Journal of Applied Electrochemistry **31**: 1033–1039, 2001.
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Comparative study on electrochemical techniques for determination of hydrogen diffusion coefficients in metal hydride electrodes

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Received 6 November 2000; accepted in revised form 2 May 2001

Key words: electrochemical techniques, hydrogen diffusion coefficient, metal hydride electrode

Abstract

The constant potential discharge technique, constant current discharge technique and electrochemical impedance spectroscopy were employed to determine the hydrogen diffusion coefficient in a metal hydride electrode of $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy with various depth of discharge (DOD) at room temperature and with a specific DOD at various temperatures. The results were compared and the advantages and disadvantages of these techniques were also discussed.

1. Introduction

In recent years, nickel–metal hydride (Ni/MH) batteries have attracted attention because of their advantages over conventional nickel–cadmium (Ni/Cd) batteries and lead-acid batteries in discharge capacity, energy density, power density, high-rate dischargeability, cycle life and environmental compatibility, and therefore extensive research has been carried out. In general, the characteristics of the Ni/MH battery, such as discharge capacity, rate-dischargeability, cycle life etc., depend on the properties of the metal hydride electrode [1]. They are determined not only by the kinetics of the process occurring at the alloy–electrolyte interface, but also by the hydrogen diffusion behaviour within the bulk of the alloy, and the latter is believed to play an important role in hydriding–dehydriding process of the metal hydride electrode [2]. The hydrogen diffusion coefficient is an important parameter in understanding the diffusion behaviour of hydrogen atoms in the metal hydride electrode, and the larger the diffusion coefficient, the faster is the hydrogen diffusion and the better is the electrode performance [3]. Thus, determination of the hydrogen diffusion coefficient is crucial for the study of hydrogen storage alloys and metal hydride electrodes.

Up to now, hydrogen diffusion in various hydrogen-storage alloys has been studied using various methods such as nuclear magnetic resonance (NMR) [4, 5], quasic-elastic neutron scattering (QNS) [6, 7] and various electrochemical techniques. Significant discrepancies, however, exist between the reported values of the hydrogen diffusion coefficient in AB_5-type hydrogen storage alloys measured with these techniques at ambient temperature. Sometimes, even the results for the same alloy determined using the same method are quite different. Using NMR, Bowman et al. [4] and Khodosov et al. [5] reported 7×10^{-9} cm^2 s^{-1} and 5×10^{-6} cm^2 s^{-1} for the hydrogen diffusion coefficient in $LaNi_5$, respectively. Lebsanft et al. [6] obtained a value of 6.1×10^{-9} cm^2 s^{-1} for the hydrogen diffusion coefficient in $LaNi_5$ with QNS, but Fischer et al. [7] reported that the hydrogen diffusion coefficient in $LaNi_5$ was on the order of 10^{-6} cm^2 s^{-1} using the same technique. Using constant current discharge technique, Zheng et al. [8] obtained a value of 6.75×10^{-11} cm^2 s^{-1} for the hydrogen diffusion coefficient in $LaNi_{4.27}Sn_{0.24}$, but Ura et al. [9] and Iwakura et al. [10] concluded that the diffusion coefficients of hydrogen in $LaNi_5$ and $MmNi_{4.2}Al_{0.5}M_{0.3}$ ($M = Cr$, Mn, Fe, Co, Ni) are of the order of 10^{-8} cm^2 s^{-1} using constant potential discharge technique. Using electrochemical impedance spectroscopy (EIS), Haran et al. [11] reported that the diffusion coefficient of hydrogen in $LaNi_{4.27}Sn_{0.24}$ varies from 1.671×10^{-10} cm^2 s^{-1} at 45% SOC (state of charge) to 3.851×10^{-11} cm^2 s^{-1} at 0% SOC.

In the present work, the hydrogen diffusion coefficient in a metal hydride electrode with $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy was determined using the constant potential discharge technique, constant current discharge technique and electrochemical impedance spectroscopy. The results are compared and the advantages and disadvantages of these techniques are also discussed.

