Study on hydrogen diffusion behavior in MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode by chronoamperometry[①]

YUAN Xian-xia(原鲜霞) , XU Nai-xin(徐乃欣)

(Shanghai Institute of Metallurgy, Chinese Academy of Sciences,
Shanghai 200050, P. R. China)

[Abstract] Hydrogen diffusion coefficients in MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode as a function of state of charge (SOC) or temperature were determined by chronoamperometry. It is found that hydrogen diffusion coefficient decreases with the increase of SOC or the decrease of temperature. The activation energy for hydrogen diffusion in the alloy electrode with 50% SOC is evaluated to be 19. 9 kJ/ mol.

[Key words] hydrogen storage alloy electrode; hydrogen diffusion coefficient, chronoamperometry

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1　INTRODUCTION

Nickel-metal hydride (Ni/ MH) batteries have been developed to meet the demands for a power source with high energy density, excellent high-rate capability, long cycle life and good environmental compatibility[1, 2], and extensive researches have been done on them[3~ 5]. The performance of the negative electrode of Ni/ MH battery is determined not only by the kinetics of the process occurring at the alloy/ electrolyte interface, but also by the hydrogen diffusion behavior within the bulk of the alloy which is believed to play an important role in hydriding / dehydriding process of the hydrogen storage alloy electrode[6]. The hydrogen diffusion coefficient is a crucial parameter to describe the diffusion behavior of hydrogen atom in hydrogen storage alloy electrode, and the larger the diffusion coefficient, the faster the hydrogen diffusion and the better the electrode performance[7].

In the present research, AB$_5$-type hydrogen storage alloy MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ was employed and the hydrogen diffusion coefficient in its electrode was determined by chronoamperometry as a function of state of charge and temperature.

2　EXPERIMENTAL

The MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy was obtained from component metals with the purity of at least 99. 9% (mass fraction) in vacuum medium frequency induction furnace. Ml is denoted as lanthanum-rich mischmetal, which is composed of 61. 11% La, 27. 16% Ce, 3. 09% Pr and 8. 64% Nd (mass fraction). To assure the homogeneity of the alloy, the ingot was turned over and remelted for five times. Then, the ingot was crushed and ground mechanically followed by capturing particles with two sequential sieves, and the average particle diameter of the resulting powders was measured by Malvern particle analyzer (Mastersizer 2000) to be 125. 2 μm.

The hydrogen storage alloy electrodes were prepared by mixing the alloy powder and nickel powder (from Inco company, Canada) in a mass ratio of 1: 4 followed by pressing at room temperature onto both sides of a nickel foam under pressure of 1. 8 × 10^8 Pa for 1min. The resulted pellet had a diameter of 15 mm and a thickness of 1. 68 mm, and the mass of it was 1. 5 g.

Electrochemical measurement of the hydrogen storage alloy electrodes was performed in a glass cell with three compartments (EG& G Princeton Applied Research Potentiostat/ Galvanostat Model 273A driven by the software of M 270). The hydrogen storage alloy electrode served as working electrode, and a nickel hydroxide electrode with an excessive capacity was employed as the counter electrode, a Hg/ HgO electrode (in 6 mol/ L KOH) was selected as the reference electrode and 6 mol/ L KOH solution as the electrolyte.

The activated hydrogen storage alloy electrode was charged at 60 mA/ g (based on the amount of alloy powder) for 7. 5 h. And after a rest of 10 min, it was discharged at 60 mA/ g for a certain period of time to reach a specified SOC (defined by Eqn. (1)) at room temperature. After the open-circuit potential got stabilized (i. e., the change of the potential was less than 1 mV in 1 h), the potential of the working electrode was stepped instantaneously by a specified amplitude and the time dependence of current response was recorded.

$$SOC = \left| 1 - \frac{I_d t_d}{Q} \right| \times 100\% \qquad (1)$$

where Q is the capacity of activated MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode, I_d and t_d are discharge current and discharge time respectively.

For the experiments at various temperatures, the electrodes were initially charged at 60 mA/g for 7.5 h and discharged at the same current to 50% SOC at ambient temperature. After a rest at a corresponding temperature for the open-circuit potential to get stabilized, the potentials of the electrodes were stepped at the same temperature and the time dependence of current responses were recorded.

