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Hydrogen transport through Pd-Ni alloy electrodeposited on Pd substrate

Abstract Hydrogen transport through a Pd-Ni alloy electrodeposited on a Pd substrate (Pd-Ni/Pd bilayer symmetric electrode) has been investigated using cyclic voltammetry and a.c. impedance spectroscopy combined with the electrochemical hydrogen permeation method. The permeation build-up current transients and the measured impedance spectra were analyzed using the time-lag method for the bilayer electrode and a complex non-linear least squares data-fitting method based upon the derived Faradaic admittance for the hydrogen absorption into and diffusion through the bilayer electrode under the permeable boundary condition, respectively. The value of the hydrogen diffusivity in the Pd-Ni layer was lower than that in the Pd layer. Furthermore, the values of the charge transfer resistance and equilibrium absorption constant for the Pd-Ni/Pd bilayer electrode were higher than those for the Pd single layer electrode. From the experimental results, the role of the thin $Ni(OH)_2$ film formed on the Pd-Ni layer surface in the hydrogen transport through the Pd-Ni/Pd bilayer electrode is discussed in terms of its passivating effect and extremely large hydrogen solubility.

Key words Hydrogen permeation · Hydrogen absorption · Hydrogen diffusion · a.c. impedance · Pd-Ni/Pd bilayer · Passivating $Ni(OH)_2$ film

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Introduction

Electrodeposited palladium (Pd) and Pd alloys have recently received much attention for electrical contact applications as a substitute for gold (Au) in view of their excellent wear resistance and good solderability combined with their low density [1–4]. Especially, electrodeposited Pd-nickel (Ni) has been reported to produce an alloy which is brighter, harder and more ductile, less catalytic towards hydrogen evolution reaction and less susceptible to the formation of microcracks resulting from the co-deposition of hydrogen [2], and has many advantages over pure Pd. However, the fear of segregated nickel oxidation has delayed their introduction.

Hydrogen transport through the metal membranes has been generally investigated [5–8] by the electrochemical hydrogen permeation method in metal-electrodeposited film bilayer electrodes. Song and Pyun [6] investigated hydrogen permeation through a bilayer of Fe/electrodeposited Ni by measuring the permeation build-up current transients. They concluded that hydrogen permeation through the bilayer is impeded by the barrier effect of the electrodeposited Ni. From the analysis of the hydrogen permeation through an $Ni(OH)_2$/Pd film bilayer [8], it was reported that hydrogen permeation through the bilayer is retarded by that through the $Ni(OH)_2$ film owing to its low hydrogen diffusivity.

In the field of electrochemistry, the measurement of the a.c. impedance at controlled potentials is an important experimental route to obtaining information about the electrochemical reaction mechanism. Lim and Pyun [9, 10] theoretically derived the Faradaic admittance for hydrogen absorption into and diffusion through a metal membrane electrode using a kinetic approach under the permeable boundary condition and analyzed the hydrogen absorption reaction into a Pd membrane electrode using the derived equation. Furthermore, Pyun et al. [unpublished work (1997)] investigated the hydro-

gen diffusion through a Pd-Au alloy electrodeposited on a Pd substrate under the permeable boundary condition using a.c. impedance spectroscopy. Hydrogen diffusion through the Pd-Au/Pd bilayer is retarded by a raised activation energy for hydrogen diffusion due to a local rearrangement of conduction electrons around the Au atoms and hydrogen, indicating that the Au atoms in the Pd-Au layer act as effective trap sites [Pyun S-I, Lee W-J, Yang T-H (1997) unpublished work]. By contrast, it was reported that hydrogen diffusion through the Pd-Ni alloy is not affected by the local rearrangement of conduction electrons by alloying Ni [11].

