Integrated preparation of long-life hydrogen storage alloy film/Ni foil composite electrode material

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Abstract. An integrated preparation method of a long-life hydrogen storage alloy film/Ni foil composite electrode material has been proposed in this paper. The hydrogen storage alloy film/Ni foil composite electrode material was prepared by magnetron sputtering. The prepared film composite electrode effectively reduces the electron/ion diffusion distance, increases the specific surface area of alloy, and reduces the contact resistance between the active material and the current collector. Furthermore, the integrated preparation of long-life hydrogen storage alloy film/Ni foil composite electrode material is realized by depositing method. This paper provides a simple and effective method for reducing the internal resistance and increasing the electrochemical reaction rate of the hydrogen storage alloy, and the prepared film composite could be a promising candidate for Ni-MH batteries.

1. Introduction

The nickel-metal hydride (Ni-MH) batteries are used in a variety of electronic devices and equipment due to their high energy density, high power density, environmental friendliness, safety and a wide range of temperature adaptability[1,2]. Ni-MH batteries are generally obtained by cold-pressing hydrogen storage alloy powder (as active material) and nickel carbonyl powder (as current collector and binder). However, this method will create a large contact resistance between the active material and the current collector. Noted that a large contact resistance could slow the electrochemical reaction kinetics, which hinders the performance improvement of the Ni-MH batteries[3-5]. Therefore, the long-life hydrogen storage alloy film/Ni foil composite electrode material could be prepared in order to reduce the contact resistance between the alloy powder and nickel carbonyl powder[6-8].

Magnetron sputtering, as a Physical Vapor Deposition (PVD), has been applied to prepare metal, semiconductor, insulator, etc. Due to the advantages of control easily, large coating area and strong adhesion[9-11]. In this work, an integrated preparation of long-life hydrogen storage alloy film/Ni foil composite electrode material has been presented. With the help of magnetron sputtering coating method, a thin film of hydrogen storage alloy with a certain thickness was deposited on a Ni foil substrate. The long-life hydrogen storage alloy films with different thicknesses and surface morphology were prepared by adjusting the background pressure, sputtering power, sputtering time and the temperature applied on substrate. This method has the following advantages: (1) increase the specific surface area of hydrogen storage alloys; (2) reduce the transmission distance of electrons and ions; (3) reduce the contact resistance between the active material and the current collector; (4) integrated production of hydrogen storage alloy film/Ni foil is realized. The integrated film composite material exhibits great potential to be candidates as the electrode for reducing the internal resistance in Ni-MH battery and increasing the...
electrochemical reaction rate[12-16].

2. Experiment

2.1. Raw Materials
The rare earth elements La, Ce, Y(99.5%) were purchased from Baotou Xinye New Material Co., Ltd., metallic elements Ni and Co(99.9%) were purchased from Jinchuan Group Co., Ltd., element Mn (99.9%) was purchased from Yiyang Jinneng New Material Co., Ltd., and element Al(99.9%) was purchased from Boyu Metal Co., Ltd.

2.2. Specimen preparation
Alloy preparation: the ingot of alloy La0.6Ce0.3Y0.1Ni3.7Co0.75Mn0.3Al0.35 was prepared by inductive melting elements La, Ce, Y, Ni, Co, Mn, Al under high-purity argon atmosphere at 1300 ºC. Then the ingot was cooled at a rapidly rate to ensure the homogeneity of the alloy. Moreover, the ingot was annealed under an Ar flow at 1000 ºC for 5 h, and mechanically ground to powders[17,18]; Target preparation: the prepared hydrogen storage alloy powders were pressed into a target (the diameter of target is 50 mm, and the thickness is 3 mm), and the target is bound with a copper backing plate by using element In. The obtained object is used for magnetron sputtering; Substrate preparation: cut the Ni foil into proper size (3.5 cm*3.5 cm), and the Ni foil was washed and dried in the following order: acetone−deionized water−3 mol/L HCl−deionized water−ethanol−vacuum drying. Subsequently, a substrate using for sputtering could be obtained; Film preparation: the atmosphere used for deportation was 99.99% purity argon. The sputtering power was controlled as the value of 100 W. The background pressure is 1 Pa. By adjusting the sputtering time \(X\) (\(X = 120, 240\) and 360 min) and the temperature applied on substrate \(Y\) (\(Y = 0\) and 150 ºC), the long-life hydrogen storage alloy film/Ni foil composite electrode material with different thicknesses and surface morphology were obtained (see Table 1).

| \(X\) (min) | S1 | S2 | S3 | CS1 | CS2 | CS3 |
|------------|----|----|----|-----|-----|-----|
| 120        | 150 | 150 |    | 0   | 0   | 0   |
| 240        | 150 | 150 |    | 0   | 0   | 0   |
| 360        | 150 | 150 |    | 0   | 0   | 0   |

2.3. Characterization
The morphology properties of the specimens were investigated by a field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, 15keV).

3. Result and discussion

3.1. Characteristics of film composite electrode
The specimen shows good elasticity since the shape could recover after bending into an arbitrary angle. It should be noted that the alloy film/Ni foil composite electrodes prepared by magnetron sputtering all have the above characteristics.

Figure 1. Photos of the alloy film/Ni foil composite electrode.
3.2. Morphological characterizations of sectional view of film composite electrodes

Figure 2a-c show the SEM images of the sectional views of CS1, CS2 and CS3, respectively. It is clear that the film thicknesses of CS1, CS2 and CS3 are 360, 640 and 800 nm, respectively, which are consistent with the increase of sputtering time. Mentioned that an obvious strip-like traces could be observed in the figure, and this is caused by alloy growth during the deposition process [19,20].

![Figure 2](image)

Figure 2. Morphological characterizations (a)-(c) are SEM images of the sectional views of CS1, CS2 and CS3, respectively.

3.3. Morphological characterizations of the surface of film composite electrode

Figure 3a-c shows the SEM images of the surface of CS1, CS2 and CS3, respectively. From the figure, there is no significant difference among samples, which are all smooth and flat. Figure 3d-f present the SEM images of the surface of S1, S2 and S3, respectively. It is clear that the film surfaces are covered with oxidized particles, which is distinct from the clean surfaces before applying a temperature of 150 °C on the Ni foil substitute. As illustrated in Figure 3d, the oxidized particles on the surface of S3 is less noticeable, while the oxidized particles became quite obvious when sputtering time is 360 min (see Figure 3f).

The film composite prepared by magnetron sputtering has a larger specific surface area and a smaller ion diffusion distance comparing with the commercial hydrogen storage alloy powder (50 ± 10 μm in diameter). Therefore, the film composite has a large charge/ion transfer rate, which is of great significance for the preparation process and future development of Ni-MH batteries.
Figure 3. Morphological characterizations. (a)-(c) are the SEM images of surface images of CS1, CS2 and CS3, respectively. (d)-(f) are the surface images of S1, S2 and S3, respectively.

4. Conclusion
In summary, a simple and effective strategy is reported to fabricate film composite for the application of Ni-MH batteries. The film composite material takes the advantages as following: (1) large specific surface area; (2) small transmission distance of electrons and ions; (3) small contact resistance; (4) good elasticity. The prepared long-life hydrogen storage alloy film composite electrode material accelerates the charge transfer rate, and successfully realizes the integrated preparation of the Ni-MH battery. This paper is of great significance for the integrated preparation of Ni-MH battery, which has a promising prospect.

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