Hydrogen diffusion in the anode of Ni/MH secondary batteries

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Abstract

Hydrogen diffusion coefficients (D) were evaluated in a $LaNi_{4.7}Al_{0.3}$ metal hydride electrode as a function of depth of discharge (DoD) using a newly developed electrochemical method which describes more precisely the practical diffusion behavior. It was found that the hydrogen diffusion coefficient in this electrode increases with increasing DoD at ambient temperature, and for this electrode at 50% DoD, the hydrogen diffusion coefficient increases with increase in temperature, and the activation energy for hydrogen diffusion is $37.3\,kJ\,mol^{-1}$. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ni/MH battery; Metal hydride electrode; Hydrogen diffusion coefficient

1. Introduction

The development of metal hydride (Ni/MH) batteries based on MH negative electrodes is one of the more important areas of electrochemical study today. Batteries based on such hydride materials have some major advantages over the more conventional lead–acid and nickel–cadmium systems. These advantages include high energy density, high rate capability, tolerance to overcharge and over-discharge, the lack of any poisonous heavy metals, and no electrolyte consumption during the charge/discharge cycle [1,2]. The characteristics of these batteries can be changed by designing the composition of the metal hydride alloy to provide optimum performance. One of the most important kinetic characteristics of a metal hydride electrode, which can be used to develop new materials for high performance batteries, is the hydrogen diffusion coefficient.

Different approaches have been proposed for the evaluation of the hydrogen diffusion coefficient in metal hydride alloys. These have included nuclear magnetic resonance (NMR) [3–5], quasi-elastic neutron scattering (QNS) [6,7], electrochemical impedance spectroscopy (EIS) [8], and various electrochemical techniques including potential-step and current-step methods [9–15]. The diffusion coefficients of hydrogen measured in various AB_5-type metal hydride electrodes using the different methods can vary by up to five orders of magnitude at room temperature for alloys with similar composition (from 10^{-10} to $10^{-15}\,m^2\,s^{-1}$) [1–15].

These widely varying values of D may be attributed to the fact that each used technique has its own theoretical background and specific simplification has been made during the deduction of the necessary formulae for calculation of D. Alloys with similar composition, or even the same composition, might have different microstructure, thermodynamic and kinetic performance due to different preparation processes which also leads to differences in D. In addition, the DoD or hydrogen concentration of a metal hydride electrode that also affects D, is usually not considered when one develops a method to measure the value of D.

The conventional potentiostatic method is widely used to study the hydrogen diffusion coefficient, as it is a simple and convenient method [8,10]. This method is applicable only for a sufficiently large time period (greater than about 5000 s) and, as a result, the calculated hydrogen coefficient is an average value for this large time interval. This method thus appears to be unsuitable for determining the diffusion coefficient at any particular time period. In this paper we describe a new and relatively simple potentiostatic method (originally presented in [16]), for determining hydrogen diffusion coefficient over a small time period (less than about 500 s). Using this method, the hydrogen diffusion coefficients were conveniently measured in $LaNi_{4.7}Al_{0.3}$ metal hydride electrode at various DoDs. The dependence of the diffusion coefficient on DoD and temperature is discussed.

2. Experimental

The $LaNi_{4.7}Al_{0.3}$ alloy was obtained from Ergenics (Hy-stor 207). It was first mechanically pulverized to a

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mean particle size of about 50 μm (270–325 mesh). The negative electrode was made by mixing the alloy powder (95 mg) with copper powder in a ratio of 1:1. A polytetrafluoroethylene (PTFE) dispersion (4 wt.%) was added to the mixture as a binder. The mixture was filled into a porous nickel foam plate with the diameter of 10.0 mm and was then pressed into a sheet of 0.6 mm thickness at a pressure of 500 MPa for 2 min.

