Electrochemical Performance of Nanocrystalline and Amorphous Mg–Nd–Ni–Cu-Based Mg₂Ni-type Alloy Electrodes Used in Ni–MH Batteries

Yanghuan Zhang · Haitao Wang · Xiaoping Dong · Wengang Bu · Zeming Yuan · Guofang Zhang

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Abstract Nanocrystalline and amorphous Mg₂Ni-type (Mg₂₄Ni₁₀Cu₂)_{100–x}Nd_x ($x = 0, 5, 10, 15, 20$) alloys were prepared by melt-spinning technology. The structures of as-cast and spun alloys were characterised by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Electrochemical performance of the alloy electrodes was measured using an automatic galvanostatic system. The electrochemical impedance spectra and Tafel polarisation curves of the alloy electrodes were plotted using an electrochemical work station. The hydrogen diffusion coefficients were calculated using the potential step method. Results indicate that all the as-cast alloys present a multiphase structure with Mg₂Ni type as the major phase with Mg₆Ni, Nd₅Mg₄₁ and NdNi as secondary phases. The secondary phases increased with the increasing Nd content. The as-spun Nd-free alloy exhibited nanocrystalline structure, whereas the as-spun Nd-doped alloys exhibited nanocrystalline and amorphous structures. These results suggest that adding Nd facilitates glass formation of Mg₂Ni-type alloys. Melt spinning and Nd addition improved alloy electrochemical performance, which includes discharge potential characteristics, discharge capacity, electrochemical cycle stability and high-rate discharge ability.

KEY WORDS: Mg₂Ni-type alloy; Nd addition; Melt spinning; Structure; Electrochemical performance

1 Introduction

Metal hydride systems are considered more accurate, efficient and safe compared with currently available hydrogen storages, and these systems are the frontiers of technology

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Y. Zhang (✉) · H. Wang · G. Zhang
Key Laboratory of Integrated Exploitation of Baiyun Obo
Multi-Metal Resources, Inner Mongolia University of Science
and Technology, Baotou 014010, China
e-mail: zhangyh59@sina.com

Y. Zhang · W. Bu · Z. Yuan
Department of Functional Material Research, Central Iron
and Steel Research Institute, Beijing 100081, China

X. Dong
College of Quality and Technical Supervision,
Hebei University, Baoding 071002, China

[1]. The Ni/MH batteries are advantageous because of their high-energy density, excellent power density and long life cycle. These properties make the Ni/MH batteries as the leading battery power source for hybrid electric vehicles [2]. The development of high-performance hydrogen storage alloys as the negative electrode of Ni–MH batteries has been extensively investigated. Consequently, a series of metal hydride electrode materials, such as rare earth (RE)-based AB₅-type, AB₂-type Laves phase, V-based solid solution and Mg-based alloys, have been fabricated. However, these batteries should be improved further to enable higher electrochemical hydrogen storage capacity. Although China and Japan have large-scale production of RE-based AB₅-type alloys [3, 4], the application of these alloys is limited by their low discharge capacity (approximately 330 mAh/g). Thus, new electrode materials that exhibit superior performance, particularly higher discharge capacity and electrochemical hydrogen storage kinetics, should be developed. Mg₂Ni-type alloys are considered

one of the most promising hydrogen storage materials that can be used in hydrogen fuel cell vehicles or negative electrodes in Ni-MH batteries [5] because of their high gaseous hydrogen absorption capacity (3.6 wt%) for Mg_2NiH_4 and large gravimetric capacity (approximately 1,000 mAh/g) [6, 7]. However, Mg_2Ni -type alloys also have drawbacks such as relatively high H-desorption temperature, slow hydriding/dehydriding kinetics and extremely poor electrochemical cycle stability, which impede the practical application of Mg_2Ni -type alloys. Despite several challenges, numerous studies have been performed to further develop alloys with enhanced properties.

