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Structure and electrochemical characteristics of $RENi_3$ alloy

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Abstract

The $RENi_3$ (RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Y) series compounds have been prepared by arc melting constituent elements under Ar atmosphere. X-ray diffraction (XRD) analysis reveals that the as-prepared alloys have different lattice parameters and cell volumes, depending on different rare earth (RE) element. The electrochemical characteristics, including the electrochemical capacity, P–C isotherms, high rate chargeability (HRC) and high-rate dischargeability (HRD), of these alloys have been studied through the charge-discharge recycle testing at different temperatures, charge currents and discharge currents. The results show that YNi_3 has the largest cell volume, smallest density, and moreover, it shows more satisfactory electrochemical characteristics than other alloys, including discharge capacity, HRC, HRD and low temperature dischargeablity.

Keywords: Metal hydride electrode; Ni-MH battery; P–C isotherms; Electrochemical characteristic; Rare earth element

1. Introduction

Recently, secondary batteries with high energy density and long durability are urgently required as a power source for portable appliances and zero emission vehicles. Due to a high specific energy, a high resistance to overcharging and overdischarging, capability of performing high rate charge/discharge, environmental friendliness, and interchangeability with the nickel-cadmium battery, the nickel-metal hydride (Ni-MH) battery has been widely investigated and applied in portable telecommunication equipment, electric tools and electric vehicles [1–3]. The Negative electrodes are the most important component in a Ni-MH battery.

AB_5 alloys, where A represents a metal that is capable of reacting exothermically with hydrogen and forming a stable hydride and B represents another kind of metal which cannot form a stable hydride but can catalyze the hydrogen reaction, are generally employed as the negative electrode material in nickel-metal hydride battery. The AB_5 type alloy has been studied extensively as the negative electrode material in Ni-MH battery [4,5], because it can easily react with hydrogen at normal temperatures and is chemical stable. However, the capacity of AB_5 type alloys is almost approaching its technical limitation nowadays because the repeated improvements to increase the capacity have already realized very high utilization of the intrinsic capacity of the alloy, and further increases in discharge capacity will be difficult.

The structure of an AB_3 compound (PuNi3-type) is obtained by combining the AB_5 with AB_2 units [$AB_5 + 2(AB_2) = 3(AB_3)$] [6]. From the viewpoint of gas-solid reactions, Oesterreicher et al. [7,8] and Takeshita et al. [9,10] have studied the hydriding characteristics of $LaNi_3$ and RT_3 phases (R = Dy, Ho, Er, Tb, Gd; T = Fe or Co), respectively. Their results showed that the hydrogen storage capacity of the AB_3 type alloy exceeds that of the well-known hydrogen storage AB_5 type alloy, which indicates that AB_3 alloy is a potential candidate for the negative electrode material. Nevertheless, it was pointed out that AB_3 type alloy is subject to the problem that the stored hydrogen in the $LaNi_3$ alloy is released sparingly after absorption [11]. Although there have been some studies on AB_3 compounds, the results are still quite incomplete. Moreover, the electrode characteristics of these alloys have been hardly investigated [12]. This study, as a part of the research work in our group, concerns the use of $RENi_3$ (RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Y) hydrogen

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storage alloys as the negative electrode material in a Ni-MH battery.

2. Experimental details

2.1. Alloy preparation and X-ray diffraction analysis

All alloy samples were prepared by arc-melting the constituent elements or master alloy on a water-cooled copper hearth under an argon atmosphere followed by annealing in vacuum for 20 h at 770 °C. The purity of the metals, i.e., La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Y, Ni, is higher than 99.9 mass%. The samples were all inverted and remelted five times to ensure good homogeneity. These alloy samples were then crushed in mortar into fine powders of 200–300 mesh.

Crystallographic characteristics of the hydrogen storage alloys were investigated by X-ray diffraction (XRD) using a Rigaku D/Max 2500PC X-ray diffractometer (Cu Ka, graphite monochromator) and JADE5 software [13]. The lattice constants and cell volume were calculated by the cell program [14] after internal theta calibration using silicon as the standard reference material.

