyzer from Netzsch instruments was used during the experiments. Approximately 10–15 mg of each dried gel powder contained in Al₂O₃ crucibles was heated from room temperature to about 800 °C at a the heating rate of 10 °C min⁻¹. TG/DTG curves (Fig. 2) indicate that the weight loss occurs in two distinct steps. The

![DSC curve of dried gel.](image1)

![XRD patterns of NiCo ferrite nanoparticles at different temperatures.](image2)
The first stage shows large weight loss over the temperature range from room temperature to 550 °C, and this can be attributed to the oxidation–reduction between nitrate and the citrate. The second step was observed between 580 °C and 800 °C with only a small weight loss, and represents the decomposition of the remaining the organic matter. It was observed that simultaneous evaluation of lattice oxygen, oxidation of complex and formulation of semiorganic carbon metals/metal oxides. It is believed that at this stage the formation of corresponding metal oxides took place [26,27]. Crystallization is observed at temperatures above 550 °C [28]. At a temperature above 800 °C, no further weight loss occurs in the samples. From the TG/DTG curves, it can be seen that the first weight loss finishes completely at 580 °C and the second is thermally stable to 800 °C.

The thermal events observed in DSC curve are in concordance with that observed in the TG/DTG curves. The DSC curve in Fig. 3 clearly shows two exothermic peaks indicating that decomposition occurs in two stages; an observation not clearly apparent from DTG curve.

The XRD patterns of all NiCo ferrite nanoparticle samples are depicted in Fig. 4. It was found that all diffraction peaks can be perfectly indexed of the cubic spinel structure of NiCo ferrite.
However, for sample a and b, the low-intensity peaks at around 53° and 63° are identified as metallic CoFe based on the standard data of the metallic CoFe (JCPDS 51-0740). The appearance of the peaks might result from the lower firing temperature and will disappear with the increasing firing temperature. The mean crystallite sizes were estimated from XRD line width of the (311) peak using the Scherrer equation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \( D \) is the mean crystallite size, \( K \) and \( \beta \) the fining constant and the half width of the relevant diffraction peak, respectively, \( \lambda \) the X-ray wavelength and \( \theta \) is the angle of diffraction. The mean crystallite sizes estimated from the (311) peak are found to be 25, 33, 42, 58 nm corresponding to the firing temperature of 550, 650, 750, 850 °C, respectively. The crystalline nature of the NiCo ferrite increases sharply as the firing temperature was increased. This demonstrates that the particle size has increased with increasing calcination temperature in a manner similar to those observed in previous studies [29–32].

Fig. 5 shows field emission scanning electron microscopy (FESEM) of the sample calcined at 750 °C. It is evident that the NiCo ferrite nanoparticles have uniform, spherical morphology. Fig. 6 shows representative TEM images of samples annealed at 550, 650, 750, and 850 °C, respectively. The particle size distributions for each are depicted in the inset. The average particle sizes for the samples are 29, 37, 48, and 69 nm, and are in good agreement with X-ray diffraction evaluation. This demonstrates that the particle size has increased with increasing calcination temperature.

Chemical and structural transformations occur during calcination and can be monitored by spectroscopic analysis. Infrared
spectroscopic studies were performed aiming to ascertain the metal–oxygen nature of the nanoparticles and map the dehydration. Fig. 7 shows the IR spectrum of the dried gels before combustion and after combustion over the range of 400–4000 cm⁻¹. Prior to combustion, Fig. 7(a), characteristic peak appeared at 3187 cm⁻¹ and 1609 cm⁻¹ corresponding to the stretching vibration of O–H group and antisymmetric stretching of carboxyl group in citric acid, respectively. In addition, the characteristic peaks of NO₃⁻ ion are also observed at 1401, 1112 and 851 cm⁻¹, respectively. This indicates that NO₃⁻ ions exist in the structure of citrate gels during the process of gelation. After combustion, Fig. 7(b) shows a characteristic peak at 574 cm⁻¹ for NiCo ferrite. By comparing Fig. 7(a) with Fig. 7(b), we can deduce that the characteristic bands of the O–H groups, the carboxyl groups, and the NO₃⁻ ions disappeared after combustion, suggesting that the O–H groups, the carboxyl groups, and the NO₃⁻ ions partook in combustion during the formation of NiCo ferrite nanoparticles.

3.3. Magnetic properties of synthesized NiCo ferrite

The field dependence of the magnetization of the as-obtained spinel NiCo ferrite nanoparticles was measured using a vibrating sample magnetometer (VSM) at 300 K with an applied field of ±7 kOe. Fig. 8 illustrates the magnetic hysteresis loops of NiCo ferrite and shows the values of saturation magnetization (Ms) to be 35.326, 38.993, 52.932, and 52.967 emu/g, corresponding to nanoparticle sizes of 25, 33, 42, and 58 nm, respectively. The remanent magnetization (Mr) values are measured to be 13.447, 18.119, 18.940, and 25.065 emu/g, respectively. The values of coercivity (Hc) are 710.79, 1172.8, 1179.7, and 1484.2 Oe for each of the nanoparticle sizes listed above. Thus, the Ms, Mr, and Hc values increase as the size of NiCo ferrite nanoparticle increases, which agree well with those previously reported [33]. The saturation magnetization values obtained in the present study are lower than those reported in the literature [34], indicating excellent magnetic property by comparison.

4. Conclusions

Nanocrystalline NiCo ferrites have been prepared by sol–gel combustion methods using spent lithium-ion batteries and nickel–metal hydride batteries as raw materials. This method provides an alternate means of recycling batteries. It is found that adjusting the calcination temperature can control the magnetic properties of the ferrite, and functional groups are identified by Fourier Transform Infrared Spectra. TG–DSC studies reveal that crystallization appears at temperatures above 550 °C. The magnetic properties of the nanoparticles are found to be directly influenced by average nanoparticle size. The values of Ms, Mr, and Hc for NiCo ferrite increase with increasing nanoparticle size.

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