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Self-supported electrodes made of $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$ and Ag or Ni for hydrogenation

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Abstract

An AB_5-type hydrogen storage alloy, $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$, was mixed with Ag flakes or Ni powder, pressed, and sintered to fabricate a durable pellet that would maintain its integrity during repeated gas phase or electrochemical hydriding and dehydriding. The molar compositions $Ag/AB_5 \geqslant 10$ and $Ni/AB_5 \geqslant 25$ could meet this requirement. After sintering, the alloy in the pellet $Ag/AB_5 = 10$ maintains the original phases, but a second phase appears in the pellet $Ni/AB_5 = 25$. The volume expansions of these two pellets after hydrogenation are 5–8%. The number and size of microholes in the pellet $Ni/AB_5 = 25$ are larger than those in the pellet $Ag/AB_5 = 10$, presumably due to different shapes of Ni powder and Ag flakes. The difference in the shape of the metallic binders also affects the discharge capacity. It is concluded that by careful control of the mixing ratio and sintering condition, the electrodes will have a potential application for charging in the gas phase and discharging in electrolyte.

Keywords: $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$; Metal hydride; Hydrogenation; Battery

1. Introduction

Pulverization of metal hydrides during absorption/desorption of hydrogen is an inherent problem that results from a combination of volume change and their brittle nature. To avoid the negative effect of pulverization in Ni-hydrides battery, it is a common practice to use fine hydride powder as the active material to fabricate the electrode. Extensive research has been aimed at improving the toughness of the electrode by using a binding material to hold the alloy powder together to accommodate the volume change [1,2], or by a different process such as sintering [3,4]. In a previous study, it was successful to sinter AB_2 with Ag at suitable ratios to make nonbreakable metal hydride pellets after hydrogen gas absorption/desorption or electrochemical charge/discharge [5]. The idea is to use such pellets as an anode for a Ni/MH battery so that it can be charged in hydrogen gas but discharged in electrolyte. The metallic powder Ag acts as a binder to maintain integrity and also as a current collector. This is feasible for a series of alloy-binder systems at different ratios.

In this work, a different class of AB_5 hydrogen storage alloy, $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$, was studied. Binders of Ni and Ag were used to determine if a similar process was suitable to prepare nonbreakable metal hydride electrodes. The gas phase and electrochemical hydrogenation properties were investigated and compared with those of conventional electrodes.

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2. Experimental

The $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$ alloy was prepared by arc melting, followed by annealing at 1100 °C under vacuum for 10 h, as reported previously [6]. It was then pulverized into a sieve of size smaller than 44 μm by repeated hydriding/dehydriding. The alloy powder was mixed with Ag flakes (~ 44 μm) or spherical Ni powder (2.5 μm) in different molar ratios, pressed at a pressure of 125 kg/cm^2 to form a pellet of diameter 14 mm, and then sintered in vacuum at 450 or 700 °C for 5 h, respectively. The phase structures of the alloy and pellets were identified by X-ray diffraction (XRD).

For activation under hydrogen gas, the alloy powder or pellets were placed in vacuum and then exposed to hydrogen gas in a volumetric system at a pressure of 2.5 MPa at 25 °C. The pressure–composition isotherms (P–C–T curves) for hydrogen absorption and desorption were measured by the Sieverts method. The P–C–T data were taken after three cycles of activation. The battery test was performed using the pellet as the negative electrode, 30 wt% KOH and 1 wt% LiOH as the electrolyte, polypropylene as the separator, and a $Ni(OH)_2$/NiOOH positive electrode. For comparison, a negative foam electrode containing only the pure alloy powder was also investigated. The negative foam electrode was prepared by pasing a mixture composed of 0.5 g of the alloy powder and 3 wt% polytetrafluoroethylene (PTFE) onto a nickel foam and then pressed at a pressure 100 kg/cm^2 to form a 3 cm × 3 cm plate. A charge/discharge rate at a current density of 60 mA/g was used. The test was started by activation from the first cycle at 50 mA h/g, the 2nd cycle at 100 mA h/g, etc., to the 6th at 300 mA h/g, then at 300 mA h/g or 1.2 times of the actual discharge capacity measured from the previous cycle, depending on which was higher. All of the discharge tests were cut off at a cell voltage of 0.9 V at 25 °C.