The present work is concerned with hydrogen transport through a Pd-Ni alloy electrodeposited on a Pd substrate (Pd-Ni/Pd bilayer symmetric electrode) under the permeable boundary condition with reference to a Pd single layer symmetric electrode. For this purpose, cyclic voltammetry and combined a.c. impedance and electrochemical permeation build-up transient measurements were carried out in aqueous 0.1 M NaOH solution on two kinds of bilayer and single layer electrode specimens. The permeation build-up current transients and the measured impedance spectra were analyzed using the time-lag equation for the bilayer electrode and the derived Faradaic admittance equation, respectively. On the basis of the hydrogen diffusivity obtained by using the time-lag equation, and such parameters, fitted to the calculated impedance spectra based upon the derived Faradaic admittance equation, as hydrogen diffusivity, charge transfer resistance and equilibrium absorption constant, the role of the thin passivating $Ni(OH)_2$ film formed on the Pd-Ni layer surface in the hydrogen transport through the Pd-Ni/Pd bilayer electrode was explored in view of its passivating effect and extremely large hydrogen solubility.

Experimental

The 99.98% pure Pd foil (Aldrich) of 50 μm thickness used as the substrate for the bilayer symmetric electrode as well as the single layer symmetric electrode was annealed under high vacuum (10^{-5} Pa) at 650°C for 2 h, cooled in the furnace, mechanically polished with silicon carbide of 2000 grit to eliminate surface oxide films, and then chemically etched in concentrated nitric acid for 30 s.

The Pd-25 atom% Ni alloy layer of about 10 μm thickness was electrodeposited on the Pd substrate (Pd-Ni/Pd bilayer symmetric electrode) from an ammoniacal bath by applying a pulse current with the average current density of 5 mA/cm^2, duty cycle of 80% and pulse period of 10 ms.

Cyclic voltammograms were obtained from the Pd-Ni/Pd bilayer electrode in aqueous 0.1 M NaOH solution with a scan rate of 0.02 V s^{-1} in the applied potential range of −1.5 to 1.0 V$_{SCE}$ using a Potentiostat/Galvanostat (EG & G PAR, M273).

The electrochemical permeation cell used in this study was similar to several cells previously described in the literature [12, 13]. The two kinds of Pd single layer and Pd-Ni/Pd bilayer symmetric membrane electrode specimens separated the permeation cell into anodic and cathodic compartments and were in contact with aqueous 0.1 M NaOH solution of pH 13. The solution was de-aerated by bubbling with nitrogen gas before and during the experiments. The surface area of the membrane specimen exposed

to electrolyte was 3.14 cm^2 on both sides. A platinum wire and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. The counter electrodes were separated from the cathodic and anodic compartments by a glass frit.

In experimental operation during electrolysis, the cathodic (entrance) side (one side of the Pd single layer electrode or the Pd-Ni side of the Pd-Ni/Pd bilayer electrode) was subjected to a constant potential of −0.75 to −0.96 V$_{SCE}$ with a Solartron 1286 ECI, while the anodic (detection) side (the Pd sides of the two kinds of electrodes 1) were potentiostatically kept at a constant potential of 0.05 V$_{SCE}$ by using a Wenking LT 78 potentiostat, which allowed any hydrogen coming through both electrodes to be oxidized to H$^+$, keeping the concentration of hydrogen at actually zero.

After steady-state hydrogen permeation was attained, the electrochemical impedance measurements were started in the cathodic compartment using a Solartron 1255 FRA in conjunction with the Solartron 1286 ECI. A single sinusoidal potential of 10 mV peak-to-peak was superimposed on the constant potential of −0.75 to −0.96 V$_{SCE}$ over the frequency range from 10^{-3} to 10^4 Hz. The frequency was scanned from high to low value. To avoid grounding problems, the Solartron 1286 ECI was operated in the main grounded mode and the Wenking potentiostat was in the floating mode. All experiments were carried out at room temperature.

