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Electrochemical Determination of the Diffusion Coefficient of Hydrogen Through an $\text{LaNi}_{4.25}\text{Al}_{0.75}$ Electrode in Alkaline Aqueous Solution

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ABSTRACT

The constant potential and constant current discharge techniques were used to determine the hydrogen diffusion coefficients in an $\text{LaNi}_{4.25}\text{Al}_{0.75}$ electrode. The values obtained were 2.97×10^{-11} and 3.30×10^{-11} cm^2/s , respectively. The advantages and disadvantages of these two techniques are discussed.

Introduction

Metal hydrides are being used as electrodes in nickel/metal-hydride batteries because of their ability to store large quantities of hydrogen and because of their many advantages over conventional lead-acid and nickel-cadmium batteries.^{1,2} The performance of a metal hydride electrode is determined by both the kinetics of the processes occurring at the metal/electrolyte interface and the rate of hydrogen diffusion within the bulk of the metal.³ Although this system has been studied extensively, understanding of the fundamental properties such as reaction mechanisms and transport phenomena have not been completed and disagreements exist in the literature.⁴⁻¹⁴ Reported values of the diffusion coefficient of hydrogen in LaNi_5 vary over three orders of magnitude at room temperature. Using nuclear magnetic resonance (NMR), Khodosov *et al.*⁴ reported a value for the hydrogen diffusion coefficient in LaNi_5 of 5×10^{-6} cm^2/s . Using the same technique Reilly and Wiswall⁵ determined a value of 2.7×10^{-8} cm^2/s for the hydrogen diffusion coefficient. Lebsanft *et al.*⁶ used a quasi-elastic neutron scattering technique (QNS) to measure the diffusion of hydrogen in LaNi_5 , FeTi , and Ti_2Ni and reported diffusion coefficient values of 6.1×10^{-9} , 1.8×10^{-12} , 2.3×10^{-10} cm^2/s , respectively. Using the same technique, Fischer *et al.*⁷ reported that the hydrogen diffusion coefficient in LaNi_5 is on the order of 10^{-6} cm^2/s . Although most measurements for the diffusion coefficient of hydrogen through metal-hydride systems were performed using NMR^{4,5,8-10} and QNS^{6,7,11,12} electrochemical techniques have been also applied^{3,13,14} to determine the hydrogen diffusion coefficient.

Electrochemical measurements using the current pulse method were carried out by Zuchner *et al.*¹³ as a function of crystal orientation and temperature to determine the diffusion of hydrogen in LaNi_5 single crystals. Their results indicated an anisotropic, orientation-dependent diffusion coefficient with a value of 10^{-8} cm^2/s . The diffusion in the [001] direction was preferred compared to that in the [100] direction.

Van Rijswijk³ using the transfer-limited portion of a potentiostatic discharge curve estimated the hydrogen diffusion coefficient in an LaNi_5 electrode to be in the order of 10^{-10} cm^2/s . Ciureanu *et al.*¹⁴ determined the diffusion coefficient of hydrogen in an $\text{Ni}_{64}\text{Zr}_{36}$ ribbon using the chronopotentiometric method. They reported hydrogen diffusion coefficient values in the range of 2.2×10^{-10} to 4.5×10^{-10} cm^2/s .

$\text{LaNi}_{5-x}\text{Al}_x$ alloys are promising hydrogen absorbing material because of their high resistance to degradation^{15,16} and because of their low equilibrium pressure when compared with Mn, Cu, Co and Cr substitutions.^{17,18} Since $\text{LaNi}_{5-x}\text{Al}_x$ alloys have been recently very well characterized in literature,¹⁹⁻²¹ we measured the hydrogen diffusion coefficient in $\text{LaNi}_{4.25}\text{Al}_{0.75}$. In this work constant-potential

and constant-current discharge techniques were used to estimate the hydrogen diffusion coefficient through a palladium-plated $\text{LaNi}_{4.25}\text{Al}_{0.75}$ electrode.

