Short communication

The electrochemical performances of $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) hydrogen storage electrode alloys

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Abstract

Amorphous hydrogen storage alloys $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) were prepared by mechanical alloying (MA). The electrochemical performances of electrode alloys were studied by cyclic charge–discharge experiment, linear polarization and electrochemical impedance spectroscopy. The capacity retention rate C_{20th}/C_{max} of quaternary $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0.05, 0.1, 0.15$) alloys are 66.2%, 75% and 76.8%, respectively, much higher than that of $Mg_{0.9}Ti_{0.1}Ni$ (31.4%). It was demonstrated that the substitution of Pd for Ni improved the cyclic stability of MgTiNi-based electrode alloy greatly. The partial substitution of Pd for Ni also led to the increase of exchange current density I_0, which concluded that the reaction activity on the surface of alloys was effectively improved.
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1. Introduction

MgNi amorphous hydrogen storage alloy is considered as a promising candidate for the cathode material of Ni-MH batteries because of its large discharge capacity [1]. However, its cycle life is not satisfied yet now, because Mg is easily oxidized in the KOH solution and the discharge capacity declines very quickly. Many elemental substitutions on Mg and/or Ni sides have been tried to improve the cycling discharge stability of MgNi alloy [2,3]. Among these efforts, it was found that the partial substitution of Ti for Mg effectively inhibited the oxidation of Mg and prolonged the cycle life of the alloy [4–7]. On the other hand, Pd was found possessing higher electro-catalytic activity than Ni for the hydrogen evolution reaction (HER) in the electrochemical cycle [8]. It was demonstrated that Pd addition not only improved the charge–discharge activities of Mg-based electrode alloys or composites [9,10], but also enhanced the anti-corrosion properties [11,12] of MgNi-based alloys. The quaternary $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) alloys were thus designed and also prepared by MA. The effects of sub-stitution of Pd for Ni on the electrochemical performances, such as cyclic stability and charge transfer activity, were intensively studied in the present paper.

2. Experimental

$Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) alloys were prepared by MA with a ball to powder weight ratio of 30:1 under Ar atmosphere for 120 h. The structures of the alloys were characterized by X-ray diffraction (XRD, Rigaku D/max-2500, Cu Kα, 50 kV, 200 mA) and transmission electron microscopy (Philips TEM F-20 TECNAI G², 200 kV).

The electrode materials to be tested were the pressed mixture of 0.1 g alloy powder with 0.3 g electrolytic Cu powder. The NiOOH/Ni(OH)₂ electrode and Hg/HgO electrode were used as counter electrode and reference electrode, respectively. The electrolyte was 6 M KOH aqueous solution at the temperature of 303 K. Charge–discharge measurements were performed upon an automatic LAND battery test instrument. The electrodes were charged for 3 h at a current density of 300 mA g⁻¹, rested for 5 min and then discharged to −0.6 V versus Hg/HgO electrode at a current density of 100 mA g⁻¹. The linear polarization curves of the electrodes were measured on Zahner Elektrik IM6e
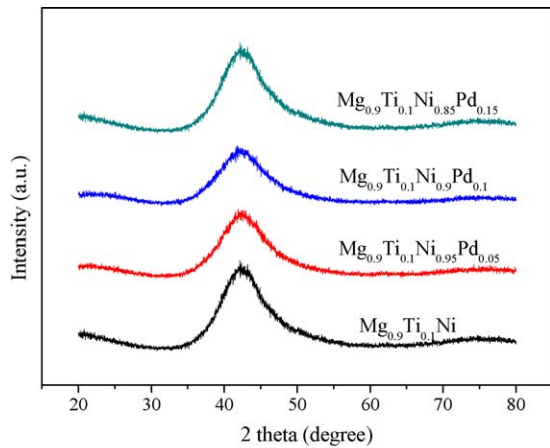
Fig. 1. XRD patterns of $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x=0$–0.15) powders after 120 h of mechanical alloying.

electrochemical workstation by scanning the electrode potential at the rate of $0.1\,mV\,s^{-1}$ from -5 to $5\,mV$ (versus open circuit potential) at the 50% depth of discharge (DOD). The electrochemical impedance spectroscopy (EIS) measurements were conducted upon the same apparatus from $5\,mHz$ to $10\,kHz$ with amplitude of $5\,mV$ versus open circuit potential at 50% depth of discharge (DOD).