Results and discussion

A typical cyclic voltammogram of the Pd-Ni/Pd bilayer electrode specimen in aqueous 0.1 M NaOH solution is presented in Fig. 1. For scans towards positive potentials the Pd-Ni/Pd bilayer electrode showed two broad peaks at −0.60 and 0.55 V$_{SCE}$, respectively. These peaks are related to oxidation of hydrogen in the electrode specimen and oxidation of $Ni(OH)_2$ to NiOOH, respectively. As the potential scan reversed, the cathodic current peaks corresponding to the formation of $Ni(OH)_2$ and decomposition of Pd oxide occurred at about 0.35 and −0.55 V$_{SCE}$, respectively. The appearance of the redox peak of the NiOOH/$Ni(OH)_2$ couple indicates that a stable $Ni(OH)_2$ film is formed on the
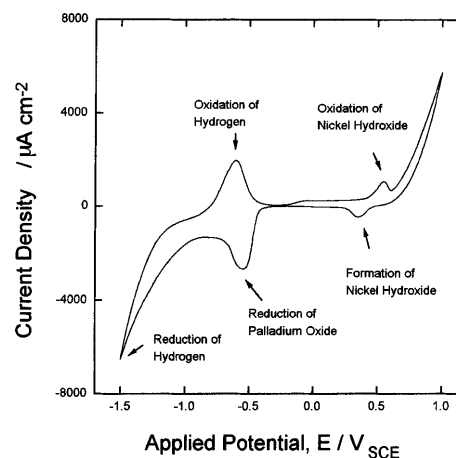

Fig. 1 Cyclic voltammogram obtained from the Pd-Ni/Pd bilayer electrode specimen in aqueous 0.1 M NaOH solution with a scan rate of 0.02 V s^{-1}
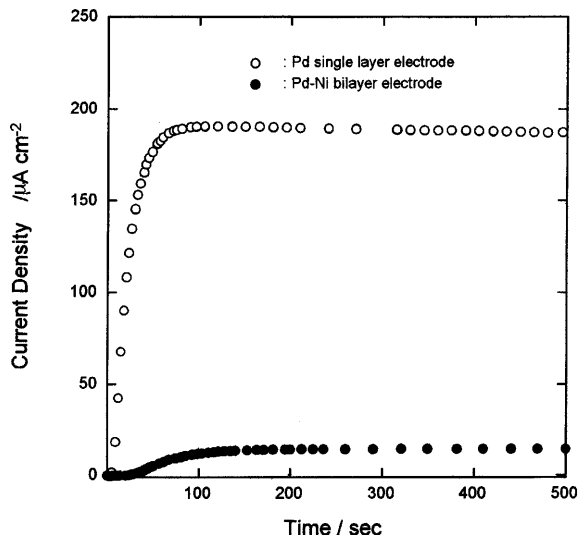
Fig. 2 Typical permeation build-up current transients obtained from the two kinds of Pd single layer and Pd-Ni/Pd bilayer electrode specimens in aqueous 0.1 M NaOH solution at a hydrogen charging potential of -0.85 V_{SCE}
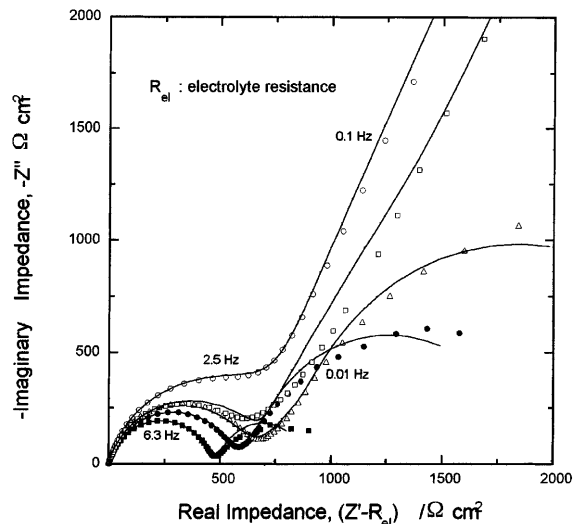