The structures of Mg and Mg-based alloys are sensitive to hydriding/dehydriding kinetics [8]. Hydrogen storage properties of these alloys are thermodynamically and kinetically affected by nanometre-scale structures. Teresiak *et al.* [9] showed that amorphous and/or nanocrystalline Mg–Ni-based alloys can electrochemically absorb and desorb large amounts of hydrogen even at room temperature. Capacity degradation has been associated with irreversible alloy oxidation caused by an electrolyte (KOH), which leads to the formation of an $\text{Mg}(\text{OH})_2$ layer on alloy particle surfaces [10, 11]. Hence, improving cycle stability by increasing alloy corrosion resistance poses a serious challenge. Adding RE (RE = La, Ce, or Y) to Mg–Ni or Mg–Cu alloys facilitates glass formation, thereby increasing corrosion resistance and improving cycle stability [12]. High-energy ball milling (HEBM) and melt spinning are effective in producing amorphous and/or nanocrystalline structures. However, milled Mg and Mg-based alloys exhibit poor cycle stability because their metastable structures are destroyed by multiple hydrogen absorbing–desorbing cycles [13]. By contrast, microstructures created by melt spinning displays higher stability during hydrogen absorbing–desorbing cycles compared with microstructures formed via HEBM [14]. Nanocrystalline and amorphous Mg-based alloys prepared by melt spinning exhibit excellent hydriding characteristics similar to the alloys produced via HEBM [15].

Previous studies have shown that substituting Ni with *M* (*M* = Co, Cu and Mn) and Mg with La remarkably improve the electrochemical and gaseous hydrogen storage performance of Mg_2Ni -type alloys [16, 17]. Therefore, adding Cu and Nd and using an appropriate melt-spinning technique may improve the electrochemical hydrogen storage performance of Mg_2Ni -type alloys. Thus, the effects of Nd content and spinning rate on the structure and electrochemical hydrogen storage performance of $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) electrode alloys were investigated.

2 Experimental

Experimental alloys with nominal compositions of $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0, 5, 10, 15, 20$) were prepared using a vacuum-induction furnace. The furnace was operated in a helium atmosphere at a pressure of 0.04 MPa to prevent Mg volatilisation. Alloys were denoted according to the Nd contents, namely, Nd₀, Nd₅, Nd₁₀, Nd₁₅ and Nd₂₀. Part of the as-cast alloys was remelted, held for 10 min at 1,450 °C, and spun by melt spinning with the use of a rotating copper roller that was cooled with water. The employed spinning rates were 10, 20, 30 and 40 m/s, which were approximately expressed by the linear velocity of the copper roller. For comparison, the spinning rate of as-cast alloy was defined as 0 m/s.

The phase structures of the as-cast and spun alloys were determined by XRD (D/max/2400). The experimental parameters employed in the method were 160 mA, 40 kV and 10°/min. XRD was performed using Cu K_α radiation filtered by graphite. A Philips SEM (QUANTA 400) linked with an energy dispersive spectrometer (EDS) was used for the morphological characterisation and chemical composition analysis of the as-cast alloys. Thin-film samples of as-spun alloys prepared by ion etching were observed using a high-resolution transmission electron microscope (HRTEM) (JEM-2100F, operated at 200 kV), and their crystalline states were confirmed by selected area electron diffraction pattern (SAEDP).

Alloys were mechanically milled to produce fine powder with a diameter of 35 μm. The alloy powder was then mixed with carbonyl nickel powder in a weight ratio of 1:4. The mixture was cold pressed under a pressure of 35 MPa to produce a round electrode pellet with a diameter of 15 mm and a total weight of 1 g. The electrochemical performance of the electrode produce was measured at 30 °C by a tri-electrode open cell. This open cell consisted of a working electrode (metal hydride electrode), a sintered $E_{\text{vs.}(\text{NiOOH}/\text{Ni}(\text{OH})_2)}/V$ counter electrode and an $E_{\text{vs.}(\text{Hg}/\text{HgO})}/V$ reference electrode that were immersed in 6 mol/L KOH electrolyte. Discharge voltage was defined as the applied or output potential difference between a negative and reference electrodes. In every cycle, an alloy electrode was first charged with a constant current density, followed by a 15-min rest. The electrode was then discharged at the same current density to a cut-off voltage of −500 mV.