Theory

Assuming that the hydride alloy is in spherical form, the diffusion equation is

$$\frac{\partial(rc)}{\partial t} = \bar{D} \frac{\partial^2(rc)}{\partial r^2} \quad [1]$$

where c is hydrogen concentration in the alloy, t is time, \bar{D} is an average (or integral) diffusion coefficient of hydrogen over a defined concentration range, and r is a distance from the center of the sphere.²² The diffusion equation may be solved under two different boundary conditions: (i) constant hydrogen surface concentration and uniform initial hydrogen concentration in the bulk alloy, and (ii) constant flux at the surface and uniform initial concentration in the bulk of the alloy. Assuming uniform initial hydrogen concentration in the bulk of the alloy, c_0 , and a constant surface concentration, c_s , the solution of the above equation is given by Crank²³

$$\frac{c - c_0}{c_s - c_0} = 1 + \frac{2a}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin \frac{n\pi r}{a} \exp\left(-\frac{\bar{D}n^2\pi^2 t}{a^2}\right) \quad [2]$$

where a is the sphere radius. The resulting diffusion current varies with time according to Eq. 3

$$i = \pm \frac{6F\bar{D}}{da^2} (c_0 - c_s) \sum_{n=1}^{\infty} \exp\left(-\frac{n^2\pi^2\bar{D}t}{a^2}\right) \quad [3]$$

For large t , Eq. 3 reduces to

$$\log i = \log\left(\pm \frac{6F\bar{D}}{da^2} (c_0 - c_s)\right) - \frac{\pi^2}{2.303} \frac{\bar{D}}{a^2} t \quad [4]$$

The \pm sign in Eq. 3 and 4 indicates the charge (–) and discharge (+) process. From the slope of a plot of $\log(i)$ vs. t , according to Eq. 4, \bar{D}/a^2 may be evaluated, and if the sphere radius is known, \bar{D} can be calculated.

The diffusion coefficient may also be determined from the amount of charge transferred. The total moles of hydrogen entering (charging) or leaving (discharging) the sphere is given by Crank²²

$$\ln\left[\frac{6}{\pi^2} \left(\frac{M_{\infty}}{M_{\infty} - M_t}\right)\right] = \pi^2 \frac{\bar{D}}{a^2} t \quad [5]$$

where M_t and M_{∞} are the amounts of hydrogen that have been transferred in or out after time t and ∞ , respectively. \bar{D}/a^2 may be estimated from the slope of the plots $\ln[6/\pi^2(M_{\infty}/M_{\infty} - M_t)]$ vs. t according to Eq. 5. In practice, it is usually not convenient to make an integration in order to estimate the amount of hydrogen as a function of time. However, if the time is known for a specified value of M_t , then \bar{D}/a^2 can be calculated from Eq. 5. For example, if $t = t_{0.95}$, then

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$$\frac{\bar{D}}{a^2} = \frac{\ln(120/\pi^2)}{\pi^2 t_{0.95}} = \frac{0.253}{t_{(0.95)}} \quad [6]$$

On the other hand, for a constant flux at the surface and uniform initial concentration of hydrogen in the bulk of the alloy, the value of \bar{D}/a^2 may be evaluated for large transition times, τ ^{22,23}

$$\frac{\bar{D}}{a^2} = \frac{1}{15\left(\frac{Q_0}{i} - \tau\right)} \quad [7]$$

where Q_0 is the initial specific capacity (C/g), i is the current density (A/g), and τ is the transient time (s), i.e., the time when the hydrogen surface concentration approaches zero. The ratio Q_0/i corresponds to the discharge time necessary completely to discharge the electrode under hypothetical conditions when the process proceeds without interference of diffusion. Rearranging Eq. 7, one obtains

$$Q_1 = Q_0 - \tau i = \frac{i a^2}{15 \bar{D}} \quad [8]$$

where Q_1 is charge of hydrogen left in the electrode when the hydrogen surface concentration is zero. According to Eq. 8, the hydrogen content left over in the electrode after discharge is proportional to the discharge current and to the square of particle size and is inversely proportional to the diffusion coefficient.

