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Preparation and electrochemical characteristics of MgNi–FeB alloys

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Abstract

To improve the electrochemical performance of the MgNi-based alloys, different amounts of iron boride powder prepared by chemical reduction method were introduced by mechanical alloying. The results of powder X-ray diffraction showed these composites had amorphous structures. Cyclic charge–discharge tests showed the cycle stability of the MgNi alloy was improved by FeB. After 50 charge–discharge cycles, the discharge capacity of the MgNi–FeB composite was 60.99% higher than that of pure MgNi alloy. From the 1st cycle to 5th cycle, the discharge capacity faded rapidly; however, from the 6th to 100th cycle the discharge capacity was much more stable. The discharge capacity of cycle 100 remained 190.7 mA h g^{-1}, which was 93.53% of the 6th cycle. The corrosion resistance of the MgNi alloy in alkaline solution was also increased by FeB, which was confirmed by the results of electrochemical impedance spectroscopy and Tafel polarization tests.

Keywords: MgNi; FeB; Hydrogen storage; Alkaline battery; Electrochemical characteristics

1. Introduction

Mg-based alloys and their composites have been investigated as negative materials of Ni–MH batteries because of their high discharge capacity, light weight, availabilities of plentiful mineral sources and low cost. Despite the merits, practical applications of these materials in secondary batteries have been hampered by their poor stability in alkaline solutions [1]. The capacity decay is associated with the irreversible oxidation of the alloy by the electrolyte (KOH) leading to the formation of a $Mg(OH)_2$ layer on the surface of the alloy particles [2].

Many efforts, such as doping additives which have good catalytic activation for electrochemical characteristics by mechanical alloying (MA), have been made to improve the electrochemical performance of MgNi alloys. Borides have attractive special initial activity, hard to be oxidized and small particle sizes which are suitable additives for improving MgNi alloys performance. The chemical reduction is a promising method to prepare nanosized boride powder. FeB which was prepared via this method had been reported before [3]. Zhang et al. [4,5] reported boron can improve the cycle stability of the $PuNi_3$-type hydrogen storage electrode.

In this work, FeB was prepared by the chemical reduction method. Then MgNi–FeB composite powder was prepared by MA. The structural and electrochemical properties were characterized.

2. Experimental

2.1. Preparation

Ultrafine amorphous FeB was synthesized by the chemical reduction method. A typical experimental procedure is as follows: 250 ml of aqueous KBH_4 solution (2.0 mol dm^{-3}) was first prepared and then adjusted to pH = 12 with potassium hydroxide to prevent violent hydrolysis. The KBH_4 solution was added dropwise to 0.1 mol dm^{-3} $FeSO_4$ aqueous solution under vigorous stirring in argon atmosphere. An ice/water bath was used to maintain the reaction temperature. After the borohydride solution was added completely, the solution was stirred for 1 h to release hydrogen to prevent burning of the precipitate in the following filtration step. The precipitate was filtered and washed with distilled water and then acetone. Finally, the product was dried in vacuum at 80 °C for 24 h. All the reagents

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were of analytical grade and used as received without purification.

The MgNi–FeB composite powder was prepared by MA. The mixtures of MgNi and FeB (mass ratio 100:5, 100:10, 100:15, 100:20) were MA for 5, 10, 15 and 20 h at a speed of 450 rpm in an argon-filled stainless steel vessel with a ball to powder weight ratio of 20:1. The amorphous MgNi alloy was prepared by the same method as our previous work [6] before the preparation of MgNi–FeB composite powder.

2.2. Structure characterization

The structure and surface configurations were characterized by X-ray diffraction (XRD, Rigaku D/Max-2500, CuKα radiation), scanning electron microscopy (SEM, Hitachi X-650) and transmission electron microscopy (TEM, FEI Tecnai 20 ST).

2.3. Electrochemical measurements

Electrodes for tests were prepared as follows: 0.8 g of the mixture of as-prepared powder and nickel powder (mass ratio 1:3) was pressed into pellet (10 mm in diameter) at 30 MPa. A sandwich of the pellet between two foamed nickel disks (20 mm in diameter) was pressed at 20 MPa, on which a nickel strip was soldered.