Fig. 3 Impedance spectra in Nyquist presentation for the hydrogen absorption into and diffusion through the Pd-Ni/Pd bilayer electrode specimen in aqueous 0.1 M NaOH solution at various hydrogen charging potentials of ○ -0.75 V_{SCE}, □ -0.80 V_{SCE}, △ -0.85 V_{SCE}, ● -0.92 V_{SCE}, ■ -0.96 V_{SCE}. *Solid line* represents the CNLS fitted spectra based upon Eq. 4 combined with Eq. 3

Pd-Ni layer surface over the whole potential range of -0.75 to -0.96 V_{SCE} applied in this work.

Figure 2 shows typical hydrogen permeation build-up current transients for the Pd single layer and the Pd-Ni/Pd bilayer electrodes in aqueous 0.1 M NaOH solution at a hydrogen charging potential of -0.85 V_{SCE}. The steady-state permeation current for the latter was lower than that for the former. This indicates that the thin passivating $Ni(OH)_2$ film formed on the Pd-Ni layer surface acts as an effective barrier to the hydrogen transport. According to the previous works by Bockris and co-workers [14–16], this prepassive film is formed at the first stage in the anodic passivation of Ni.

The classical method of obtaining the hydrogen diffusivity in metal membrane is to evaluate the time-lag, one of the characteristic time intervals obtained from the permeation current transients. The time-lags t_L for the single layer [5, 12] and bilayer [6, 8, 13, 17] under the potentiostatic boundary condition are expressed as follows

$$t_L = l^2/(6D) \qquad \text{for the single layer} \qquad (1)$$

and

$$t_L = \left[\frac{l_1}{D_1} + \frac{Kl_2}{D_2}\right]^{-1}\left[\frac{l_1^2}{D_1}\left\{\frac{l_1}{6D_1} + \frac{Kl_2}{2D_2}\right\} + \frac{l_2^2}{D_2}\left\{\frac{l_1}{2D_1} + \frac{Kl_2}{6D_2}\right\}\right] \qquad \text{for the bilayer} \qquad (2)$$

where l denotes the thickness of layer, D is the hydrogen diffusivity, subscripts "1" and "2" refer to the Pd-Ni layer and Pd layer, respectively, and K is the hydrogen solubility ratio at the Pd-Ni/Pd interface. We assumed that at all times the ratio of the hydrogen concentration on the Pd-Ni side to that on the Pd side just near the interface is equal to the hydrogen solubility ratio K at the Pd-Ni/Pd interface [18].

Figure 3 shows the Nyquist plots obtained from the Pd-Ni/Pd bilayer electrode in aqueous 0.1 M NaOH solution in the applied cathodic potential range of -0.75 to -0.96 V_{SCE}. The first arc appearing in the high frequency regions corresponds to the charge transfer reaction, and the second arc in the low frequency regions is presumably due to relaxations arising from the hydrogen adsorption-absorption and hydrogen diffusion through the Pd-Ni/Pd bilayer electrode. With decreasing potential, the sizes of the first arc representing the charge transfer reaction and of the second arc including the mass transfer reaction became smaller. The Warburg impedance for the hydrogen diffusion in general followed a straight line with a slope of 45° in the low frequency regions of the Nyquist plots.

In view of the hydrogen absorption and diffusion mentioned above, the Faradaic admittance Y_f for the diffusion-controlled indirect hydrogen absorption into the Pd-Ni/Pd bilayer electrode under the permeable boundary condition with the assumption of no hydrogen evolution was derived using Lim and Pyun's kinetic approach [9] as follows:

$$Y_f = \frac{1}{R_{ct}}\left(1 - \frac{B}{j\omega + B + \frac{J_s^t}{\Gamma_{eq}}}\right) \qquad (3)$$