2. Theory

Assuming that the alloy particles in the metal hydride electrode are in spherical form with uniform size, the diffusion equation can be written as

$$\frac{\partial C(r,t)}{\partial t} = D\frac{\partial^2 C(r,t)}{\partial r^2} + D\frac{2}{r}\frac{\partial C(r,t)}{\partial r} \tag{1}$$

where D is the hydrogen diffusion coefficient (cm^2 s^{-1}), r is the distance from the centre of the sphere (cm), t is time (s), and $C(r,t)$ is the hydrogen concentration at the site of r in the alloy and at the time of t.

The diffusion equation (1) can be solved with appropriate initial conditions and boundary conditions resulting in a final formula used to calculate diffusion coefficient.

2.1. *Constant potential discharge technique (CPDT)*

When the surface of the electrode is held at a constant potential, the hydrogen concentration on the electrode surface is also constant (C_s). Assuming that the initial hydrogen concentration in the bulk of the alloy is uniform (C_0), the solution of the diffusion equation (1) given by Schneider [12] can be rearranged to give the following [13]:

$$i = \pm\frac{6FD}{d^2}(C_0 - C_s)\sum_{n=1}^{\infty}\exp\left(-\frac{n^2\pi^2 Dt}{d^2}\right) \tag{2}$$

When t is large enough, Equation 2 reduces to

$$\log i = \log\left[\pm\frac{6FD}{\delta d^2}(C_0 - C_s)\right] - \frac{\pi^2 D}{2.303\, d^2}t \tag{3}$$

where i is the diffusion current after the application of a constant potential, d is the sphere radius of the alloy particles, δ is the diffusion layer thickness, the ± sign indicates the charge (−) or discharge (+) process. So, D can be calculated from the slope of log i against t if the sphere radius d is known.

2.2. *Constant current discharge technique (CCDT)*

When the discharge process is carried out at constant current, it is reasonable to assume that a constant flux of hydrogen flows through the electrode surface. Supposing the initial hydrogen concentration in the bulk of the alloy is uniform (C_0), the diffusion equation (1) can be solved and the value of D can be evaluated for large transition time τ [12] with the known value of sphere radius d by

$$D = \frac{d^2}{15\left(\frac{Q_0}{i_d} - \tau\right)} \tag{4}$$

where Q_0 is the initial capacity in the electrode (C), i_d is the constant discharge current (A), and τ is the transition time (s), that is, the time required for hydrogen concentration on the electrode surface to become zero and a drastic potential change occurs to compensate the hydrogen surface concentration decrease in order to keep the constant discharge current.

2.3. *Electrochemical impedance spectroscopy (EIS)*

When a small sinuous a.c.-voltage is imposed on an electrode system, the concentration gradient of hydrogen at the electrode surface can be expressed as

$$\left[\frac{\partial C(r,t)}{\partial r}\right]_{r=d} = \frac{I_{\max}\sin\omega t}{nFD} \tag{5}$$

where $I_{\max}$ is the amplitude of responding a.c. current, ω is angular frequency, F is faradaic constant (96 485 C mol^{-1}), n is the number of transferred electrons. Similarly, on the assumption that the initial hydrogen concentration in the bulk alloy is uniform (C_0), the diffusion equation (1) can be solved and a formula for the impedance of the electrode will be obtained which can be used to evaluate the hydrogen diffusion coefficient.

Theoretically, the electrochemical impedance spectrum of an electrode system can be illustrated as Figure 1 [14]. It is obvious that charge transfer controls the electrode reaction at high frequency and semiinfinite diffusion, which appears as a straight line with slope of 1 (noted as the 45° line in the following paragraphs) dominates the electrode process at medium frequencies. At low frequency the finite size of the alloy particle limits the extent of the diffusion behaviour and a 'redox capacitance', displayed as a vertical line is observed. In an experimental Nyquist plot, however, because of porosity [15] or fractal geometry effects [16, 17] of the