Experimental

The alloy was prepared by arc melting under argon atmosphere and was stored under argon atmosphere. The following procedure was used to prepare the LaNi_{4.25}Al_{0.75} pellet electrode. The LaNi_{4.25}Al_{0.75} powder was passed through a 230 mesh sieve, which gave a particle size of less than 60 μm . The alloy was chemically activated by immersing the alloy for 30 s in an aqueous 1M HF prior to electroless plating with palladium. According to Hout *et al.*²⁴ and Ciureanu *et al.*,²⁵ immersion of several alloys in 1M HF removed the oxide layers, significantly improving their electrocatalytic activity. Since the alloy was not exposed to air until after it was palladium plated, we expect the thickness of any oxide layer that may have formed on the surface of alloy to be negligible. The electroless plating process was carried out in a chamber filled with argon. After cleaning the alloy with HF, the LaNi_{4.25}Al_{0.75} alloy was microencapsulated with a thin film of palladium (approximately 0.5 μm thick) by electroless deposition using hypophosphite as a reducing agent. The alloy powder was immersed in an electroless plating solution containing 1.7 g/liter PdCl₂, 160 ml/liter NH₄OH, 26 g/liter NH₄Cl, and 10 g/liter NaH₂PO₂·H₂O. The palladium to alloy ratio by weight was 1:5. Microencapsulation with palladium was carried out in order to prevent the LaNi_{4.25}Al_{0.75} alloy from oxidizing during the discharge process. Since the Pd film was less than 1 μm and palladium has a relatively high diffusivity, the diffusion resistance of the film was assumed to be negligible.

A good electrical connection to the pellet was achieved through the following procedure: (i) a piece of platinum wire was passed several times through a platinum mesh; (ii) the platinum mesh and the wire were then pressed together to obtain good electrical connection; (iii) next, the pellet electrodes were prepared by mixing palladium-plated LaNi_{4.25}Al_{0.75} alloy powder with 2.5% of polytetrafluorethylene (PTFE) powder followed by hot-pressing the material between two platinum meshes in a cylindrical press. A pellet with a diameter of 0.8 cm and thickness of 0.5 mm was formed at approximately 300°C using a pressure of 5 t/cm². A pellet containing 112 mg of LaNi_{4.25}Al_{0.75} alloy was then inserted between two pieces of Plexiglas holders with small holes on each side. The electrode was immersed in the test cell filled with a 6M KOH electrolyte solution. A piece of Pt gauze on each side of the electrode were used as counterelectrodes.

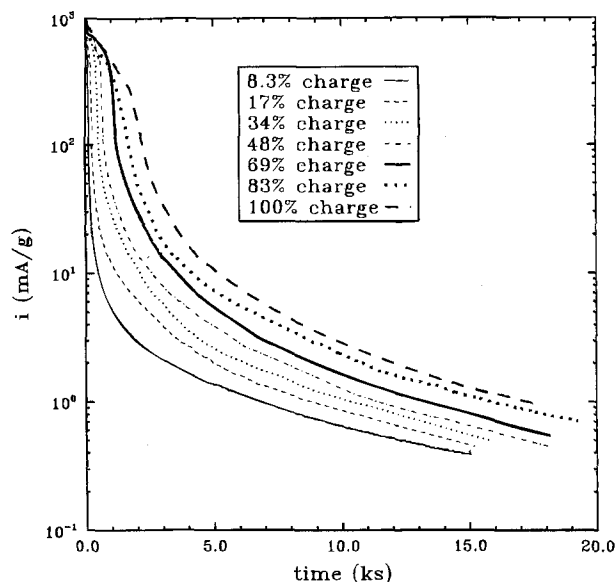


Fig. 1. Constant potential discharge curves at different state of charge. Discharge potential = -0.30 V (Hg/HgO).

The experiments were carried out using an Hg/HgO reference electrode using the Model 342C SoftCorr System with the EG&G Princeton Applied Research potentiostat/galvanostat Model 273 at 25°C.

Results and Discussion

To estimate the diffusion coefficient parameter \bar{D}/a^2 , the following procedure was carried out: the alloy was activated by fully charging and discharging the electrode for ten cycles. Then the electrodes with different states of charge were equilibrated until an equilibrium potential was reached.