The electrochemical cell was equipped with three compartments. The negative metal hydride electrode was placed in the central compartment and two positive electrode plates were placed on either side. The MH electrode and counter electrode were separated by a porous frit. The experimental apparatus was set in a water bath at controlled (±0.5 K) temperatures to maintain a practically constant temperature during each kinetic run. The charge/discharge and potentiostatic tests were conducted using a Solartron 1285 Potentiostat with Corrware software. The electrochemical capacity of the positive electrode was designed to be higher than that of the negative electrode. The electrolyte was a 6 M KOH aqueous solution. A Hg/HgO/6 M KOH electrode was used as the reference electrode. A Luggin capillary tube, which was connected to the reference electrode and working electrode, was placed close to the working electrode in order to minimize the ohmic drop across the electrolyte solution.

The metal hydride electrodes were first activated by charge/discharge cycles to ensure that the electrode was electrochemically stable. When charge/discharge cycles are carried out, the average particle size decreases and then remains constant after being fully activated (25 charge/discharge cycles). After complete activation of the MH electrode at room temperature, the MH electrode was charged at a constant current (80 mA g^{-1}) until the hydrogen concentration reached its saturated value at room temperature. The electrochemical discharge process was carried out at constant potentials so that the thermodynamic force (i.e., $E_{applied} - E_{eq}$) for the MH electrode reaction remains constant. The decrease in discharge current was monitored as a function of time. Before each potential step, a small current density (5 mA g^{-1}) has been applied to partially remove the adsorbed hydrogen on the particle surface.

Since hydrogen diffusion does not become the rate-determining process immediately after the application of a positive potential step, a certain time, which depends on the applied potential and discharge state, must elapse before D can be determined (for the saturated state, this is approximately 40–70 s). Thus, when we determined the dependence of D on the DoD, the potential step was always larger than +0.6 V versus Hg/HgO so as to make more steps available. After discharging for 25 s at each potential step, the discharge process was terminated until the open-circuit (i.e., equilibrium potential) became stabilized (i.e., the change of the potential was less than 0.1 mV for 1 min). This procedure was used to ensure that each subsequent potential step was also applied after equilibrium had been reached for the preceding step.

The DoD is defined by:

$$\text{DoD} = \frac{j_d t_d}{Q} \times 100\% \tag{1}$$

Here Q is the capacity of the activated metal hydride electrode; j_d and t_d are discharge current and discharge time, respectively. For the experiments at various temperatures, the electrodes were initially charged at 80 mA g^{-1} for 5 h and discharged at the same current to 50% DoD at ambient temperatures, after a rest of 1 h at the specified temperature for the open-circuit potential to become stabilized, the discharge current was measured.

3. Results and discussion

Assuming that the alloy particles in the metal hydride electrode are in spherical form with uniform size, the diffusion of hydrogen inside the particle can be written as (Fick's second law):

$$\frac{\partial C(r, t)}{\partial t} = D \left[\frac{\partial^2 C(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r, t)}{\partial r} \right] \tag{2}$$

where D is an average (or integral) diffusion coefficient of hydrogen (m^2 s^{-1}); r is the radial distance from the center of the sphere (m); t is the time (s); $C(r, t)$ is the hydrogen concentration in the alloy with respect to radius and time (mol H m^{-3}). Supposing that the initial hydrogen concentration in the bulk of the alloy is uniform (C_0), when a dc voltage is imposed on the metal hydride electrode system, the initial and boundary conditions can be mathematically represented as:

$$C(r, 0) = C_0; \quad 0 \leq r \leq a; \quad t = 0 \tag{3}$$

$$C(a, t) = C_s; \quad r = a; \quad t > 0 \tag{4}$$

$$C(0, t) = C_0; \quad r = 0; \quad 0 < t < \tau \tag{5}$$

$$D \left[\frac{\partial C(r, t)}{\partial r} \right]_{r=a} = \pm \frac{j(t)}{nFA} \tag{6}$$

