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# Enhanced electrochemical kinetics of magnesium-based hydrogen storage alloy by mechanical milling with graphite

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ABSTRACT

Magnesium nickel alloy ($Mg_2Ni$) which used as the negative electrode material in the nickel-metal hydride (Ni/MH) secondary battery is modified by graphite via mechanical milling. The effects of graphite on the $Mg_2Ni$ are systematically investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) and a series of electrochemical tests. The results show that the cycle stability of the $Mg_2Ni$ alloy is improved with the addition of 10 wt.% graphite and the discharge capacity at the 20th cycle increase from 116.9 mA $g^{-1}$ to 178.5 mA $g^{-1}$. The Tafel polarization test indicates better corrosion resistance of the $Mg_2Ni$/graphite composite. Meanwhile, the results of electrochemical tests indicate that both the charge-transfer reaction rate on the surface of the alloy and the hydrogen diffusion rate inside the bulk of alloy are boosted with the introduction of graphite.

## Introduction

Nickel/metal hydride (Ni/MH) secondary battery has been widely used in portable electric devices, electric vehicles and other power sources due to their high energy density, element abundance and environment friendliness [1]. $AB_5$-type alloy is one of the most successful negative electrode material in the MH/Ni battery family and have been commercialized for over decades [2]. As the requirements for rechargeable battery are continuous increasing, the traditional alloys are no longer satisfactory with respect to specific capacity and cycle life in the future [3]. Recently, Mg-based hydrogen storage alloys have attracted great concern owing to its distinguished high theoretical capacity of 2200 mAh $g^{-1}$ in forming $MgH_2$ [4] or 1080 mAh $g^{-1}$ in forming $Mg_2NiH_4$ [5] and have been considered as one of the most promising candidates for the negative electrode material of the next generation MH/Ni battery [6]. However, sluggish hydriding/dehydriding kinetics at room temperature and poor corrosion resistance in alkaline electrolyte still restrain Mg or Mg-based alloys from practical applications. Hence, a great deal of attentions have been paid on improving hydriding/dehydriding kinetics and cyclic stability of Mg or Mg-based alloys [7–10].

In the past several years, surface modification and composition adjustment have been proved are two effective methods to improve the electrochemical performance of the Mg-based hydrogen storage alloys. Shen [11] found that electroplating polyaniline on La-Mg-Ni-based alloy could increase its capacity retention and kinetics due to the catalysis and

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corrosion resistance of the plated polymer layer. Chen [12] reported that the introduction of nano-nickel by mechanical milling improves both discharge capacity and cycle stability of $Mg_2Ni$ alloys. Meanwhile, the cycle stability of Mg-based alloys has also been meliorated by the introduction an appropriate amount of Al, Li, Si, Ti, Zr, B, or Pd [7,8,10,13–15]. Among all kinds of modification materials, carbonaceous materials are a special group of materials which have been proved both experimentally and theoretically to have hydrogen absorption ability of its self [16–19] or have positive effects on the performance of Mg-based hydrogen storage alloys [20–25]. Liu [26] found that the high temperature reduced graphene oxide has excellent catalytic effect on the hydrogenation/dehydrogenation of $MgH_2$ when the graphene nano-sheet closely stick to alloy particle. Imamura [27–30] conducted a series of work and demonstrated that milling Mg-based alloy with carbonaceous materials could facilitate the adsorption/desorption of gaseous hydrogen and proposed the synergetic effect and the "dangling carbon bond" mechanism. Huang [31] synthesized graphene/nano-Ag composite (G/A) and reported its favorable effect on improving discharge capacity, cycle life, discharge potential and electrochemical kinetics of Mg-Ni-La-type hydrogen storage alloy. Although Mg and Mg-based alloy have been intensively studied for several years as a promising candidate for hydrogen storage, most of the pure Mg related studies are focused on the gaseous hydrogen absorption properties and the electrochemical hydrogen storage properties are often studied on the basis of La-Mg-Ni alloy and its derivatives [32–35]. Meanwhile, those $Mg_2Ni$ alloy related researches which intend to improve the electrochemical hydrogen storage performance are usually involve complex process of introducing other element to change the composition of alloys or to form a functional layer on the surface of alloys [36–38]. On the other hand, the graphite as a very common and widely available material has been used to improve the performance of various hydrogen storage alloys for a long history. For instance, Iwakura [39] reported the positive effects of ball-milling as well as graphite on the electrochemical and physicochemical characteristics of $Mg_2Ni$ alloy and conducted several similar researches on the modification of Mg-base hydrogen storage alloy by graphite [40–42]. Bobet [43] also reported the improved hydriding kinetics of magnesium by milling with graphite. However, those graphite-involved researches mostly focused on the gaseous hydrogen sorption capacities or the electrochemical discharge capacities of the Mg-based alloy, and studied less on the kinetics and the mechanism. Therefore, in order to get better understanding about the mechanism and find out better solution for the modification towards the $Mg_2Ni$ alloy, it is necessary to obtain some detailed information about the kinetics.