with

$$R_{ct} = -\frac{1}{F\left(\frac{\partial v_1}{\partial \eta}\right)}, \quad B = -\left(\frac{\partial v_1}{\partial \Gamma}\right),$$

and

$$l_{eq} = \frac{1}{K_{eq}} = \frac{\Gamma}{C_s} = \frac{\Gamma_{max}\theta}{C_s} = \frac{\Gamma_{max}k_{-3}}{k_3}$$

where R_{ct} is the resistance of the charge transfer at the electrolyte/electrode interface, l_{eq} the inverse of the equilibrium absorption constant K_{eq}, J_s^t the oscillated flux of hydrogen, v_1 the Volmer adsorption reaction rate, Γ the surface concentration of adsorbed hydrogen, C_s the concentration of hydrogen in the electrode, Γ_{max} the maximum surface concentration of adsorbed hydrogen, θ the surface coverage, and k_3 and k_{-3} the forward and backward rate constants of hydrogen transfer from adsorbed to absorbed state and from absorbed to adsorbed state, respectively. Y_f for the single layer is taken from the previous work [9].

The double layer impedance, $Z_{dl} = 1/(j\omega C_{dl})$, is represented by the constant phase element (CPE), defined as $Z_{CPE} = 1/T(j\omega)^{\varphi}$ [19], where $T = C_{dl}^{\varphi}(R_s^{-1} + R_{ct}^{-1})^{1-\varphi}$ and φ is the fractional parameter representing the degree of the depression of a semicircle. Hence, the total impedance Z_{total} is expressed as

$$Z_{total} = R_{el} + \frac{1}{T(j\omega)^{\varphi} + Y_f} \tag{4}$$

where R_{el} is the resistance of the electrolyte. The real (Z') and imaginary (Z'') components of the impedance spectra in the complex plane measured at each applied potential were analyzed using a complex non-linear least squares (CNLS) data-fitting method suggested by Macdonald et al. [19] and modified in this laboratory [20] to estimate the kinetic parameters including D_H from Eq. 3.

The hydrogen diffusivities (D_Hs) in the second Pd layer and the first Pd-25 atom % Ni alloy layer are plotted against applied potential in Fig. 4, calculated on the basis of time-lag Eqs. 1 and 2 and the Faradaic admittance (Eq. 3). The value of D_H in the second Pd layer was calculated from the measured t_L and l values to be $(1.76 \pm 0.11) \times 10^{-7}$ cm^2 s^{-1}, which is comparable to that $(1.0 \times 10^{-7}$ to 6.0×10^{-7} cm^2 s^{-1} at 25°C) reported in previous work [21]. It should be stated that the D_H in the first Pd-Ni layer, $(4.1 \pm 1.6) \times 10^{-9}$ cm^2 s^{-1}, obtained from the permeation build-up transients, was smaller by about two orders of magnitude than that, $(1.4 \pm 0.6) \times 10^{-7}$ cm^2 s^{-1}, determined from the measured impedance spectra, which has almost the same value in the Pd-26 atom % Ni alloy, 1.6×10^{-7} cm^2 s^{-1}, at 25°C as that obtained by the electrochemical time-lag method in the previous work [22]. The D_Hs in the first Pd-Ni layer and the second Pd layer obtained from the measured impedance spectra showed negative potential dependences, probably because of the relaxation of the hydrogen evolution reaction.

The hydrogen permeation and a.c. impedance measurements were conducted before and after the steady-state concentration profile for hydrogen was attained,
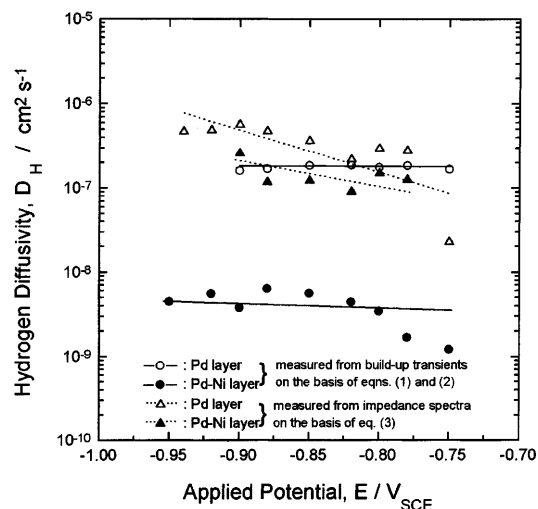