3. Results and discussions

3.1. The phase structure of the alloys

Fig. 1 shows the X-ray diffraction patterns for the $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x=0$–0.15) quaternary alloys after 120 h ball milling. For each alloy, a broad Bragg peak was observed at approximately $42°$ (2θ). No secondary phase or residual starting materials were observed. It was suggested that these alloys prepared by MA were amorphous alloys. In Fig. 2, the selected area
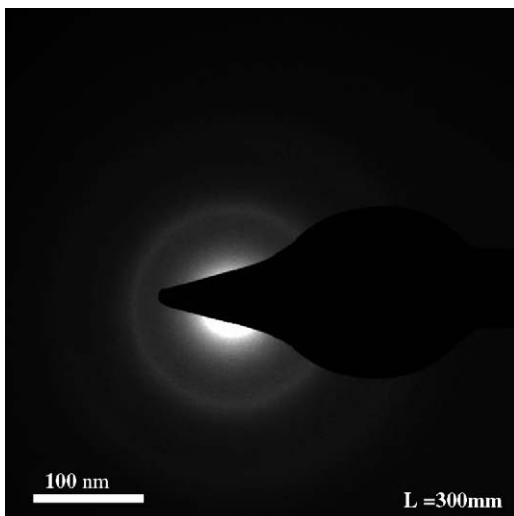

Fig. 2. The transmission electron microscopy image of $Mg_{0.9}Ti_{0.1}Ni_{0.9}Pd_{0.1}$ alloy after 120 h mechanical alloying.

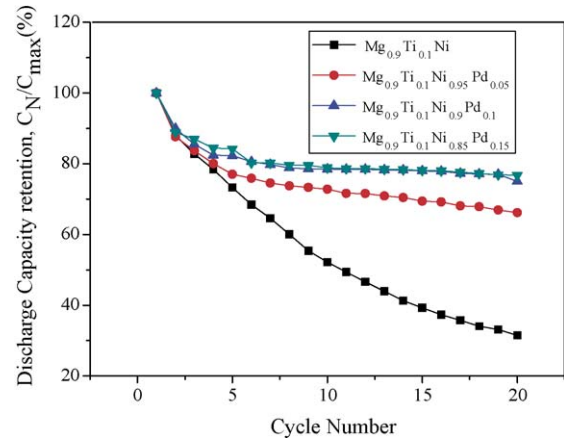Fig. 3. The discharge capacity retention curve of $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x=0$–0.15) electrode alloys at 303 K.

electron diffraction (SAED) image of $Mg_{0.9}Ti_{0.1}Ni_{0.9}Pd_{0.1}$ alloy exhibited a broad and ambiguous ring, which indicated that the long-range ordered structure of the alloy had disappeared after 120 h ball milling. The TEM image confirmed the amorphous nature of these alloys.

3.2. Discharge capacity and cyclic stability

Fig. 3 shows the discharge capacity retention of $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x=0$–0.15) electrode alloys as a function of cycle number. Table 1 gives their maximum discharge capacities, which are the initial capacities in this study. The table also shows that the discharge capacity retention rates after 20 cycles are 31.4%, 66.2%, 75% and 76.8% for $Mg_{0.9}Ti_{0.1}Ni$, $Mg_{0.9}Ti_{0.1}Ni_{0.95}Pd_{0.05}$, $Mg_{0.9}Ti_{0.1}Ni_{0.9}Pd_{0.1}$ and $Mg_{0.9}Ti_{0.1}Ni_{0.85}Pd_{0.15}$, respectively. It is obvious that, the discharge capacity retention rate of quaternary alloys is greatly improved because of the substitution of Pd for Ni. This phenomenon agreed well with those results of Pd coating on the surface of MgNi alloy [11,12], which suggested that Pd could effectively inhibit the corrosion of Mg on the surface of the alloys. In this study, Pd dissolved into the amorphous alloy thoroughly by means of mechanical alloying. No separate Pd powder was found according to the XRD patterns in Fig. 1. Therefore, the homogenously dispersed Pd in the alloy can prevent not only the outer surface but also the inner from the permeation and oxidation of KOH solution, thus inhibited the corrosion of the alloys and enhanced its cyclic stability greatly.

Table 1
The discharge capacities and their retention rates of the $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x=0$–0.15) electrode alloys, C_{max}, C_{10} and C_{20} denote the maximum discharge capacity, the discharge capacity after 10th cycle and 20th cycle, respectively

x	C_{max} (mAh g^{-1})	C_{10}/C_{max} (%)	C_{20}/C_{max} (%)
0	455	55.4	31.4
0.05	290.3	73.3	66.2
0.10	239.1	78.6	75
0.15	184.2	79.5	76.8

Table 2
Electrochemical kinetic parameters of the $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) electrode alloys

x	Charge transfer reaction resistance, R_{ct} (mΩ)	Polarization resistance, R_p (mΩ)	Exchange current density, I_0 (mA g^{-1})
0	1135	1480	176
0.05	498	853	303
0.10	742	1075	231
0.15	907	1380	185

