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Electrochemical properties of Mg-based hydrogen storage materials modified with carbonaceous materials prepared by hydriding combustion synthesis and subsequent mechanical milling (HCS + MM)

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ARTICLE INFO

Article history:

Received 23 April 2010

Received in revised form

18 June 2010

Accepted 3 July 2010

Available online 1 August 2010

Keywords:

Mg-based hydrogen storage materials

Hydriding combustion synthesis

Electrochemical properties

Mechanical milling

Carbonaceous materials

ABSTRACT

Mg₂Ni-based hydride was prepared by hydriding combustion synthesis (HCS), and subsequently modified with various carbonaceous materials including graphite, multi-walled carbon nanotubes (MWCNTs), carbon aerogels (CAs) and carbon nanofibers (CNFs) by mechanical milling (MM) for 5 h. The structural properties of the modified hydrides were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). All of the modified hydrides show amorphous or nanocrystalline-like phases. The hydride modified with graphite exhibits the most homogenous distribution of particles and the smallest particle size. The effects of the modifications on electrochemical properties of the hydride were investigated by galvanostatic charge/discharge, linear polarization, Tafel polarization, electrochemical impedance spectroscopy and potentiostatic discharge measurements. The results show that the maximum discharge capacity, the high rate dischargeability (HRD), the exchange current density and the hydrogen diffusion ability of the hydride modified with the carbonaceous materials are all increased. Especially, the hydride modified with graphite possesses the highest discharge capacity of 531 mAh/g and the best electrochemical kinetics property.

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1. Introduction

Presently, nickel–metal hydride batteries (Ni/MH) have been extensively applied in everyday life due to their superior charge/discharge capability and pollution-free nature. However, unsatisfactory theoretical specific capacities and high cost of the commercial anode materials (i.e. LaNi₅-based and Zr–Ti-based hydrogen storage alloys) restrict their further developments.

Consequently, the development of high specific capacity and economical metal hydride as anode materials is crucial

for the large-scale applications of Ni/MH batteries. Mg-based hydrogen storage materials have attracted considerable interests among the most promising candidates in view of their high theoretical specific capacity, light weight, abundant resources, low cost, etc [1–4]. However, either poor cycling stability or low practical discharge capacity hinders their potential application. In order to overcome the above shortcomings, much research such as mechanical milling (alloying) [5,6], element substitution [7–9], Mg-based composite preparation [10,11], surface modification [12,13] and novel preparation methods [14,15] has been conducted. Mechanical

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doi:10.1016/j.ijhydene.2010.07.031

milling/alloying has been widely used to synthesize Mg-based alloys with amorphous or nanocrystalline microstructure, which possesses higher discharge capacity than crystalline alloys [5].

Hydriding combustion synthesis, put forward in 1997 by Akiyama et al. [16], has been considered as a valuable method to prepare Mg-based hydrogen storage alloys on account of its short process time, low energy consumption and high purity and activity of product [17–22]. By ways of HCS, Mg₂Ni alloy can be directly synthesized from the powder mixture of magnesium and nickel at 850 K, which is below the melting point of magnesium. As a consequence, the evaporation of magnesium can be prevented effectively. Furthermore, the preparation and hydrogenation of hydrogen storage alloy proceed in a single process, which avoids the repeated remelting and activating process as compared with the conventional ingot melting. Based on the above advantages of HCS and MM, we have prepared Mg₂Ni-based hydrides with high discharge capacity and activity by the process of HCS + MM (MM for only 5 h) previously [23,24].

It has been widely reported that carbonaceous materials, such as graphite and multi-walled carbon nanotubes are effective additives for improving the electrochemical properties of Mg-based hydrogen storage alloys [25–31]. Thus, the aim of the present work is to investigate the influences of various carbonaceous additives (including graphite, MWCNTs, CAs and CNFs) on the structural and electrochemical properties of the Mg₂Ni-based hydride prepared by the process of HCS + MM.