The EIS and Tafel polarisation curves of the alloys were measured at 30 °C using an electrochemical workstation (PARSTAT 2273) to determine the electrochemical kinetics of the alloy electrodes. Several electrochemical charging and discharging cycles were performed to activate the materials. This procedure was conducted prior to the measurement of the impedance

Fig. 1 SEM images and typical EDS results of as-cast $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys: **a** Nd_0 ; **b** Nd_{10} ; **c** Nd_{20}

and polarisation curves. The fresh electrodes were fully charged. The electrodes were then allowed to rest for 2 h, until the open circuit potential was stabilised. The EIS of the electrodes was measured at 50% depth of discharge (DOD). Parameters employed were as follows: frequency range from 10 kHz to 5 mHz; signal amplitude of 5 mV for potentiostatic or galvanostatic measurements and 60 points per decade of frequencies. Tafel polarisation curves were measured in the potential range from -1.2 to $+1.0$ V (vs. Hg/HgO) with a scan rate of 5 mV/s. To test potentiostatic discharge, fully charged test electrodes were discharged at 500 mV potential steps for 5,000 s on an electrochemical workstation (PAR-STAT 2273) with the use of electrochemistry corrosion software (CorrWare).

3 Results and Discussion

3.1 Microstructure Characteristics

SEM images and EDS results of the as-cast $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys are illustrated in Fig. 1. The as-cast Nd_0 alloy showed a typical dendritic structure. Morphologies of the as-cast alloys changed with Nd addition. SEM and EDS analyses showed that all the Nd-doped alloys exhibited a multiphase structure, including Mg_2Ni , $\text{Nd}_5\text{Mg}_{41}$ and NdNi phases.

Phase components and structural characteristics of the as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys were analysed by XRD, as shown in Fig. 2. All as-cast alloys exhibited multiphase structures. Nd

Fig. 2 XRD patterns of as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys: **a** as-cast; **b** as-spun (40 m/s); **c** Nd_{10} alloys

addition generated NdNi and $\text{Nd}_5\text{Mg}_{41}$ secondary phases along with the main phase Mg_2Ni , the amount of which increased with the increasing Nd content. The as-spun Nd_0 alloy exhibited extremely sharp diffraction peaks, suggesting its crystalline structure with a grain size of approximately 20 nm. The grain size was calculated using Scherrer's equation based on the FWHM values of the major diffraction peak (203) in Fig. 2b. The Nd-doped alloys displayed completely different diffraction peaks from that of the Nd_0 alloy even if they were spun at the same spinning rate. Extremely broad and flat diffraction peaks indicate that the as-spun Nd-doped alloys had an amorphous structure, which can be attributed to Nd addition that facilitated glass formation in Mg_2Ni -type alloys. The broad and diffuse diffraction peaks of the as-spun (10 m/s) Nd_{10} alloy exhibited amorphous and nanocrystalline structures (Fig. 2c). Increasing the spinning rate resulted in broader and flatter diffraction peaks for the Nd_{10} alloy. This result implies the increasing amounts of the amorphous phase, which was confirmed by the TEM images (Fig. 3). The as-spun Nd_0 alloy was extremely disordered and nanostructured. Some crystal defects, such as subgrains and grain boundaries, were observed. ED patterns appeared as sharp multi-halos that corresponded to nanocrystalline structure. The as-spun Nd_{10} alloy exhibited a nanocrystalline structure embedded in an amorphous matrix, and its electron diffraction patterns consisted of a broad and dull halo, indicating the existence of an amorphous structure. This result was in good agreement with the XRD results as shown in Fig. 2.

