



Significantly improved electrochemical hydrogen storage properties of magnesium nickel hydride modified with nano-nickel



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HIGHLIGHTS

- The HCS product of Mg_2NiH_4 is modified with nano-nickel via mechanical milling.
- The discharge capacity and cycle stability are dramatically improved.
- A novel $NiH_{0.75}$ phase is observed and the formation mechanism is discussed.
- Some insights into “electrochemical catalytically” enhanced mechanism are proposed.

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ABSTRACT

Magnesium nickel hydride (Mg_2NiH_4) used as negative electrode material in nickel-metal hydride (Ni-MH) secondary battery is modified by nano-nickel via mechanical milling. In this paper, we systematically investigate the microstructure and electrochemical properties of the modified system with different milling durations. X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) analyses confirm the amorphous transformation of Mg_2Ni -based hydride and a novel $NiH_{0.75}$ nanocrystalline with a diameter of about 5 nm embedding or covering on the surface of the base particle has been observed. Its formation mechanism and positive effects on electrochemical properties of the Mg_2NiH_4 have also been elaborated. Electrochemical measurements show that the 5 h milled composite possesses markedly increased discharge capacity up to 896 mAh g^{-1} . With prolonging the milling duration from 5 h to 40 h, the discharge capacity at the 10th cycle increases from 99 mAh g^{-1} to 359 mAh g^{-1} . Besides, the discharging procedure changes from stepwise processes to one single-step process with increasing the milling duration. Tafel polarization test shows that the nano-nickel modified system exhibits a much better anti-corrosion ability during charging/discharging cycles. Meanwhile, both the charge-transfer reaction on the alloy surface and hydrogen diffusion inside the alloy bulk are enhanced with nano-nickel modification.

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1. Introduction

Since the discovery of the reversible hydrogen storage alloy in the late 1960s, nickel-metal hydride (Ni/MH) batteries have been developed as one of the most important energy storage carriers thanks to their high energy density and good environmental compatibility with tremendous development in the last few decades. Future Ni/MH batteries are expected to store a large amount of energy without the increase in weight to satisfy the portable equipment and mobile applications [1–4].

Among the hydride-forming materials, Mg-based alloys, especially Mg_2Ni , exhibit promising properties as negative electrode materials in Ni/MH batteries because of their higher hydrogen storage capacity, lower specific weight and less cost compared with the commercial $LaNi_5$ -type alloys. Considering the objectives proposed by the U.S. Department of Energy (DOE) for the future hydrogen storage materials, magnesium and its alloys are expected to meet the target of high hydrogen storage capacity [2,5]. What is undesirable with it is that the lower practical discharge capacity, as well as the inferior cyclic stability stemming from the severe oxidation of Mg in alkaline solution restrains its practical application [6–8]. Meanwhile, the charging/discharging process is a solid–liquid reaction, and the reaction rate is affected very much on the solid–liquid interface. Hence, it is very necessary to modify the

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surface of hydride particles, aiming to protect the base materials and accelerate the electrochemical reaction.

In the past several decades, surface modification has been proved to be an effective method to improve the comprehensive electrochemical performance of the Mg_2Ni electrode alloys. Besides the traditional surface modification methods, namely acid, alkali and F-treatments which usually affect the surface composition of parent alloy, several groups have reported the improvement in capacity degradation of the alloy electrodes by microencapsulating the alloy particles with various coating layers such as Ni, Cu, Co, polymer, etc via electroless [9–12]. Luo [13] found that surface modification with Ni–P coatings by electroless plating effectively improves the cycle stability of Mg_2Ni -based alloy. Hwang [14] reported that electroless Ni coating can effectively improve the discharge capacity of Mg_2Ni alloys. Shen [15] reported that surface modification with polyaniline by electroless deposition improves the high rate discharge ability (HRD) of the AB_5 -type alloy electrode. However, the electroless coating process is complex due to its special self-catalyzed chemical reactions. Impurity elements like P, S, B, may inevitably be introduced, increasing the charge transfer resistance and hindering the diffusion of H as well. Coating layers introduced by mechanical milling (MM) have been confirmed to be effective in improving the performance of hydride electrodes by preventing corrosion of the disintegrated alloy, bringing about a superior electric catalytic activity. Among the commonly used dopants, including the transition metals, oxides and various carbon sources (graphite, CNTs, carbon black, etc) [8,16–20], Ni exhibits remarkable positive effects in terms of the utilizing of hydrogen absorbability and desorbability of the Mg_2Ni -type alloy electrodes, which has been attributed to the outstanding catalytic activity and electrical conductivity of Ni [21,22].

In our previous work, we have reported a novel method of preparing Mg_2NiH_4 with high activity and discharge capacity, namely hydriding combustion synthesis with subsequent mechanical milling (HCS + MM) [23]. However, the as-prepared HCS + MM product still needs investigation due to the severe corrosion of Mg in alkaline solution. In order to improve the electrochemical performance, especially the cycle stability of the HCS + MM product, a further modification is thus needed. Therefore, in this work, nano-nickel is introduced to modify the Mg_2NiH_4 via mechanical milling. The influence of milling duration on the structures and electrochemical properties of the hydride is investigated in detail. These results not only lead to an optimized Mg_2NiH_4 /nano-nickel composite system, but also provide some insight into the “electrochemical catalytically” enhanced mechanism of nano-nickel.