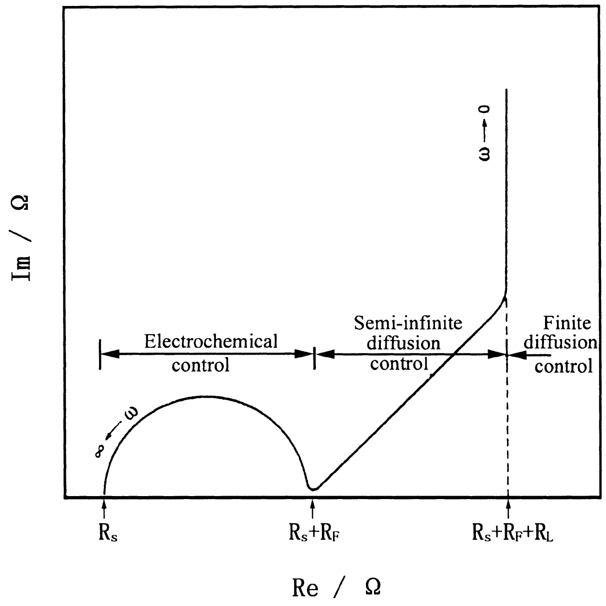

Fig. 1. Theoretical Nyquist plot of an electrode system.

electrode surface, the 'redox capacitance' rarely appears and the semiinfinite diffusion-controlled region deviates from the 45° line. But, the fact is that the slope of the diffusion-controlled impedance increases gradually. The region between the 45° line and the vertical line is generally considered as the transition region which contains information on hydrogen diffusion behaviour.

According to Haran et al. [11], the slope of the Nyquist plot in the transition region can be expressed as

$$\frac{\mathrm{d(Im)}}{\mathrm{d(Re)}} = \frac{T_4[-T_3 + (S_3S_5 + S_4S_7 - S_1S_6 + S_2S_8)\psi] - 2T_3(S_4S_3 + S_2S_1)\psi}{T_4[-T_5 + (S_3S_6 + S_4S_8 - S_1S_5 + S_2S_7)\psi] - 2T_5(S_4S_3 + S_2S_1)\psi} \tag{6}$$

where Im and Re are the real components and imaginary components of the electrochemical impedance, respectively, d(Im)/d(Re) is the slope of the Nyquist plot, all T_i ($i = 3$–5) and S_j ($j = 1$–8) are functions with the only unknown variable ψ, and

$$\psi = \sqrt{\frac{\omega d^2}{2D}} \tag{7}$$

Equation 6 involves only the unknown parameter ψ (given by Equation 7) and can be used to extract the diffusion coefficient by equating it to the slope in the transition region [11].

3. Experimental details

The $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy was prepared from component metals of purity of at least 99.9 wt % in a vacuum medium frequency induction furnace. To assure the homogeneity of the alloy, the ingot was turned over and remelted five times. Then, the ingot was crushed and ground mechanically followed by capturing particles with two sequential sieves, and the particle size of the resulting powders was measured by a Malvern particle analyser Mastersizer2000, which gave an average particle diameter of 125.2 μm.

The metal hydride electrodes were prepared by mixing the alloy powder and nickel powder (Inco Company, Canada) in a weight ratio of 1:4 followed by pressing at room temperature onto both sides of a nickel foam under a pressure of 1.8×10^8 Pa for 1 min. The resulted pellet had a diameter of 15 mm and a thickness of 1.68 mm and weighed 1.5 g.

Electrochemical measurements on the metal hydride electrodes were performed in a glass cell with three compartments by means of a EG&G Princeton Applied Research potentiostat/galvanostat (model 273A) and lock-in amplifer (model 5210) driven by M270 software or Powersine in the Powersuite package. In addition to the metal hydride electrode as working electrode, a nickel hydroxide electrode, with an excessive capacity, was employed as the counter electrode, a Hg/HgO (6 M KOH) as the reference electrode and 6 M KOH solution as the electrolyte.

The activated metal hydride electrode was charged at 60 mA g^{-1} (based on the amount of alloy powder) for 7.5 h, after a rest of 10 min, it was discharged at 60 mA g^{-1} for a certain period of time to reach a specified depth of discharge (DOD) at room temperature. After the open-circuit potential (OCP) was stabilized (i.e., the variation of the potential was less than 1 mV in 1 h), the working electrode was discharged at 15 mA g^{-1} to the cut-off potential of −0.6 V vs Hg/HgO. The time dependence of the potential was recorded to determine the diffusion coefficient with CCDT. Alternatively, the electrochemical impedance of the electrode was measured, followed by a constant potential discharge, the potential step amplitude of which was 50 mV, since the a.c. impedance technique has been proved to be capable of holding the electrode at constant state during the measurement [18]. The impedance spectra of the electrodes were recorded from 100 kHz to 0.001 Hz with a.c. perturbation of ±5 mV as amplitude.