where a is the radius of the particle sphere (m); t is the time (s); C_0 is the initial hydrogen concentration in the bulk of the alloy throughout the sample (mol H m^{-3}); C_s is the hydrogen concentration at the particle surface (mol H m^{-3}); τ is the time (s) at which the boundary condition shown in Eq. (5) becomes invalid; n denotes the number of Faradays (or electrons) involved in the reaction ($n = 1$ for this electrochemical system); F is Faraday's constant (96,487 C mol^{-1}); A is the surface area of the particles (m^2 g^{-1}); $j(t)$ is the diffusion current density (A g^{-1}). The initial and boundary conditions (Eqs. (3) and (4)) imply that the sphere is initially at a uniform concentration C_0, and the surface concentration is kept constant at C_s during the experiment. The (±) sign in Eq. (6) indicates the charge (+) and discharge (−) process when the current density is always considered to be a positive value. Application of the Laplace transformation

method to Eq. (2) together with the initial and boundary conditions Eqs. (3)–(5), for small times gives [17]:

$$\frac{C - C_0}{C_s - C_0} = \frac{a}{r} \sum_{m=0}^{\infty} \left[\text{erfc} \frac{(2m+1)a - r}{2\sqrt{(Dt)}} - \text{erfc} \frac{(2m+1)a + r}{2\sqrt{(Dt)}} \right] \quad (7)$$

Simplifying Eq. (7) and combining with Eq. (6), we can obtain:

$$j(t) = \pm FAD(C_s - C_0) \left(\frac{1}{\sqrt{\pi D}} \frac{1}{\sqrt{t}} - \frac{1}{a} \right) \quad (8)$$

The equations given above are written for the case where the only species reacting at the electrode are supplied by hydrogen diffusion. Additional current densities due to reaction of adsorbed hydrogen, double layer charging/discharging, or oxide film formation or removal may also contribute to the current densities measured upon application of a potential step to the electrode. However, these processes may not play important roles for the current variation after a certain time when hydrogen diffusion in the solid solely governs the reaction since the intercepts on the j axis of the $j(t)$ versus $t^{-1/2}$ plots are generally negative for the discharge reaction of a MH electrode at different applied potentials (such behavior has been observed in the experiments to be described). The intercepts will mainly be determined by the first term, i.e., $\pm FDA(C_s - C_0)/a$ and the other additional currents can be neglected.

The diffusion coefficient of hydrogen is then found by measuring the ratio of intercept I (A g^{-1}), and slope S (A g^{-1} s$^{1/2}$) from a linear plot of $j(t)$ versus $t^{-1/2}$ (Fig. 1):

$$D = \left(\frac{I}{S} \right)^2 \frac{a^2}{\pi} \quad (9)$$

This method does not require a knowledge of either the hydrogen concentration or the surface area (A) of alloy particles.
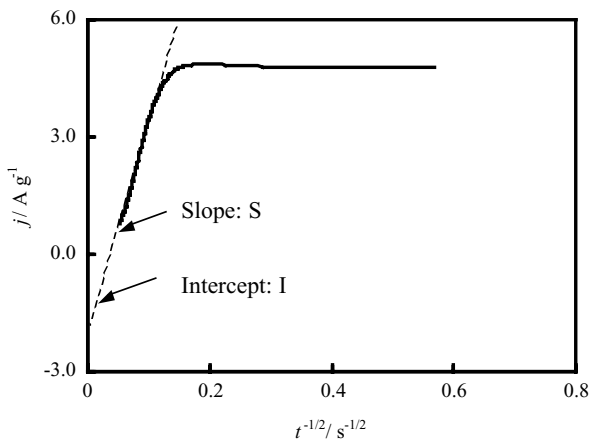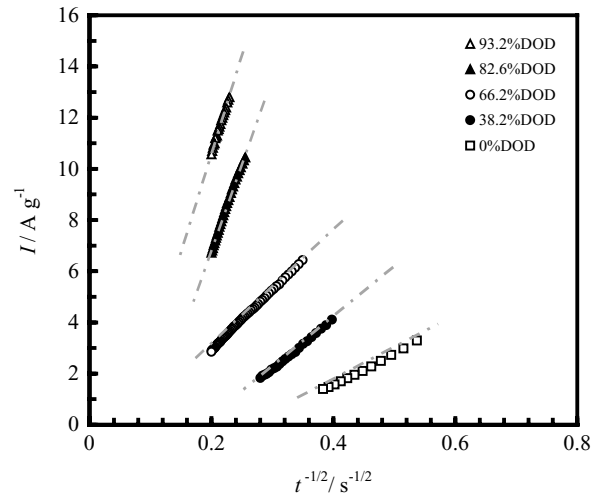

Fig. 2. $j(t)$ as a linear function of $t^{-1/2}$ for LaNi$_{4.7}$Al$_{0.3}$ metal hydride electrode at various DoD at room temperature.