Fig. 4 Dependences of the hydrogen diffusivities D_Hs in the second Pd layer and the first Pd-Ni layer on applied potential, determined from the permeation build-up transients using time-lag Eqs. 1 and 2, and obtained from the impedance spectra using the Faradaic admittance Eq. 3

respectively. Thus, the D_H determined from the impedance spectra is less sensitive to the effect of the impeding sites on the hydrogen transport than that obtained from the hydrogen permeation transients. This result is in good agreement with the previous works on the hydrogen diffusion through a Pd-Au/Pd bilayer [Pyun S-I, Lee W-J, Yang T-H (1997) Unpublished work] using a.c. impedance spectroscopy combined with the electrochemical hydrogen permeation technique and on the hydrogen diffusion through Fe/Fe passivating oxide film [23] using the hydrogen permeation and modulation techniques. The hydrogen diffusion through the Pd-Au layer is impeded by the Au atoms residing in the inner layer due to the local rearrangement of conduction electrons, whereas the hydrogen transport through the Pd-Ni layer is not inhibited by the Ni atoms in the inner layer because Ni and Pd have similar electronic structures, but rather by the passivating Ni(OH)$_2$ film formed on the Pd-Ni layer surface, as shown in Fig. 1.

The value of D_H in the Pd-Ni layer obtained from the permeation build-up transients was markedly reduced as compared to that determined from the measured impedance spectra. The reduced D_H means a prolonged time-lag, which includes the time interval required for reduction of NiOOH to Ni(OH)$_2$. The hydrogen transport through the passivating Ni(OH)$_2$ film proceeds by the process which breaks the bond of OH$^-$—H$^+$ [6]. The hydrogen transport within the hydroxide must occur by the activated hopping of a H$^+$ from one OH$^-$ to another. The necessary breaking of the bond with the initial OH$^-$ causes the mobility of a hydrogen in a hydroxide to be considerably lower than that in the metal phase of that hydroxide [7].

Figure 5 demonstrates the dependences of the charge transfer resistance R_{ct} on applied potential for the
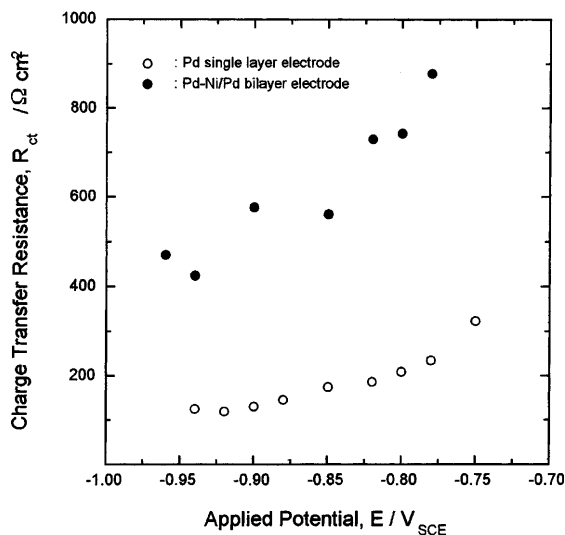
Fig. 5 Applied potential dependences of the charge transfer resistance R_{ct} obtained from the impedance spectra of the Pd single layer and Pd-Ni/Pd bilayer electrode specimens in aqueous 0.1 M NaOH solution