For the experiments at various temperatures, the electrodes were initially charged at 60 mA g^{-1} for 7.5 h at ambient temperature, then the electrochemical cell was moved to a container at a constant specified temperature controlled by a thermostat. After sufficient time for the OCP to become stabilized, the electrodes were discharged at 15 mA g^{-1} to –0.6 V vs Hg/HgO. Alternatively, after the electrodes had been discharged to 50% DOD at room temperature, the electrochemical cell was moved to the container at a constant specified temperature. When the OCP had stabilized, similar electrochemical impedance and constant potential discharge measurements were carried out.

4. Results

4.1. *Determination of hydrogen diffusion coefficient with CPDT*

The potential step amplitude of 50 mV was selected after preliminary tests with different amplitudes were carried out. The potentiostatic discharge curves of a $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy electrode at various DOD are shown in Figure 2.

The current–time response as a semilogarithmic plot (log i against t) is a straight line when t is larger than 250 s. The hydrogen diffusion coefficients in the electrode evaluated from the slope of the linear part in Figure 2 are represented in Figure 3. The diffusion coefficients range from 1.11×10^{-9} cm^2 s^{-1} (0% DOD) to 1.01×10^{-8} cm^2 s^{-1} (80% DOD) and increase with the increase in DOD. This is in good agreement with the results of Iwakura [10] that the hydrogen diffusion

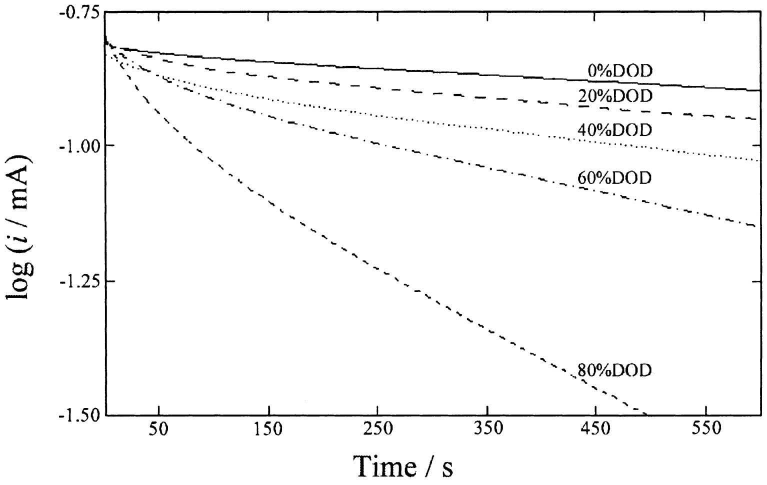

Fig. 2. Time dependence of responding current of $\mathrm{MlNi_{3.65}Co_{0.75}\,Mn_{0.4}Al_{0.2}}$ alloy electrode at various DOD after application of a potential step of 50 mV at room temperature.

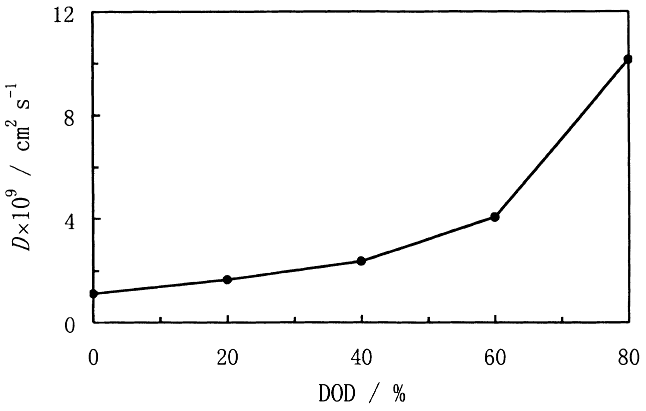

Fig. 3. DOD dependence of hydrogen diffusion coefficient in $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy electrode determined by CPDT at room temperature.