3   RESULTS AND DISCUSSION

3.1   Selection of potential step amplitude

Various potential step amplitudes were used in chronoamperometry to measure hydrogen diffusion coefficient in hydrogen storage alloy electrode. Miyamura[8], GENG[9], CAI[10], Imakura[11] and Ura[12] used + 2 mV, + 10~ + 50 mV, + 100 mV, + 200 mV and + 900 mV respectively as the potential step amplitude for determining hydrogen diffusion coefficient in AB$_5$-type hydrogen storage alloy electrode. LI et al[13] emphasized that it was of great importance to select a proper potential step amplitude, and an improper step amplitude might introduce chemical reactions other than the oxidation of hydrogen or cause the responding current to decrease rapidly to the noise level. So, the effect of potential step amplitude on the responding current was studied in this work in order to select a proper potential step amplitude.

The chronoamperometric curves of fully discharged (0% SOC) MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with various potential step amplitudes are shown in Fig. 1. It can be seen that the discharge current decreases rapidly to the noise level when the step amplitude is low (such as + 10 mV or + 20 mV). The responding current is almost the
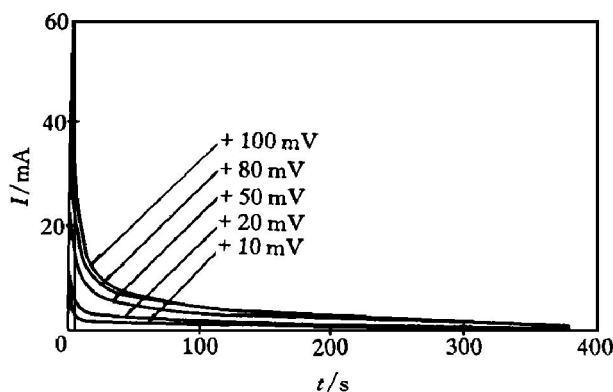
Fig. 1   Chronoamperometric curves of fully discharged MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with various potential step amplitudes

same with high step amplitude of + 80 mV and + 100 mV, which indicates that the hydrogen diffused from the bulk is completely oxidized on the electrode surface and the hydrogen concentration on the electrode surface is zero. So, + 50 mV is selected as the potential step amplitude in the following measurement.

3.2   Selection of time region

Assuming that the alloy particles in the hydrogen storage alloy electrode are in spherical form with uniform size, the current response flowing through the electrode after application of a potential step can be described by Eqn. (2) for the short-time region and Eqn. (3) for the long-time region, respectively[12].

Short-time region:

$$I = - nFSD(C_0 - C_s) \left| \frac{1}{\sqrt{\pi D t}} + \frac{1}{r} \right| \qquad (2)$$

Long-time region:

$$\lg I = \lg \left| \pm \frac{6FD}{r^2}(C_0 - C_s) \right| - \frac{\pi^2 D}{2.303 r^2} t \qquad (3)$$

where I is responding current (A), n is the number of the transferred electrons, F is faradaic constant (96 485 C/mol), S is electrochemical active area (cm^2), D is diffusion coefficient (cm^2/s), C_0 is initial hydrogen concentration in the electrode (mol/cm^3), and C_s is hydrogen concentration on the electrode surface after a potential step (mol/cm^3), r is the sphere radius of the alloy particles (cm), t is time (s). It is obvious that the value of D can be obtained by calculating the slope and intercept of $I - t^{-1/2}$ curves for the short-time region or the slope of $\lg I - t$ curves for the long-time region if the sphere radius r is known.

The data presented in Fig. 1 are replotted as Fig. 2. It exhibits approximately straight lines which are consistent with the expression of Eqns. (2) and (3). The values of D calculated are listed in Table 1.

Table 1   Hydrogen diffusion coefficient in fully discharged MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode

Potential step amplitude/mV	$D/(\text{cm}^2 \cdot \text{s}^{-1})$	
	Short-time region	Long-time region
+ 10	6.80×10^{-11}	1.16×10^{-8}
+ 20	3.63×10^{-10}	1.19×10^{-8}
+ 50	1.05×10^{-8}	1.28×10^{-8}
+ 80	9.30×10^{-8}	1.30×10^{-8}
+ 100	2.16×10^{-7}	1.36×10^{-8}