2.2. Electrochemical measurements

The well-mixed alloy powder and carbonyl nickel powder in a weight ratio of 1:5 were pressed into tablets for the metal hydride electrode, with dimensions of 13 mm diameter, thickness of 1.5 mm. The weight of each electrode was about 0.9 g.

The electrochemical properties were then measured in a standard three electrode cell consisting of a working electrode (metal hydride electrode), a counter-electrode ($NiOOH/Ni(OH)_2$ electrode) and a reference electrode (Hg/HgO). The electrolyte in the cell was 6 M KOH aqueous solution. Charge and discharge tests were carried out on a DC-5 battery testing instrument controlled by computer. The emphasis of these charge/discharge tests was on the electrochemical capacity and stability of the negative electrode, thus the capacity of the positive electrode plate was designed to be much higher than that of the negative electrode. These experimental cells were first charged at 293 K at a current of 60 mA g^{-1} for 5.5 h, then rested for 30 min before discharging at the same discharge current density to the cut off voltage of −0.60 V versus Hg/HgO.

P–C–T curves were electrochemically obtained by converting the equilibrium potential of the metal hydride to the equilibrium pressure of hydrogen on the basis of Nernst equation using electrochemical data [15] as reported in reference [16]. The equilibrium potential curves were obtained by alternating the following two processes: (1) a pulse discharge of (25 mA g^{-1} × 0.25 h) and (2) a rest period until the potential became almost constant. The equilibrium potential change of approximately 30 mV corresponds to the equilibrium pressure change by one order of magnitude. Since the measured potentials have an error of 1–2 mV, the calculated pressure values are accurate to within 10% [16].

To evaluate the high rate dischargeability (HRD) (in the range of 90–900 mA g^{-1}), the charging current density was kept constant at 60 mA g^{-1} and the obtained discharge capacity was denoted as C_i. On the other hand, when the high rate chargeability (HRC) (90–900 mA g^{-1}) was investigated, the discharge current density was held at 60 mA g^{-1} and thus we got the discharge capacity (C_j). HRD (or HRC) are generally defined as the ratio of the discharge capacity C_i (or C_j) at the cut off voltage of −0.6 V to the maximum capacity C_{max}, namely: $HRD = C_i/C_{max} \times 100\%$, $HRC = C_j/C_{max} \times 100\%$, respectively.

For investigating the electrocatalytic activity of the hydrogen electrode reaction, the linear polarization curves of the electrode were plotted on a EG&G PARC's Model 273 Potentiostat/Galvanostat station by scanning the electrode potential at the rate of 0.1 mV/s from −5 to 5 mV (versus open circuit potential) at 50% depth of discharge (DOD) at 293 K. The polarization resistance R_p can be obtained from the slope of the linear polarization curves. Moreover, the exchange current density (I_0), which is a measure of the catalytic activity of electrode, was calculated from the slopes of polarization curves by the following equation [17]

$$I_0 = \frac{RT}{FR_P}$$

where R is the gas constant; T, the absolute temperature; F, the Faraday constant; and R_p, the polarization resistance. The potentiostatic discharge technique was used to evaluate the coefficient of diffusion within the bulk of the alloy electrodes. After being fully charged followed by a 30 min open-circuit lay-aside, the test electrodes were discharged with +500 mV potential-step for 500 s on a EG&G PARC's Model 273 Potentiostat/Galvanostat station, using the M352 CorrWare electrochemical/corrosion software.

The hydride electrodes were charged at different temperatures (T = 233, 253, 293, 333 K) (the charged capacity was represented by C_c) and then discharged at 293 K to determine the dependence of charge efficiency on temperature (the obtained discharge capacity was denoted as C_d). The charge efficiency was defined as the ratio of the discharge capacity C_d at the cutoff voltage of −0.6 v to the charge capacity C_c. In contrast if they were charged at 293 K and discharged at various temperatures, the discharge efficiency can be evaluated.

3. Results and discussion

3.1. Structure characteristics

Fig. 1 shows the XRD patterns of the alloys with different chemical compositions. The results indicate that these alloys all are homogenous with a single phase corresponding to a hexagonal $PuNi_3$ type structure. Careful examination of the diffraction angle reveals a peak shift upon changing the com-