3.2 Electrochemical Performances

3.2.1 Discharge Potential and Discharge Capacity

The variations in discharge potential of the as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys as a function of discharge capacity at a current density of 40 mAh/g are shown in Fig. 4. The discharge potentials of the alloy electrodes decreased during the discharging process, which indicates that the output power of the battery was not constant. The discharge potential characteristic, which is directly related to output power stability, is an important characteristic of alloy electrodes. This parameter is characterised by a potential plateau of the discharge curve of the alloy. Longer and more horizontal discharge potential plateau signifies better discharge potential characteristics of the alloy. Both melt spinning and Nd addition remarkably improved the discharge potential characteristics of the alloys, i.e. enhanced discharge potential and lengthened discharge plateau (Fig. 4). Melt spinning and Nd addition enabled the discharge capacity of alloys to increase remarkably. The relationship between discharge capacities of alloys and Nd content is described in Fig. 5. Increasing alloy discharge capacities were observed with the increasing Nd content (up to $x = 10$). However, excessive amounts of Nd ($x > 10$) resulted in reduced discharge capacity. Nd-doped alloys exhibited higher discharge capacity than Nd-free alloy, suggesting that Nd addition positively contributes to the discharge capacity of the alloy. When Nd content was $x = 10$, the as-cast and spun alloys yielded maximum discharge capacity, namely, 86.4, 200.5,

Fig. 3 HRTEM images and SAED patterns of as-spun Nd₀ and Nd₁₀ alloys: **a** Nd₀, 10 m/s; **b** Nd₀, 40 m/s; **c** Nd₁₀, 10 m/s; **d** Nd₁₀, 40 m/s

266.3, 402.5 and 452.8 mAh/g, corresponding to the spinning rates of 0, 10, 20, 30 and 40 m/s, respectively. At fixed Nd content, the discharge capacity of the alloy markedly increased with the increasing spinning rate. For instance, when the spinning rate was increased from 0 to 40 m/s, discharge capacity increased from 42.5 to 100.6 mAh/g for the Nd₀ alloy and from 86.4 to 402.5 mAh/g for the Nd₁₀ alloy. The increase in discharge capacity, which was caused by melt spinning, was more pronounced in the Nd-doped alloys than that in an Nd-free alloy. The positive effect of Nd addition to the discharge capacity of an alloy was caused by several reasons. First, glass formation, which was facilitated by Nd addition, enabled the Mg–Ni-based alloy to possess superior discharge property because of the adequate proportion of amorphous and nanocrystalline structures in the alloy [18]. Second, the secondary phases Mg₆Ni and NdNi played a catalytic role in activating the Mg₂Ni phase to reversibly absorb/desorb hydrogen in an alkaline electrolyte.

Excessive amounts of Nd ($x > 10$) caused undesirable discharge capacity reduction, as shown by the sharp decrease in the Mg₂Ni phase. Nanocrystalline and amorphous structures that were formed during melt spinning improved discharge capacity. Nanocrystalline and amorphous structures had larger grain boundaries, and they possessed maximum hydrogen concentration distribution [19]. These structures promoted the hydriding/dehydriding ability of Mg₂Ni-type alloys, as reported by Kumar *et al.* [20] and Teresiak *et al.* [9].

3.2.2 Cycle Stability

Cycle stability is one of the major parameters that are used to evaluate the applicability of an alloy as a negative electrode material. This parameter is characterised by the capacity retaining rate (S_n), which is defined as $S_n = C_n / C_{\max} \times 100\%$, where $C_{\max}$ is the maximum discharge capacity and C_n is the discharge capacity at the n th

Fig. 4 Discharge potential curves of as-spun (40 m/s) $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloys **a**; as-cast and as-spun (10–40 m/s) Nd_{10} alloy **b**