2. Experiment details

The HCS product was prepared from commercial Mg (99.9 mass% in purity and <150 μm in particle size) and Ni (99.7 mass% in purity and 2–3 μm in particle size) powders. The powders were mixed in 2:1 of Mg/Ni molar ratio by an ultrasonic homogenizer in acetone for 1 h. After completely dried in air, the well-mixed powder was placed directly into the synthesis reactor without compacting. Before heating, the reactor was evacuated by a rotary pump, then argon at 0.1 MPa was introduced and the reactor was evacuated again. This cleaning procedure was repeated twice to remove any oxygen in the system. During HCS process, the mixed powder was heated from room temperature to 850 K at the rate of 7 K/min and held for 1 h under 1.9 MPa hydrogen pressure. In order to increase the degree of hydrogenation of Mg₂Ni, the samples were hold at 623 K for about 1 h during the cooling process. Subsequently, the samples were cooled down to room temperature under hydrogen atmosphere. After that, the HCS product was mechanically milled with 3 wt% (vs. the HCS product) commercial graphite, MWCNTs, CAs and CNFs for 5 h at a speed of 400 rpm and 40:1 in ball-to-powder using a planetary-type ball mill under argon atmosphere, respectively.

All the testing electrodes were prepared as follows: 0.1 g HCS + MM product was mixed with 0.4 g carbonyl nickel powder, and then cold-pressed into a pellet of 10 mm diameter and about 1 mm thickness under a pressure of 12 MPa. The electrochemical measurements were performed in 6 M KOH aqueous solution using a three-compartment cell comprised of

a metal hydride testing electrode, a sintered NiOOH/Ni(OH)₂ counter electrode and a Hg/HgO reference electrode. The charge/discharge cycles were carried out with a LAND Battery Test instrument. As the initial anode are in their hydride state, all the testing electrodes were first discharged at 30 mA/g up to –0.6 V (vs. Hg/HgO), and then charged at 300 mA/g for 2 h after resting for 10 min at 30 ± 1 °C. The discharge capacities of electrodes were evaluated by the mass of active substances. The discharge capacities at different discharge current densities (100, 200, 400 mA/g) were measured to investigate the high rate dischargeability (HRD). Linear polarization, Tafel polarization, electrochemical impedance spectroscopy (EIS) and potentiostatic discharge of the electrodes were performed at room temperature on a CHI660C electrochemical workstation at 50%, 100%, 50% depth of discharge (DOD) and 100% depth of charge (DOC), respectively. Linear polarization and Tafel polarization were measured at scanning rates of 0.1 mV/s and 1 mV/s from –5 to +5 mV and –300 to 1500 mV (vs. open circuit potential), respectively. The EIS spectra of the electrodes were obtained in the frequency range of 100 kHz–5 mHz with an AC amplitude of 5 mV under open circuit conditions. The obtained EIS spectra were analyzed by ZPLOT electrochemical impedance software. As for potentiostatic discharge, electrodes were discharge at +600 mV potential steps for 3600 s.

The crystal structures of the samples were characterized by X-ray diffraction (XRD) on an ARL X'TRA diffractometer with Cu K_α radiation. The morphologies of the samples were analyzed by a JSM-6360LV scanning electron microscopy (SEM).

3. Results and discussion

3.1. Structural and morphological characteristics

Fig. 1 shows the XRD patterns of the bare (unmodified) and modified Mg₂Ni-based hydrides. It can be seen from Fig. 1(a) that the HCS product consists of the main phase Mg₂NiH₄ and

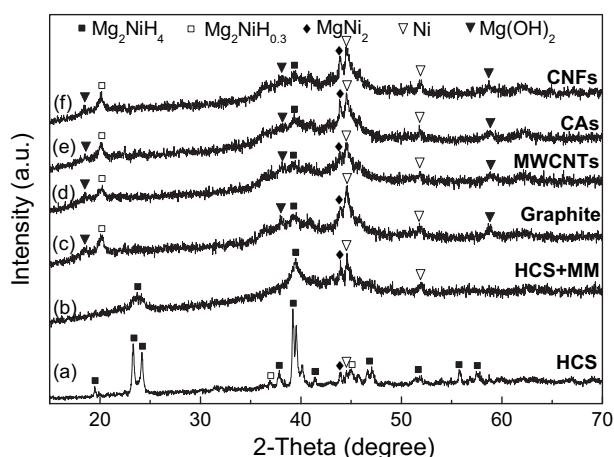


Fig. 1 – XRD patterns of the Mg₂Ni-based hydride modified with various carbonaceous additives: (a) HCS product; (b) HCS + MM product; (c) HCS + MM-Graphite product; (d) HCS + MM-MWCNTs product; (e) HCS + MM-CAs product; (f) HCS + MM-CNFs product.

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