2. Experimental

2.1. Sample preparation

The HCS product of Mg_2NiH_4 was prepared from commercial magnesium powder (99.9 wt.% in purity and $<150\ \mu m$ in particle size) and nickel powder (99.7 wt.% in purity and $2\text{--}3\ \mu m$ in particle size). They were mixed in 2:1 of Mg:Ni molar ratio by an ultrasonic homogenizer in acetone for 1 h. After being completely dried, the well-mixed powder was placed directly into the synthesis reactor without compressive treatment. The hydriding combustion synthesis reactor used in the present work is the same as that reported in our previous work [24]. During HCS process, the mixed powder was heated to 850 K at the rate of $7\ K\ min^{-1}$ and held for 1 h under 1.8 MPa hydrogen pressure. Subsequently, the sample was cooled down to room temperature under hydrogen atmosphere. The XRD pattern of the as-prepared HCS product of Mg_2NiH_4 is shown in Fig. S1. It can be seen the HCS product is composed of the main

phase of Mg_2NiH_4 and the minor phase of $Mg_2NiH_{0.3}$.

The HCS product and commercial nano-nickel powder (99.7 wt.% in purity and $\leq 50\ nm$ in particle size) were mixed in 1:2 M ratio. Then the powder mixtures were put into the stainless steel vials (volume 100 ml) for mechanical milling. The milling was carried out under argon atmosphere at room temperature using a planetary-type ball mill at a speed of $400\ r\ min^{-1}$ and ball to powder ratio of 40:1. In order to investigate the influence of milling duration, the samples were milled for 5, 10, 20 and 40 h, respectively.

2.2. Sample characterization

All the testing electrodes were prepared as follows: 0.1 g sample powder was mixed with 0.4 g Ni powder, and then cold-pressed into a pellet of 10 mm diameter and about 1 mm thickness under a pressure of 12 MPa. Electrochemical measurements were performed in a three-electrode cell in 6 M KOH at $30 \pm 1\ ^\circ C$, using sintered $Ni(OH)_2/NiOOH$ as the counter electrode and Hg/HgO as the reference electrode. The discharge capacities of electrodes were evaluated by the amount of active substance of Mg_2NiH_4 . The discharge capacity and the cycle life were determined by the galvanostatic method using CT2001A Land battery testing system. The electrodes were discharged at $30\ mA\ g^{-1}$ to a cut-off potential of $-0.6\ V$ (vs. Hg/HgO) and then charged at $300\ mA\ g^{-1}$ for 2 h after 5 min rest. To investigate the HRD of the alloy electrodes, discharge capacities at different current densities ($100, 200, 400\ mA\ g^{-1}$) were measured at the first cycle.

Linear polarization curves were measured at a scanning rate of $0.1\ mV\ s^{-1}$ from -5 to $5\ mV$ (vs. open circuit potential) at 50% depth of discharge (DOD). Tafel polarization curves were measured at a scanning rate of $1\ mV\ s^{-1}$ from -300 to $300\ mV$ (vs. open circuit potential) at 100% DOD. Electrochemical impedance spectroscopy (EIS) studies of the electrodes were performed in a frequency range of 100 kHz to 5 MHz with an AC amplitude of 5 mV at 50% DOD under open-circuit conditions, using ZPLOT electrochemical impedance software. For the potentiostatic discharge, the electrodes were discharged at $+600\ mV$ (vs. open circuit potential) potential step and 100% depth of charge (DOC) for 3600 s. The above electrochemical tests were performed at room temperature in the 6 M KOH aqueous solution on a CHI660C electrochemical workstation.

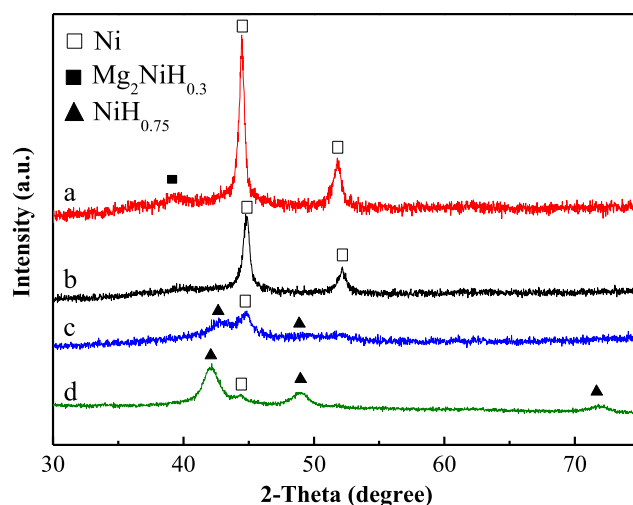


Fig. 1. XRD patterns of the Mg_2NiH_4 /nano-nickel composite milled for different durations: (a) 5 h, (b) 10 h, (c) 20 h, (d) 40 h.

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