Fig. 5 Evolution of the discharge capacity of as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloys with varying Nd contents

charge–discharge cycle. Larger S_n values result in better alloy cycle stability. The variations in the S_n values of as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloys as a function of cycle number are illustrated in Fig. 6; this result shows the degradation process of the discharge capacity. Qualitative description of the degradation rate of the discharge capacity during charging–discharging cycles can be observed from the slope of the curves, i.e. smaller curve slopes imply better alloy life cycle. Both melt spinning and Nd addition reduced the slopes of the curve, indicating that Nd addition and melt spinning positively contributed to the cycle stability of the alloy. The relationships between the S_{20} values of as-spun (40 m/s) alloys and Nd content are shown in Fig. 6a, whereas the relationship between the S_{20} values of an Nd_{10} alloy and spinning rate is illustrated in Fig. 6b. The S_{20} value of as-spun (40 m/s) alloy increased with the increasing Nd content (up to $x = 10$). However, further increase in Nd content resulted in decreased S_{20} values. Increasing Nd

content from $x = 0$ to $x = 20$ caused the S_{20} value to increase from 41.1% ($x = 0$) to 89.7% ($x = 10$) and then later declined to 83.8% ($x = 20$). Moreover, increasing the spinning rate from 0 to 40 m/s increased the S_{20} value of the Nd_{10} alloy from 53.2 to 89.7%. The amelioration of the cycle stability of the alloy caused by Nd addition and melt spinning may be explained as follows. Discharge capacity degradation of the Mg_2Ni alloy during charge–discharge cycling was due to the formation and thickening of the $\text{Mg}(\text{OH})_2$ surface layer. This condition prevented the hydrogen atoms from diffusing in or out of the alkaline solution [21]. Moreover, the hydrogen storage material underwent volume change during charge–discharge process. This condition caused the alloy to crack and pulverise, which then facilitated oxidation on the material surface (Fig. 7). Alloy particles with a size of approximately 30 μm and aggregated ultrafine Ni powders were observed. Several cracks on the alloy particle surfaces were also observed after electrochemical cycle, and a rough and gossypine layer covered the alloy particles. XRD result indicates that the layer formed was $\text{Mg}(\text{OH})_2$, as illustrated in Fig. 7d. However, fewer cracks were found on the Nd_{10} alloy particle surface after cycling than that in the Nd_0 . This result suggests that Nd addition enhanced the anti-pulverisation ability of the alloy. In addition, the thickness of the covering layer on the Nd_{10} alloy particle surface was lesser than that in the Nd_0 alloy, which indicates that Nd addition improved the anti-corrosion and anti-oxidation ability of the Mg_2Ni alloy. A similar result was reported by Teresiak et al. [9]. The positive effect of Nd addition was attributed to two aspects. First, the addition of RE (La, Nd, Sm, Y) improved the cell volume of the Mg_2Ni alloy [17], which in turn decreased the expansion/contraction ratios during hydrogen absorption/desorption so as to enhance the anti-pulverisation capability. Second, glass formation, which

Fig. 6 Evolution of the S_n values of as-spun (40 m/s) $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloys **a**; as-cast and as-spun (10–40 m/s) Nd_{10} alloy **b**

Fig. 7 SEM images and XRD pattern of as-spun (40 m/s) Nd_0 and Nd_{10} alloys before and after electrochemical test: **a** Nd_0 alloy before electrochemical test; **b** Nd_0 alloy after electrochemical test; **c** Nd_{10} alloy after electrochemical test; **d** XRD pattern of the Nd_0 alloy after electrochemical test

was facilitated by Nd addition, formed an amorphous phase that improved not only the anti-pulverisation ability but also the anti-corrosion and anti-oxidation abilities of the alloy electrode in a corrosive electrolyte [9, 16]. These phenomena explained why Nd-doped alloys exhibited higher cycle stability than Nd-free alloy.