To investigate the effect of DoD on hydrogen diffusion coefficient, the experiments were carried out at successive discharge stages of the MH electrode under a constant potential step. Since hydrogen diffusion becomes the rate-determining step after a certain time and this time period becomes shorter at higher potentials, a large potential step (+0.6 V versus Hg/HgO) was employed. j versus $t^{-1/2}$ plots of the LaNi$_{4.7}$Al$_{0.3}$ metal hydride electrode with various DoD at room temperature are shown in Fig. 2 and the calculated values of D as a function of DoD are shown in Fig. 3 (an average diameter spherical particles, a, is 6 μm). It can be seen that the hydrogen diffusion coefficient increases from 3.7×10^{-14} to 8.6×10^{-13} m^2 s^{-1} with the increase in DoD of the metal hydride electrode from 0 to 93%. This is in good agreement with the result of Iwakura et al. [18] that the hydrogen diffusion coefficient in a MmNi$_{4.2}$Al$_{0.5}$M$_{0.3}$ (M = Cr, Mn, Fe, Co, Ni) alloy increases with decreasing hydrogen concentration. The probable reason for the DoD dependence of hydrogen diffusion coefficient is that
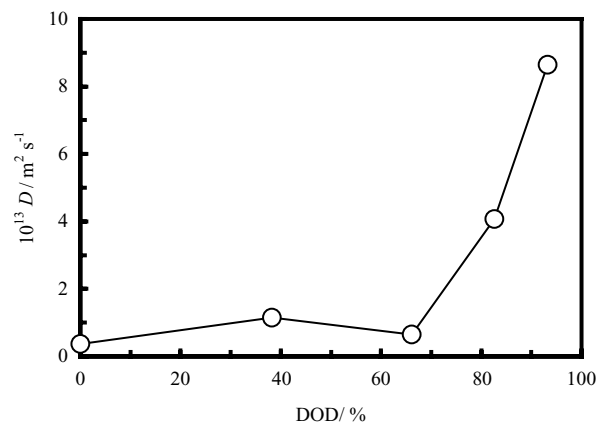

Fig. 1. Illustration of the determination of intercept I, and slope S from a linear plot of $j(t)$ vs. $t^{-1/2}$.

Fig. 3. Hydrogen diffusion coefficients in LaNi$_{4.7}$Al$_{0.3}$ metal hydride electrode as a function of DoD at room temperature.

diffusion coefficient of a species is related to its mobility. One factor that restricts hydrogen mobility is its concentration, i.e., DoD. With increasing hydrogen concentration (low DoD), the mutual interaction of atomic hydrogen in a metal or an alloy will lower its mobility, thus lowering the hydrogen diffusion coefficient. Another factor is that at these higher concentrations (low DoD), transitory trapping of hydrogen by the dislocation structure in the β-hydride takes place. The attractive interaction between hydrogen and dislocations decreases its diffusivity as has been shown in several papers [19–21].

The calculated value of D in the $LaNi_{4.7}Al_{0.3}$ metal hydride electrode saturated with hydrogen is $3.7 \times 10^{-14} \, m^2 \, s^{-1}$ which is similar to previous results for alloys of similar composition [10,15]. Zheng et al. [10] used the constant potential and constant current discharge techniques to measure the values of D in a $LaNi_{4.25}Al_{0.75}$ power electrode. They reported values of D of 2.97×10^{-11} and $3.30 \times 10^{-11} \, cm^2 \, s^{-1}$ estimated from the potentiostatic and galvanostatic discharge experiments, respectively. Van Rijswick [15] using the transfer-limited portion of a potentiostatic discharge of curve estimated the value of D in an $LaNi_5$ electrode to be in the order of $10^{-10} \, cm^2 \, s^{-1}$. Although some authors [8,10] have measured the dependence of D on DoD, the values of D thus obtained are the average values over a relatively large discharge time such as several hours, and it is difficult to determine the accurate dependence of D on DoD. The present method can overcome this difficulty.