Initially, the activated electrode was discharged at constant potential at different states of charge. It was found that the discharge current per unit mass becomes constant when the applied potential is between -0.50 and -0.30 V vs. Hg/HgO in 6M KOH indicating that the hydrogen which diffuses from the electrode is completely oxidized. In order to secure a zero concentration of hydrogen at the surface of each individual particle, the electrode was discharged at a constant anodic potential -0.30 V (Hg/HgO) by taking into account the ohmic voltage drop through the pellet. Discharge curves obtained for seven different charge states are

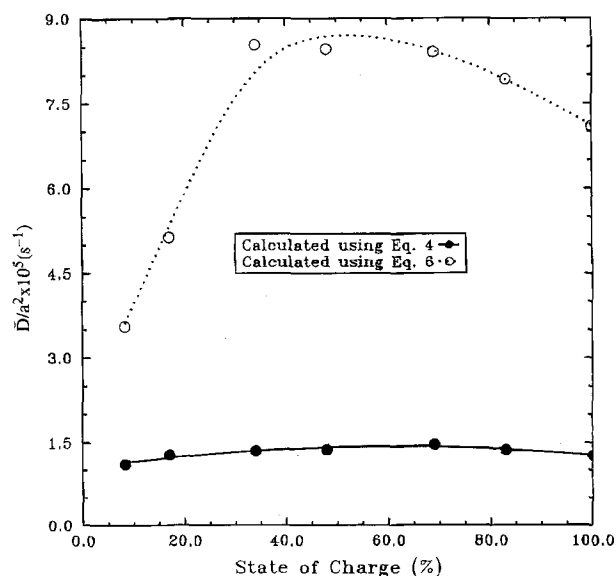


Fig. 2. Dependence of \bar{D}/a^2 upon the state of charge.

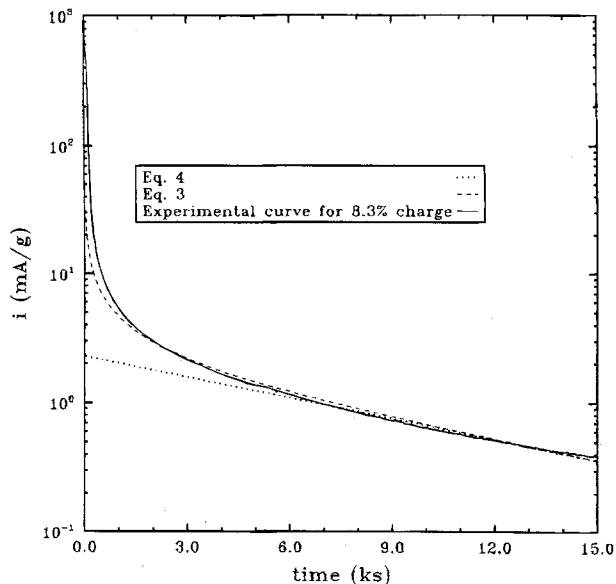


Fig. 3. Comparison of theoretical results with experimental data at 8.3% state of charge.

given in Fig. 1. For large times in Fig. 1 an approximately linear relationship exists between $\log i$ and t , which is consistent with Eq. 4. From the slope of the linear portion of the corresponding curves in Fig. 1, the ratios of \bar{D}/a^2 were estimated by using Eq. 4. These ratios for different states of charge are presented in Fig. 2. As shown in Fig. 2, the ratio of \bar{D}/a^2 is almost independent of state of charge with an average value of \bar{D}/a^2 of $1.32 \times 10^{-5} \text{ s}^{-1}$. Assuming that the average particle radius is $15 \mu\text{m}$, the effective diffusion coefficient of hydrogen through $\text{LaNi}_{4.25}\text{Al}_{0.75}$ electrode was estimated to be $2.97 \times 10^{-11} \text{ cm}^2/\text{s}$. This value is very close to the diffusion coefficient values of hydrogen in nickel alloys, which are in the range of 2.0×10^{-11} to $5.6 \times 10^{-11} \text{ cm}^2/\text{s}$, estimated using a permeation technique.²⁶⁻²⁸

In order to show the validity of Eq. 4, both Eq. 3 and Eq. 4 were plotted in Fig. 3, and the plots were compared with the experimental data obtained at 8.3% state of charge. Equation 4 is a good approximation only for large times and, as shown in Fig. 3 can be used to estimate \bar{D}/a^2 only four times larger than 6,000 s.