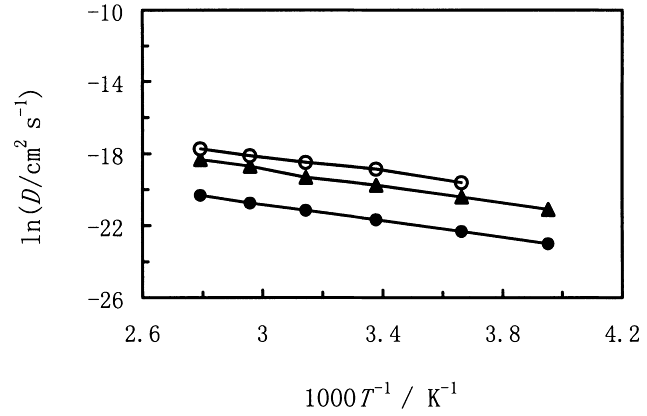

Fig. 4. Temperature dependence of hydrogen diffusion coefficient in $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy electrode determined by various electrochemical techniques (states of the measured electrode: (▲) CPDT—50% DOD, (●) CCDT—0% DOD, (○) EIS—50% DOD).

coefficient in $\mathrm{MmNi_{4.2}Al_{0.5}M_{0.3}}$ (M = Cr, Mn, Fe, Co, Ni) increases with decrease in hydrogen concentration in it.

The hydrogen diffusion coefficients in $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy with 50% DOD at various temperatures were also evaluated and are shown in Figure 4. The hydrogen diffusion coefficient increases with the increase in temperature, and an approximately linear relationship exists between ln D and the reciprocal of the absolute temperature ($1/T$). According to the Arrhenius equation, the activation energy for hydrogen diffusion in $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy with 50% DOD was calculated to be 19.8 kJ mol^{-1}. This is in good agreement with 19.9 kJ mol^{-1} for the hydrogen diffusion activation energy in $\mathrm{MmNi_{4.2}Al_{0.5}Co_{0.3}}$ determined by Iwakura [10].

4.2. *Determination of hydrogen diffusion coefficient with CCDT*

The constant current discharge curves of $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy at various DOD are shown in Figure 5 and the calculated hydrogen diffusion coefficient as a function of DOD are shown in Figure 6. The hydrogen diffusion coefficient also increases with increase in DOD. But, in comparison with the results obtained with CPDT, which are shown in Figure 3, it increases more slowly.

The estimated hydrogen diffusion coefficients in $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy with 0% DOD as a function of temperature are also shown in Figure 4 along with the results of other techniques and the activation energy for hydrogen diffusion in this electrode evaluated with the Arrhenius equation is 19.0 kJ mol^{-1}. This is in good agreement with the results of CPDT.

4.3. *Determination of hydrogen diffusion coefficient with EIS*

Nyquist plots of the $\mathrm{MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}}$ alloy electrode with various DOD at room temperature are shown in Figure 7. Similarly to Motupally et al. [18], the data points with slopes in the range from −1.5 to −2.5 in the transition region were used for determining the

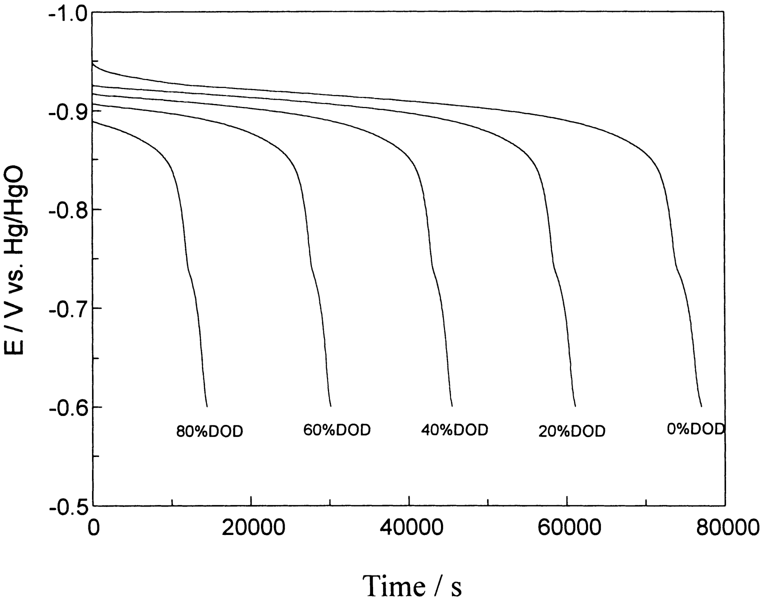

Fig. 5. Constant current discharge curves of $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode with various DOD at 15 mA g^{-1} at room temperature.