3. Results and discussion

3.1. Gas-phase hydrogenation

After three cycles of hydrogen absorption/desorption under a hydrogen pressure of 4 MPa, the pellets with the molar ratios $Ag/AB_5 \geqslant 10$ and $Ni/AB_5 \geqslant 25$ (i.e., weight ratios of 2.53 and 3.44, respectively) could maintain their integrity without breaking. The XRD patterns of $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$ and two mixed pellets $Ag/AB_5 = 10$ and $Ni/AB_5 = 25$ are shown in Fig. 1(a). The AB_5 alloy belongs to a hexagonal

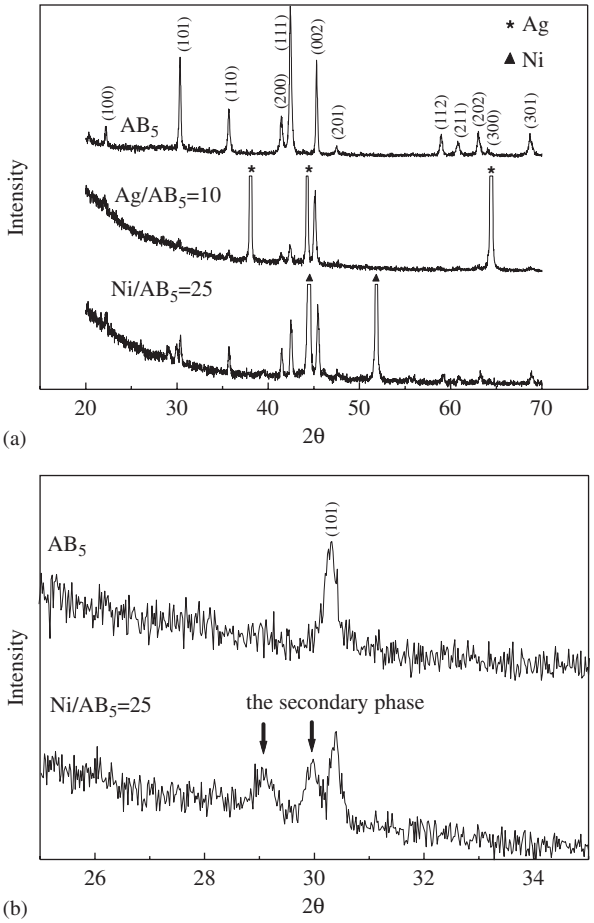

Fig. 1. (a) XRD patterns of $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$ and the pellets $Ag/AB_5 = 10$ and $Ni/AB_5 = 25$. (b) Magnified XRD patterns of $LaNi_{4.25}Al_{0.15}Co_{0.5}V_{0.1}$ and the pellet $Ni/AB_5 = 25$.

structure of $CaCu_5$, as reported previously by Lai et al. [6]. The main diffraction peaks in the pellet $Ag/AB_5 = 10$ indicate that Ag and the original structure of the alloy are maintained. For the pellet $Ni/AB_5 = 25$, in addition to Ni and the AB_5 phase, some additional peaks are present, as shown more clearly in Fig. 1(b). These peaks belong neither to the phase of La_2Ni_7 nor to $LaNi_3$ [7]. This indicates that a reaction between Ni and the AB_5 alloy has occurred during sintering.

The volume expansion of the pellets $Ag/AB_5 = 10$ and $Ni/AB_5 = 25$ after 3 cycles of hydrogenation were about 8% and 5%, respectively. Figs. 2 and 3 show the SEM morphologies of both pellets before and after hydrogenation. Although some microcracks are observed in the pellet $Ag/AB_5 = 10$ after hydrogenation, its integrity is preserved. The number and pore size of the microholes in the pellet $Ni/AB_5 = 25$ are larger than those in the pellet $Ag/AB_5 = 10$. The distinct