Values of \bar{D}/a^2 calculated using Eq. 6 are also given in Fig. 2 for comparison. The \bar{D}/a^2 values obtained using Eq. 6 are much higher than those calculated from Eq. 4. The $t_{0.95}$

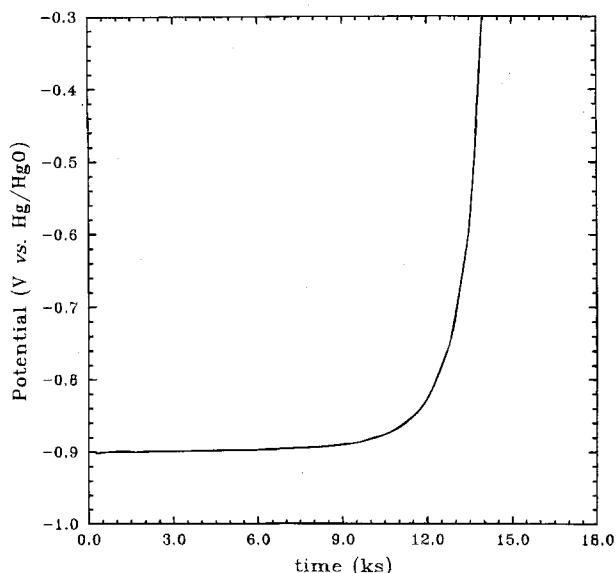


Fig. 4. Constant current discharge curve at $i = 57.1 \text{ mA/g}$.

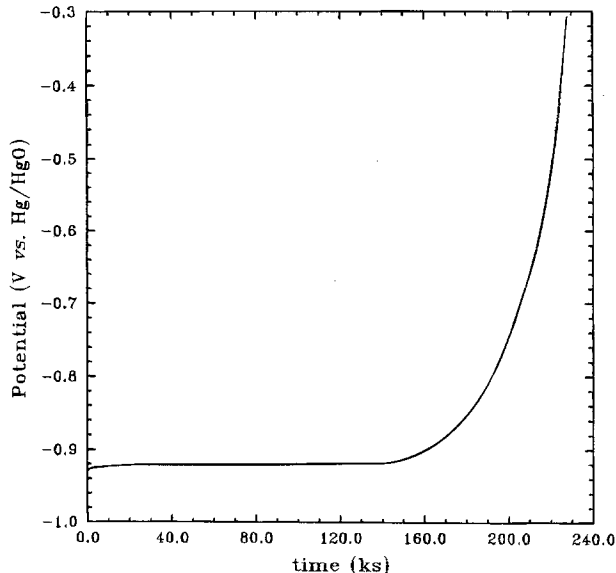


Fig. 5. Constant current discharge curve at $i = 4.57 \text{ mA/g}$.

value for each discharge curve was obtained by determining the time at which the electrode was 95% discharged. For example, the discharge curves obtained at 8.3 and 17% and state of charge have $t_{0.95}$ values of 7×10^3 and 5×10^3 s, respectively. All others have an average value of $t_{0.95}$ approximately 3×10^3 s, which is far from the linear portions of $\log i$ vs. t curves observed in Fig. 1. Thus, Eq. 6 is not valid in these cases and is not recommended for estimating the diffusion coefficient.