It can be found from Table 1 that the hydrogen diffusion coefficient in short-time region depends remarkably on the potential step amplitude, and the increase of step amplitude from + 10 mV to + 100 mV causes the calculated values of D to increase four orders of magnitude. The potential step amplitude,
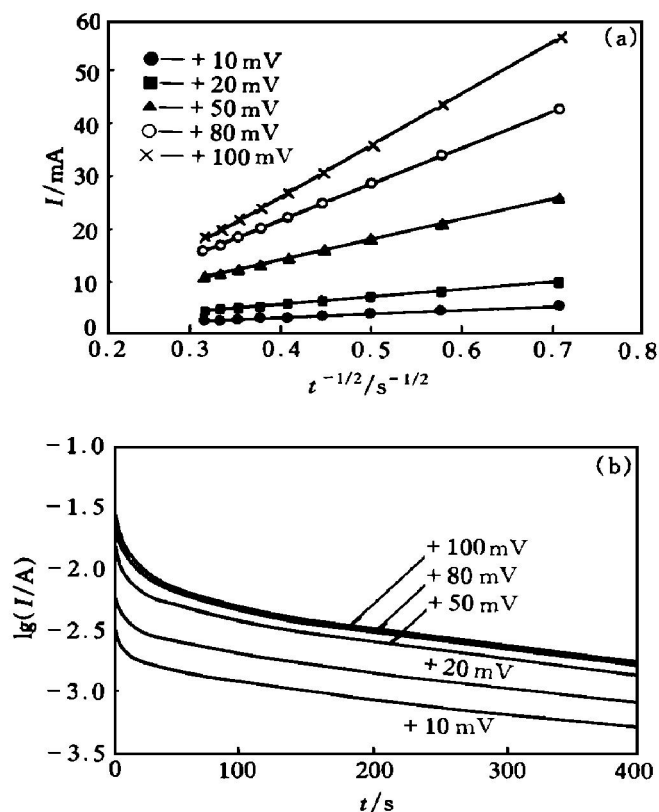
Fig. 2 Relationship of I and t of
fully discharged MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy
electrode with various potential step amplitudes

however, affects only slightly the diffusion coefficients in long-time region. Table 1 also indicates that the hydrogen diffusion coefficients are comparable for the potential step amplitude of + 50 mV. When the potential step amplitude is less than + 50 mV, the diffusion coefficient in long-time region is two or three orders of magnitude larger than that in short-time region. For the potential step amplitude larger than + 50 mV, the results in long-time region are less than that in short-time region. Similar results were obtained by Nishina et al[7, 12] in determining hydrogen diffusion coefficient for Pd and LaNi$_5$ alloy particles. Since the electrode at a given state has a fixed hydrogen diffusion rate, the hydrogen diffusion coefficient in it determined with the same method should not change remarkably with the potential step amplitude. Therefore, it should be recognized that the long-time calculation gives more reliable value for diffusion coefficient than the short-time calculation.

3. 3   Determination of hydrogen diffusion coefficient

The chronoamperometric curves of MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode at various state of charge are shown in Fig. 3.

It is obvious that lg$I$ —t plot is a line when t is larger than 250 s. So, the diffusion coefficient in the electrode can be determined from the slope of the linear part in Fig. 3, and the obtained values are repre-
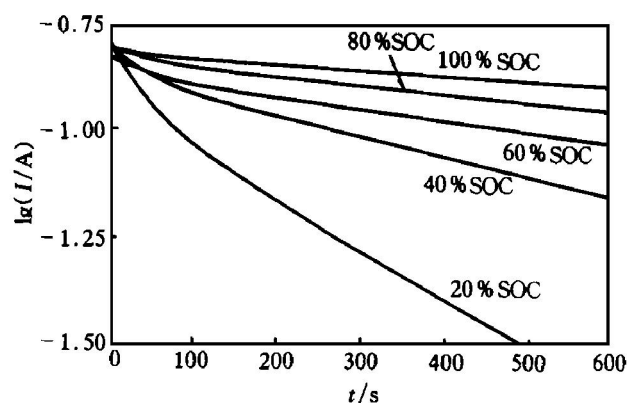