Electrochemical tests employed a three-electrode system, as-prepared electrode as working electrode, $NiOOH/Ni(OH)_2$ as counter electrode, HgO/Hg as reference electrode and 5 mol dm^{-3} KOH aqueous solution as electrolyte. Charge–discharge cycle tests were performed using an automatic battery-testing instrument controlled by a computer. Test sequence was that charge at 100 mA g^{-1} for 6 h, discharge at 25 mA g^{-1} to −0.6 V vs. HgO/Hg, rest for 10 min between charge and discharge.

CHI 660b electrochemical workstation was used for Tafel polarization (scan rate: 1 mV s^{-1}, −1.2 to −0.2 V vs. HgO/Hg) and electrochemical impedance spectroscopy (EIS) (at open circuit potential, amplitude 5 mV, 10^4–10^{-1} Hz) measurements. All the experiments were conducted at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of FeB, MgNi and MgNi–FeB composite (mass ratio 100:15). Compared to XRD patterns of MgNi, the Ni peak becomes weak after MgNi–FeB MA 15 h. This suggests FeB facilitated the formation of amorphous composite during MA process.

Fig. 2 shows the SEM photographs of MgNi and MgNi–FeB (mass ratio 100:15) composite. The MgNi–FeB particle size was bigger than that of pure MgNi alloy, and there were some layer structures in MgNi–FeB alloy. The cycle stability of the alloy electrodes may benefit from the MgNi–FeB particle size.

Fig. 3 shows the TEM photographs of the FeB and MgNi–FeB alloy. The FeB particles (Fig. 3A and B) were spherical with an average particle size of around 2 μm in diameter. FeB exhibited small size and its particles appeared to be interconnected. The MgNi–FeB particles (Fig. 3C and D) were irregular spheres with diameters of about 3 μm. MgNi–FeB particles exhibited high dispersion, and the crystallinity was low. That indicated this composite particle has low crystal

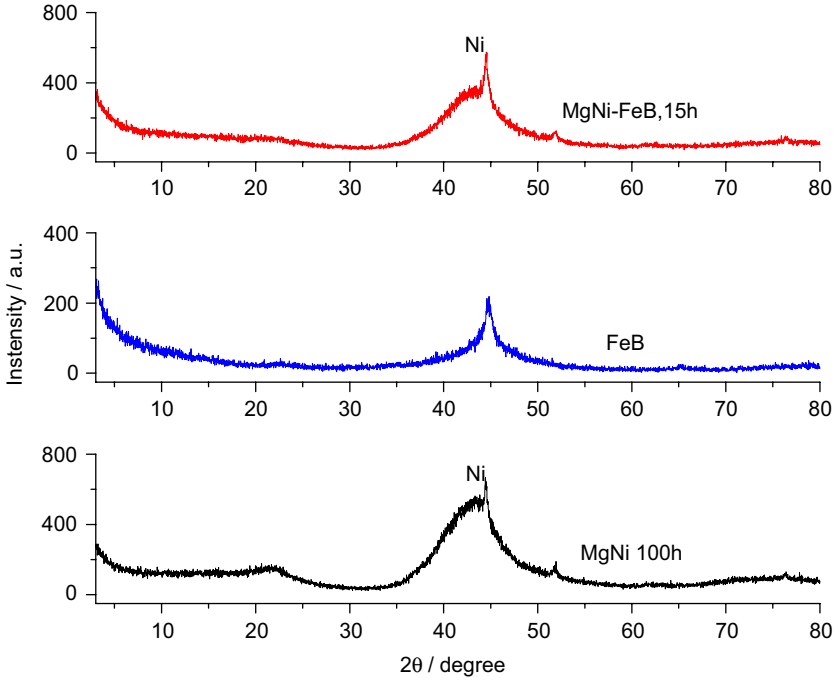

Fig. 1. XRD patterns of MgNi, FeB and MgNi–FeB (mass ratio 100:15) 15 h.