Next, two discharge curves were obtained under constant current conditions. In the absence of any other oxidation process, the discharge process carried out at a constant current should establish a constant hydrogen flux condition. In these galvanostatic cases, the experiment was terminated at a potential of -0.30 V (Hg/HgO) to secure the same conditions as under potentiostatic conditions. The galvanostatic discharge curve presented in Fig. 4 was obtained at a constant current per unit mass of 57.1 mA/g . The curve shown in curve Fig. 5 was obtained at a constant current per unit mass of 4.57 mA/g . In order to evaluate the diffusion coefficient using Eq. 7 it is necessary to estimate the transient time τ . As shown in Fig. 4 and 5, after a certain period of time, a drastic potential change occurred to compensate the hydrogen surface concentration decreasing in order to keep a constant current. The estimated transition times in Fig. 4 and 5 are 1.39×10^4 s and 2.28×10^3 s, respectively. The initial charge in the electrode, Q_0 , was 1062 C/g , and the charges remaining in the electrode after discharge for τ seconds were estimated from Fig. 4 (constant current discharge curve obtained at $i = 57.1 \text{ mA/g}$) and Fig. 5 (constant current discharge curve obtained at $i = 4.57 \text{ mA/g}$) as 268 and 20 C/g , respectively. The calculated values of \bar{D}/a^2 using Eq. 7 are $1.42 \times 10^{-5} \text{ s}^{-1}$ and $1.51 \times 10^{-5} \text{ s}^{-1}$, respectively. Thus, using $a = 15 \mu\text{m}$, the effective diffusion coefficient of $3.30 \times 10^{-11} \text{ cm}^2/\text{s}$ was estimated, which is close to the measured values under constant-potential conditions.

Conclusion

The constant hydrogen surface concentration condition, necessary to satisfy Crank's equation was established only when the discharge potential is anodic enough to cause the hydrogen which diffuses from the bulk of the hydride to the surface to be oxidized instantly. To satisfy this condition, the $\text{LaNi}_{4.25}\text{Al}_{0.75}$ electrode was discharged at a constant anodic potential of -0.3 V (Hg/HgO) . A linear relationship was found to exist between $\log i$ and t for large times, which is consistent with Eq. 4. From the slope of the linear portion of $\log i$ vs. t curve, the hydrogen diffusion parameter \bar{D}/a^2 was established to be $1.32 \times 10^{-5} \text{ s}^{-1}$. Assuming that the average particle radius $a = 15 \mu\text{m}$, the effective diffusion

coefficient of hydrogen through $\text{LaNi}_{4.25}\text{Al}_{0.75}$ was calculated to be $2.97 \times 10^{-11} \text{ cm}^2/\text{s}$. This value agrees well with a previously obtained hydrogen diffusion coefficient value of $2.0 \times 10^{-11} \text{ cm}^2/\text{s}$, estimated in nickel alloys using a permeation technique.²⁶⁻²⁸ Note that when the potentiostatic discharge technique is used to estimate the diffusion coefficient, electroless palladium plating is a necessary pretreatment to prevent oxidation of the alloy.

An average value for the diffusion coefficient of hydrogen was also determined from the amount of charge transferred during a constant current discharge. This value was obtained using $a = 15 \mu\text{m}$ and agrees well with the value obtained during potentiostatic discharge.

In the galvanostatic mode, it was possible to prevent substrate oxidation because the experiments were carried out at sufficiently negative potentials. However, it was found that the galvanostatic technique has the following disadvantages when it was used to determine the hydrogen diffusion coefficient through $\text{LaNi}_{4.25}\text{Al}_{0.75}$: (i) the transition time is not well defined and (ii) Eq. 7 is valid only for small discharge currents, which increases the duration of the experiment.

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LIST OF SYMBOLS

a	sphere radius, cm
c	hydrogen concentration in a sphere alloy, mol/cm ³
c_s	surface hydrogen concentration of a sphere, mol/cm ³
c_0	initial hydrogen concentration in a sphere, mol/cm ³
\bar{d}	density of the alloy, g/cm ³
D	integral diffusion coefficient of hydrogen, cm ² /s
F	Faraday's constant, 96,487 C/equiv.
i	current density, A/g
M_t	the amount of hydrogen entering or leaving the sphere at time t , mol
M_∞	the amount of hydrogen entering or leaving the sphere at infinite time, mol
Q_0	the initial charge in the electrode, C/g
Q_1	the charge remaining after discharge for τ seconds, C/g
t	time, s
$t_{0.95}$	the time at $M_t = 0.95 M_\infty$, s
τ	transient time, s
r	distance, cm

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