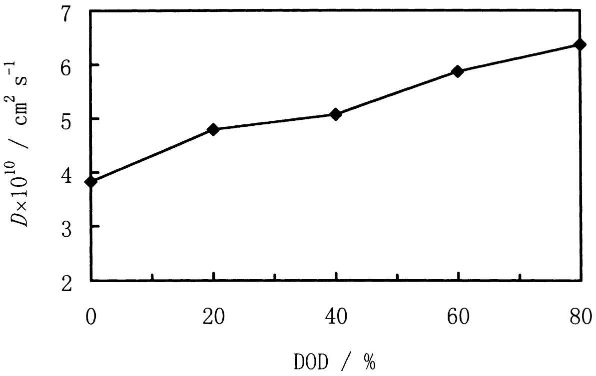

Fig. 6. DOD dependence of hydrogen diffusion coefficient in $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode determined by CCDT at room temperature.

diffusion coefficients by the following procedure [19]: the real and imaginary parts of the EIS data in the transition region were fitted to a polynomial function

$$\mathrm{Im} = a\mathrm{Re}^2 + b\mathrm{Re} + c \tag{8}$$

Thus, the fitting parameters a, b and c were determined and then the slope at each data point were obtained by differentiating the polynomial function. Next, Equation 6 was solved for ψ at each data point. Finally, with the known value of ψ, angular frequency ω and radius of the spherical alloy particles d, the hydrogen diffusion coefficient D was calculated using Equation 7.

The calculated values of D as a function of DOD are shown in Figure 8. It can be seen that increasing DOD from 0% to 80% caused the hydrogen diffusion coefficient at room temperature to increase from 3.46×10^{-9} cm^2 s^{-1} to 2.0×10^{-8} cm^2 s^{-1}. The evaluated values of D for the electrode with 50% DOD at various temperatures are shown in Figure 4 along with the results of the other two techniques. According to the Arrhenius equation, the activation energy for hydrogen diffusion in $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy with 50% DOD is 17.9 kJ mol^{-1}.

5. Discussion

5.1. *DOD dependence of hydrogen diffusion coefficients*

Three electrochemical measurements reported here unanimously indicated that the hydrogen diffusion coefficient in the $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode increases with increase in DOD. The probable reason for this is that at lower DOD the hydrogen concentration is higher and the number of vacant sites available for hydrogen to occupy is less than that at higher DOD. This makes hydrogen diffusion in the metal hydride electrode with lower DOD more difficult. On the other hand, hydrogen diffusion in a metal hydride electrode might be related to the transformation of the electrode active material between metal hydride in the β phase and solid solution in the α phase and the interaction between the absorbed hydrogen atoms and the constituent metals.

5.2. *Comparison of the used electrochemical techniques*

According to this study, the values of hydrogen diffusion coefficients in the $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode determined by various electrochemical techniques are not exactly the same. In addition to the uncertainty or inaccuracy of some parameters used in these techniques as a cause, this is mainly due to the fact that each technique has its own essential conditions and proper application conditions, and different simplifications were made during the deduction of the formulae