Fig. 3 Current —time responses of
MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with
potential step of + 50 mV at room temperature

sented in Fig. 4. It is shown that the diffusion coefficients range from 1.28×10^{-8} cm^2/s (0% SOC) to 1.11×10^{-9} cm^2/s (100% SOC) and decrease with the increase of SOC. This is in good agreement with the results of Iwakura et al[11]. At high SOC, the hydrogen concentration is larger and the vacant sites available for hydrogen to occupy are less than that at low SOC. Hydrogen must change from absorbed β phase to α phase (namely, structure transformation of the active material from metal hydride to solid solution) before diffusion. So the diffusion of hydrogen is influenced not only by its concentration but also by structure change of the active material at high SOC. But at low SOC, hydrogen concentration is so small that hydrogen atom exists as dissolved hydrogen, and the available sites for hydrogen to occupy is sufficient, so diffusion of hydrogen will not be limited by the two factors described above and the diffusion coefficient is larger.
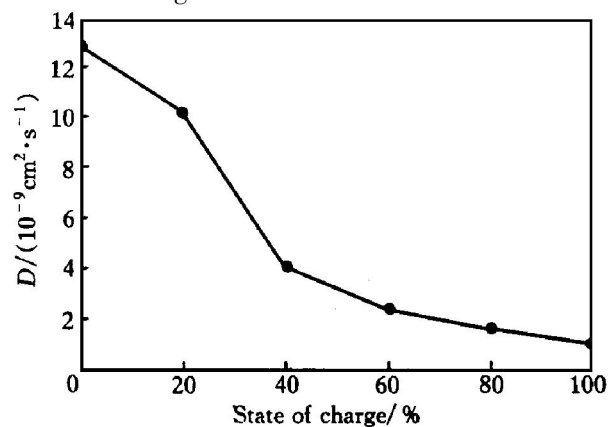

Fig. 4 Dependence of D on SOC in
MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode at
room temperature

The chronoamperometric curves of MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with 50% SOC at various temperatures are shown in Fig. 5. It also can be seen that the plot of lg$I$ —t curve is linear when t

is larger than 250 s, and the evaluated values of D from the slopes of these lines as a function of temperature are shown in Fig. 6 which indicates that the hydrogen diffusion coefficient in MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with 50% SOC increases with the increase of temperature, and an approximately linear relationship exists between ln$D$ and 1/T. According to Arrhenius equation, the activation energy for hydrogen diffusion in MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with 50% SOC is calculated to be 19.9 kJ/mol. This is in good agreement with the results determined by Iwakura[11].

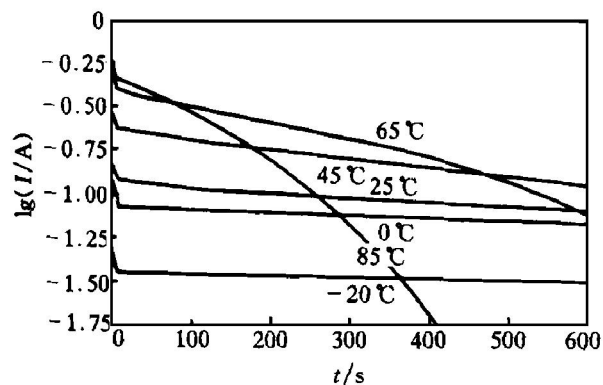**Fig. 5**   Current —time responses of MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with 50% SOC at various temperatures
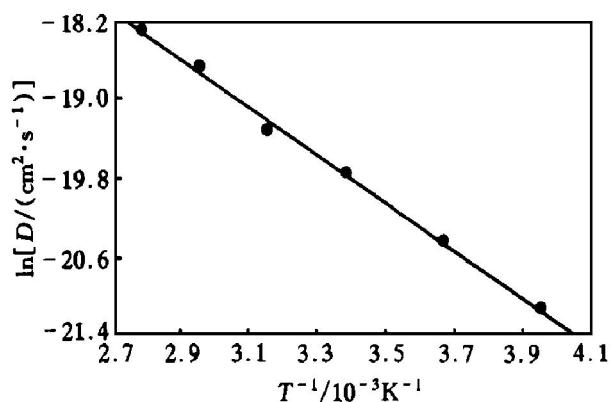
Fig. 6   ln$D$ —1/T curve of MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with 50% SOC

4   CONCLUSIONS

1) Calculation of hydrogen diffusion coefficient in the long-time region by chronoamperometry gives more reliable value in hydrogen storage alloy electrode than that in the short-time region.

2) Hydrogen diffusion coefficient in MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode decreases with the increase of state of charge at room temperature.

3) Hydrogen diffusion coefficient in MlNi$_{3.75}$Co$_{0.65}$Mn$_{0.4}$Al$_{0.2}$ alloy electrode with 50% SOC increases with the increase of temperature, and the activation energy for hydrogen diffusion in it is 19.9 kJ/mol.

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