3.2.3 HRD and Electrochemical Kinetics

Electrochemical hydrogen storage kinetics is regarded to be equally important as discharge capacity and cycle stability. This parameter is symbolised by HRD, which is defined as $\text{HRD} = C_{i, \max} / C_{40, \max} \times 100\%$, where $C_{i, \max}$

Fig. 8 Evolution of the HRDs of of as-spun (40 m/s) $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys **a**; as-cast and as-spun (10–40 m/s) Nd_{10} alloy **b**

and $C_{40, \max}$ are the maximum discharge capacities of the alloy electrode that was charged and discharged at current densities of i and 40 mA/g, respectively. Variations in HRD values of as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys as a function of discharge current density are illustrated in Fig. 8. Melt spinning and Nd addition affected the HRD of the alloy. The relationship between the HRD ($i = 200$ mA/g) values of the as-spun (40 m/s) alloys and the Nd content is shown in Fig. 8a, whilst the relationship between the HRD values of the Nd_{10} alloy and the spinning rate is illustrated in Fig. 8b. Increasing Nd content from $x = 0$ to $x = 20$ initially increased the HRD value of as-spun (40 m/s) alloy from 57.3% ($x = 0$) to 65.9% ($x = 10$) and then decreased to 59.8% ($x = 20$). Although the addition of excess amounts of Nd ($x > 10$) caused undesirable reduction in the HRD values, the HRD values of Nd-doped alloys were higher than that in Nd-free alloy. This observation showed that Nd addition positively contributed to the electrochemical kinetics of the alloy. The HRD value of an Nd_{10} alloy initially increased and then decreased with the increasing spinning rate.

The high-rate discharge ability of a metal hydride electrode is primarily dominated by the charge-transfer rate on an alloy electrode surface and hydrogen diffusion capability in an alloy bulk [22]. Thus, investigating the hydrogen diffusion coefficient and charge-transfer rate of alloy electrodes is important. Diffusion coefficients of hydrogen atoms can be obtained by measuring the semilogarithmic curves of anodic current versus the working duration of an alloy (Fig. 9). According to the model established by White and coworkers [23], the diffusion coefficient of hydrogen atoms in an alloy bulk can be calculated using the slope of the linear region of corresponding plots, as shown in the following formulae:

$$\lg i = \lg \left(\pm \frac{6FD}{da^2} (C_0 - C_s) \right) - \frac{\pi^2 Dt}{2.303a^2}, \quad (1)$$

$$D = \frac{2.303a^2}{\pi^2} \frac{d \lg i}{dt}, \quad (2)$$

where i is the diffusion current density (A/g), F the Faraday constant, D the hydrogen diffusion coefficient (cm^2/s), C_0 the initial hydrogen concentration in the alloy bulk (mol/cm^3), C_s the hydrogen concentration on the alloy particle surface (mol/cm^3), $a = 1.4 \times 10^{-3}$ cm is the alloy particle radius, d the density of the hydrogen storage alloy (g/cm^3) and t is the discharge time (s). The hydrogen diffusion coefficient D represents the hydrogen diffusion rate in the bulk. A larger D leads to faster diffusion of hydrogen atoms in the alloy, which enhances the electrochemical kinetics of alloy electrodes [24]. The variations in hydrogen diffusion coefficient D which was calculated by Eq. (2) as a function of Nd content and spinning rate are illustrated in Fig. 9. The D values of as-cast and spun alloys increased with the increasing Nd content and spinning rate.

Tafel polarisation curves of as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0-20$) alloys were measured to determine the electrochemical hydrogen absorption/desorption kinetics, as shown in Fig. 10. A point of inflexion was observed in each anodic polarisation curve, implying the presence of a critical value, which was denoted as the limiting current density (I_{lim}). The result indicates that oxidation occurred on the alloy electrode surface and the generated oxidative product prevented further penetration of hydrogen atoms [25]. Therefore, I_{lim} may be viewed as a critical current density of passivation, which is mainly determined by the solid state diffusion of hydrogen in a metal hydride electrode [26]. The I_{lim} values of the alloys vary with Nd content and spinning rate, which are presented in Fig. 10. I_{lim} values of the alloys

Fig. 9 Semilogarithmic curves of anodic current versus time responses of as-spun (40 m/s) $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloys **a**; as-cast and as-spun (10–40 m/s) Nd_{10} alloy **b**

Fig. 10 Tafel polarisation curves at 50% DOD of as-spun (40 m/s) $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloys **a**; as-cast and as-spun (10–40 m/s) Nd_{10} alloy **b**

continuously increase with the increasing Nd content and spinning rate.