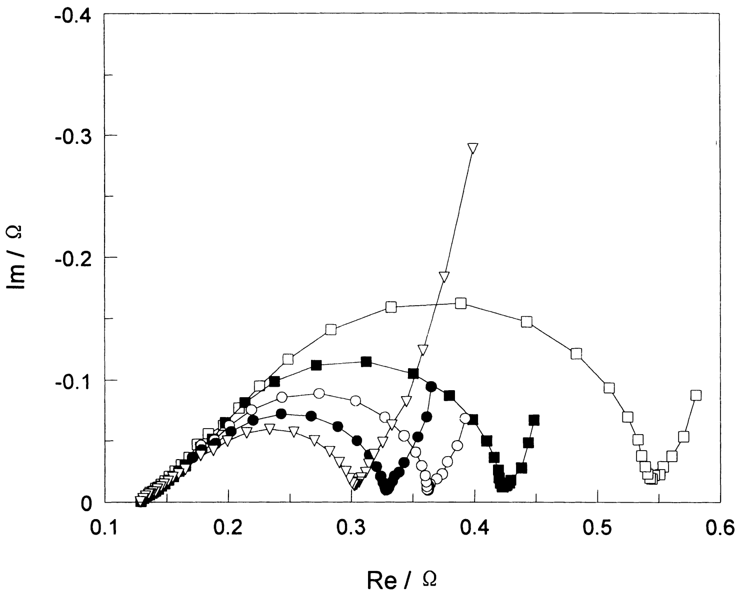

Fig. 7. Nyquist plots of $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode with various DOD at room temperature (the amplitude of a.c. perturbation was 5 mV and the frequency covered from 100 kHz to 0.001 Hz). Key: (□) 0% DOD, (■) 20% DOD, (○) 40% DOD, (●) 60% DOD and (▽) 80% DOD.

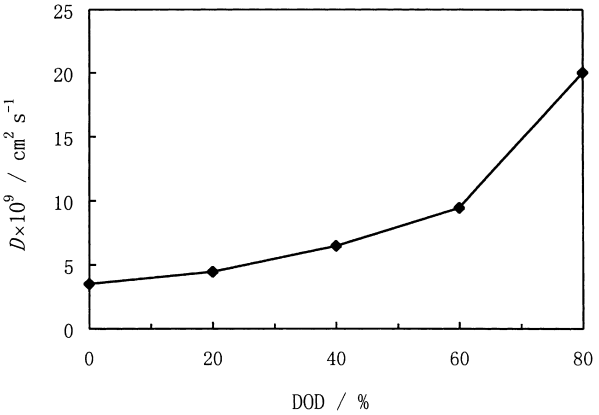

Fig. 8. DOD dependence of hydrogen diffusion coefficient in $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode determined by EIS at room temperature.

for calculation of the D value in individual technique. This makes some difference between these techniques.

For the CPDT technique, the hydrogen concentration dependence of D was neglected during the derivation of Equation 3 [8]. However, CPDT measurement was carried out along with the changing hydrogen concentration in the electrode. Thus, the calculated hydrogen diffusion coefficient is an average value over this hydrogen concentration range and cannot accurately reflect its DOD dependence.

CCDT measurements were carried out under successively changing hydrogen concentrations that led to an average diffusion coefficient over the previous DOD and the fully discharged state. So, similarly to CPDT, CCDT cannot be used to exactly determine the DOD dependence of hydrogen diffusion coefficient. Besides, Equation 4 is valid only for small discharge currents which increase the duration of the experiment, and the difficulty in accurately defining the transition time τ usually leads to errors in the calculated diffusion coefficient [8]. Further analysis of the results indicates that the values of D determined from CCDT increase much more slowly than that from CPDT and EIS. The probable reason is that the diffusion coefficients calculated from this technique are mainly determined from the values of $(Q_0/i_d - \tau)$ which are embodied at the late stages of the discharge process and are almost the same for electrodes of the same alloy with various DOD. This makes CCDT unsuitable for comparison of hydrogen diffusion coefficients in metal hydride electrodes with various DOD.

EIS measurement was carried out with a small a.c. voltage perturbation. The small positive and negative deviations from the OCP ensured that the electrode stayed at almost constant state during the measurement. This is the distinctive characteristic of the EIS technique. Thus, the hydrogen diffusion coefficient determined by EIS can accurately reflect its DOD dependence and the hydrogen diffusion behaviour in the metal hydride electrode in the given state.

In brief, all three above-mentioned electrochemical techniques can be used for studying hydrogen diffusion behaviour in a metal hydride electrode. However, for investigation of the DOD dependence of the hydrogen diffusion coefficient, EIS is most appropriate.

6. Conclusions

The hydrogen diffusion coefficient in $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode increases with increase in DOD and temperature, and the activation energies for hydrogen diffusion in this electrode lie in the range $17.9 \sim 19.8$ kJ mol^{-1}.

Hydrogen diffusion coefficients in $MlNi_{3.65}Co_{0.75}Mn_{0.4}Al_{0.2}$ alloy electrode determined by CPDT, CCDT and EIS differ. CPDT and CCDT can only measure an average value of diffusion coefficient, which means that the results are not capable of accurately reflecting their DOD dependence. For investigation of the DOD dependence of the hydrogen diffusion coefficient, EIS is more appropriate than CPDT and CCDT.

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