j versus $t^{-1/2}$ plots of $LaNi_{4.7}Al_{0.3}$ metal hydride electrode with 50% DoD at various temperatures are shown in Fig. 4 and the measured values of D as a function of temperature are shown in Fig. 5. It is obvious that the hydrogen diffusion coefficient increases with increase in temperature. The activation energy for hydrogen diffusion in this electrode is calculated to be $37.3 \, kJ \, mol^{-1}$ using the Arrhenius equation. This is in good agreement with the results of $35.4 \, kJ \, mol^{-1}$ obtained by Züchner and Rauf [22] for hy-
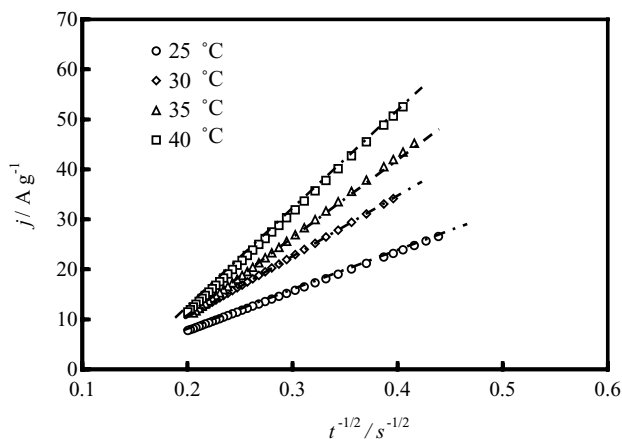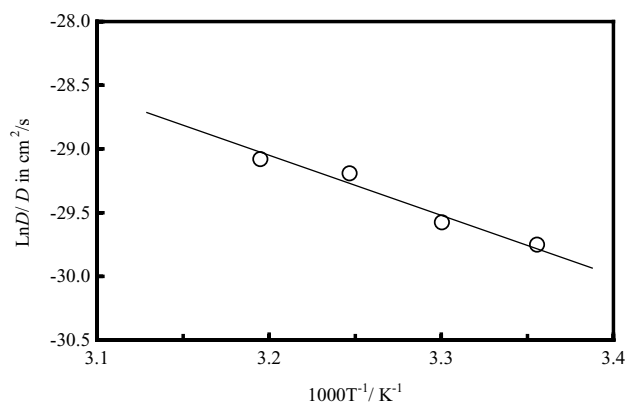

Fig. 5. Temperature dependence of hydrogen diffusion coefficient in $LaNi_{4.7}Al_{0.3}$ metal hydride electrode with 50% DoD.

drogen diffusion in $LaNi_5$ using a current pulse relaxation method.

It is suggested that any comparison of hydrogen diffusion coefficients in different metal hydrides, or in the same metal hydride, should be made for values obtained at the same DoD, i.e., hydrogen concentration.

4. Conclusions

1. The hydrogen diffusion coefficient in a $LaNi_{4.7}Al_{0.3}$ metal hydride electrode increases with increase in DoD and is in the range of 3.1×10^{-14} to $8.6 \times 10^{-13} \, m^2 \, s^{-1}$ at room temperature.
2. The hydrogen diffusion coefficient in a $LaNi_{4.7}Al_{0.3}$ metal hydride electrode at 50% DoD increases with increase in temperature, and the activation energy for hydrogen diffusion is $37.3 \, kJ \, mol^{-1}$.

Acknowledgements

Fig. 4. $j(t)$ as a linear function of $t^{-1/2}$ for $LaNi_{4.7}Al_{0.3}$ metal hydride electrode with 50% DoD at various temperatures.

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