3.3. Reaction activity on the surface of the alloys

Fig. 4 illustrates the electrochemical impedance spectroscopy of $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) electrode alloys at 50% DOD and 303 K. All the EIS spectra of these electrodes consisted of a smaller semicircle in the high-frequency region and a larger semicircle in the low-frequency region followed by a straight line. These spectra were characterized by an equivalent circuit as that proposed by Kuriyama et al. (also in Fig. 4) [13]. The circuit elements were evaluated by nonlinear least squares fit using the simulation software (see Table 2). It is obvious that, with increase of Pd content, the charge transfer reaction resistance R_{ct} related to the low-frequency region of EIS spectra decreased significantly from 1135 mΩ ($x = 0$) to 498 mΩ ($x = 0.05$). Thereafter, R_{ct} rose up with further increase of x. For Mg-based electrode alloys, the reaction activity was usually determined by B-site elements with high electro catalytic activities, for instance, Ni or Pd, etc. [1,9]. In this case, Ni and Pd synergistically determined the charge transfer process in the double layer of surface. When Pd amount is lower than 0.05, the effect of Pd addition on R_{ct} exhibited significantly. However, with the content increasing above 0.05, the variation of Ni content dominated the reaction activities. It is found that with the gradual decrease of Ni amount in the alloy, the reaction activity turned to decline and the charge transfer resistance R_{ct} raised gradually. In principle, the charge transfer reaction resistances of the substituted $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0.05$–0.15) quaternary electrode alloys were lower than that of $Mg_{0.9}Ti_{0.1}Ni$.

Fig. 5 shows the linear polarization curves of the $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) electrode alloys at 50% DOD and 303 K. The slope of the linear curve is the polarization resistance R_p of the corresponding electrode alloy (listed in Table 2). The variation of R_p with Pd content x was consistent with that

Fig. 5. Linear polarization curves of the $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) electrode alloys at 50% DOD and 303 K.

of charge transfer resistance R_{ct}. It is noted that the R_p values decreased first from 1480 mΩ ($x = 0$) to 853 mΩ ($x = 0.05$) and then increased to 1380 mΩ ($x = 0.15$). It is well known that the exchange current density I_0 could be calculated by following equation [14]:

$$I_0 = \frac{RT}{FR_p} \tag{1}$$

in which R, T, F denotes the gas constant, absolute temperature and Faraday constant, respectively. In this equation, the exchange current density I_0 were proportional inversely with R_p, upon which the reaction activity over the alloy's surface was expressed directly. From Table 2, it can be seen that the exchange current density of electrode alloys increased first from 176 mA g^{-1} ($x = 0$) to 303 mA g^{-1} ($x = 0.05$) and then decreased to 185 mA g^{-1} ($x = 0.15$) with the increase of Pd content. When x increased from 0 to 0.05, the I_0 values of the electrode alloys increased accordingly. While x increased further from 0.05 to 0.15, the I_0 values of the electrode alloys decreased. It was demonstrated that only within the composition range from $x = 0$ to 0.05, Pd can play a positive role on the charge transfer or current exchange over the particle surface of the quaternary Mg–Ti–Ni-based alloys. Excessive Pd addition might result in the decline of reaction activity in this study.

4. Conclusions

The cyclic stability of the electrode alloys was significantly improved with increase of Pd addition because of the corrosion inhibiting roles of Pd for the electrode alloys. Partial substitution of Pd for Ni can effectively enhance the electrochemical activity
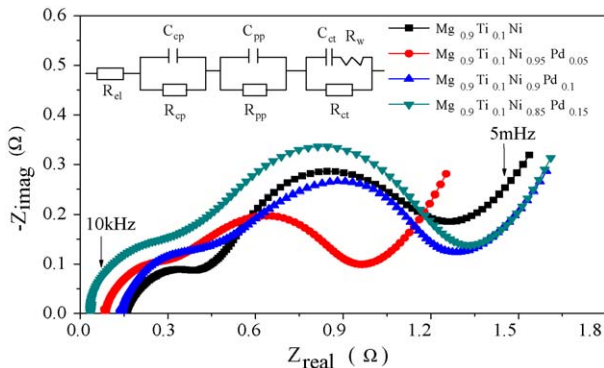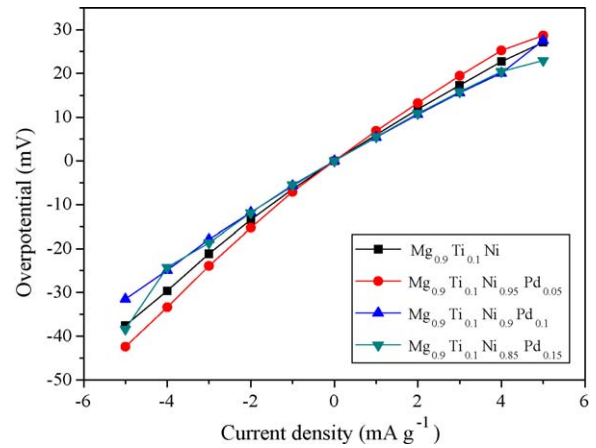

Fig. 4. The electrochemical impedance spectroscopy (EIS) of the $Mg_{0.9}Ti_{0.1}Ni_{1-x}Pd_x$ ($x = 0$–0.15) electrode alloys at 50% DOD and 303 K.

of electrode alloys. With the increase of Pd amount from 0 to 0.05, the charge transfer resistance R_{ct} on the alloy's surface decreased significantly.

Acknowledgements

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