In this work, graphite is introduced to modify the $Mg_2Ni$ alloy via mechanical milling, a set of electrochemical parameters are obtained and the modification effects as well as the possible mechanisms are discussed. The improvement in the discharge capacity, the high rate dischargeability (HRD), the electrochemical impedance spectroscopy (EIS), the linear polarization, the anode polarization and the hydrogen diffusion properties of the $Mg_2Ni$ alloy, which respectively reflect the total energy storage capacity and cycle stability, the ability of discharge at a high current density, the detailed internal resistance, the rate of charge transfer on the surface of alloy, the limited discharge current density and the rate of hydrogen diffusion in the bulk of alloy, are all investigated in detail. It is expected to provide some new information about the positive effect of graphite on the $Mg_2Ni$ alloy, especially in the aspect of kinetics and mechanism.

## Experimental

### Sample preparation

The $Mg_2Ni$ alloy was prepared from magnesium powder (99.9 wt.% in purity and <50 μm in particle size) and nickel powder (99.9 wt.% in purity and <50 μm in particle size). They were mixed in 2: 1 of Mg: Ni molar ratio by hand mixing in agate mortar for 5 min and then loaded into a stainless steel vessel (volume 70 ml) for mechanical milling. The milling was conducted under argon atmosphere at room temperature using a planetary-type ball mill at a speed of 350 r $min^{-1}$ and with the ball to powder mass ratio of 20:1. The ball milling duration was selected as 40 h by milling for 30 min in the clockwise direction then cooling for 15 min and then milling for 30 min in the reverse direction in order to prevent overheat of the vessels and obtain better homogeneity. The milling vessels were vacuumed and recharged with high purity Ar gas for three times before milling and opened every 10 h during milling procedure in order to crush the aggregation on the inside wall of the vessels. The as-prepared $Mg_2Ni$ alloy were then mixed with the same Ni powder in 2: 1 of $Mg_2Ni$: Ni mass ratio and milled for another 10 h under the same condition for the purpose of increasing amorphous phase and improving the overall performance of $Mg_2Ni$ alloys according to Chen's result [12]. It should be aware that this $Mg_2Ni$ alloy composite is not a stoichiometrically $Mg_2Ni$ alloy, however, it still can be denoted as $Mg_2Ni$ alloy without any ambiguity in this work. This $Mg_2Ni$ alloy then mixed with 10 wt.% graphite and mechanically milled for another 3 h at a comparative low speed of 200 r $min^{-1}$ to obtain $Mg_2Ni$/graphite (M/G) composite, which was used to investigate the effect of graphite on the electrochemical properties of $Mg_2Ni$ alloys. All the above mentioned operations were performed in glovebox filled with dry Ar gas in order to minimize the oxidation.

### Sample characterization

The X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Focus diffractometer, made in Germany, with Cu K$\alpha$ radiation ($\lambda = 0.154$ nm), 2θ range from 1 to 135° and the maximum operating power is 40 KV and 40 mA. The morphologies and microstructures were observed by a HITACHI S-4300 scanning electron microscopy (SEM), which offers resolution capabilities of 1.5 nm at 15 kV and 5.0 nm at 1 kV and magnification from 20 to 500,000.

All the electrodes were prepared by following procedure: 0.1 g sample powder was completely mixed with 0.4 g Ni powder and then cold-pressed into a piece of nickel foam with diameter of 10 mm under a pressure of 25 MPa. Electrochemical measurements were performed in a three-electrode

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