The charge-transfer ability on an alloy electrode surface may be qualitatively evaluated using its EIS. The EIS of as-cast and spun $(\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2)_{100-x}\text{Nd}_x$ ($x = 0\text{--}20$) alloy electrodes are shown in Fig. 11, in which enlarged semicircles in high-frequency domains are presented. The EIS contained two distorted capacitive loops in high and middle frequencies and a line in low frequency, which represented the electrochemical processes. These processes were elucidated and modelled by Kuriyama *et al.* [27]. The smaller semicircle in the high-frequency region corresponds to the contact resistance between the alloy powder and the conductive material. The large semicircle in the middle-frequency region refers to the charge-transfer resistance on an alloy surface. The straight line in the low-frequency region refers to the atomic hydrogen diffusion in the alloy. The larger the radius of the semicircle in the middle-frequency region, the higher the charge-transfer resistance of the alloy electrode. The radii of the large semicircles of the alloy

electrodes in the middle-frequency region expanded with the increasing Nd content and spinning rate. The straight lines on the EIS of the as-spun (40 m/s) Nd_{20} alloy and the as-spun (>30 m/s) Nd_{10} alloy nearly disappeared, suggesting that Nd addition and melt spinning remarkably impaired the charge-transfer ability on the alloy electrode surface.

Hydrogen diffusion is dominated by the strength of metal–hydrogen interaction and alloy structure [28]. Cui *et al.* [29] reported that an increase in lattice constants and cell volume caused a decrease in the diffusion activation energy of hydrogen atoms, which enhanced hydrogen diffusion. In addition, diffusion ability of hydrogen atoms is very sensitive to grain size [30]. A crystalline material, when melt spun, becomes partially disordered and its structure changes to nanocrystalline with several new crystallites and grain boundaries (Fig. 3). Consequently, crystal defects such as dislocations, stacking faults and grain boundaries are introduced and may aid hydrogen diffusion in materials by providing many sites with low

Fig. 11 Electrochemical impedance spectra of as-cast and spun ($\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2$) $_{100-x}\text{Nd}_x$ ($x = 0$ –20) alloys at 50% DOD: **a** as-spun (40 m/s); **b** Nd_{10} alloys

diffuse activation energy. Experimental results indicate that Nd addition and melt spinning negatively affected the charge-transfer, which were attributed to the structural change that originated from Nd addition and melt spinning. Increased cell volume caused by Nd addition and the presence of ultra-refined grains by melt spinning enhanced the anti-pulverisation ability of the alloy during electrochemical cycling. This condition indicates that fewer fresh alloy surfaces were formed, which impaired the charge-transfer ability. Investigation of the electrochemical kinetics showed that Nd addition and melt spinning enhanced hydrogen atom diffusion in the alloy but impaired charge-transfer ability. Hence, the beneficial and harmful impacts incurred by Nd addition and melt spinning led to the maximum HRD value of the alloy with varying Nd contents and spinning rates.

4 Conclusions

The as-spun Nd-free alloy exhibited a nanocrystalline structure, whereas the as-spun Nd-doped alloys showed an amorphous structure. This result confirms that Nd addition facilitates the glass formation in Mg_2Ni alloys. Both Nd addition and melt spinning positively contributed to the electrochemical performance of alloys, including discharge capacity, potential characteristic and cycle stability. HRD values of the alloy electrodes initially increased and then decreased with varying Nd contents and spinning rates. This phenomenon was due to the enhanced hydrogen atom diffusion and impaired charge-transfer rate caused by Nd addition and melt spinning rate. Furthermore, Nd addition improved the anti-corrosion and anti-pulverisation abilities. These improved abilities caused the enhanced cycle stability of Mg_2Ni -type alloys.

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