Fig. 6 Dependences of the equilibrium absorption constant K_{eq} on applied potential obtained from the impedance spectra of the Pd single layer and Pd-Ni/Pd bilayer electrode specimens in aqueous 0.1 M NaOH solution

Volmer adsorption reaction on the Pd single layer and Pd-Ni/Pd bilayer electrodes in aqueous 0.1 M NaOH solution. As the applied potential decreased from −0.75 to −0.96 V_{SCE}, the R_{ct} value of the Pd-Ni/Pd bilayer electrode decreased more steeply than that of the Pd single layer electrode. This tendency results from more facile water reduction to electrolytic hydrogen on the Pd-Ni layer surface at a falling applied cathodic potential. Hence, the R_{ct} value of the Pd-Ni/Pd bilayer electrode was greater than that of the Pd single layer electrode, which means that the hydrogen overpotential for the Volmer reaction on the Pd-Ni layer surface is increased due to the passivating $Ni(OH)_2$ film formed on the layer surface [14–16].

Figure 6 presents the dependences of the equilibrium absorption constant K_{eq} on applied potential for the hydrogen absorption reaction into the Pd single layer and Pd-Ni/Pd bilayer electrodes in aqueous 0.1 M NaOH solution. At local equilibrium between the adsorbed and absorbed hydrogen, the equilibrium absorption constant K_{eq} can be defined as the ratio of the hydrogen concentration beneath the surface to that concentration on the surface as previously introduced by Breger and Gileadi [24]. The K_{eq} value of the Pd single layer electrode first slowly increased from 1.14×10^3 to 5.81×10^3 cm^{-1} with decreasing applied potential from −0.75 down to −0.88 V_{SCE} and then abruptly increased to 5.56×10^4 cm^{-1} at −0.90 V_{SCE}. The abrupt increase of the K_{eq} value at −0.90 V_{SCE} indicates that β-PdH is formed because of the increased hydrogen concentration just beneath the electrode surface. This result is in good agreement with the result reported by Yang and Pyun [25]. However, the K_{eq} value of the Pd-Ni/Pd bilayer electrode remained nearly constant, higher by about two orders of magnitude than
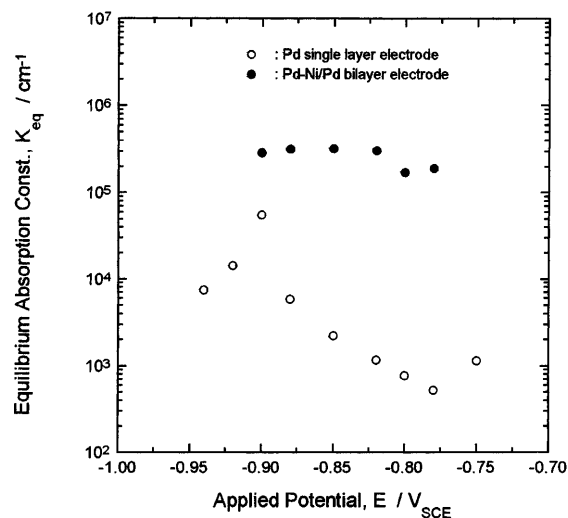
that of the Pd single layer, irrespective of applied potential from −0.75 to −0.96 V_{SCE}. This means that the absorbed hydrogen concentration beneath the Pd-Ni/Pd bilayer electrode surface is increased by the extremely large hydrogen solubility in the passivating $Ni(OH)_2$ [8].

Conclusions

The present work is concerned with hydrogen transport through a Pd-Ni alloy electrodeposited on a Pd substrate (Pd-Ni/Pd bilayer symmetric electrode) in aqueous 0.1 M NaOH solution under the permeable boundary condition as compared to that through a Pd single layer symmetric electrode using cyclic voltammetry and a.c. impedance spectroscopy combined with the electrochemical hydrogen permeation method. From the experimental results the conclusions are drawn as follows.

1. The hydrogen diffusivity D_H in the first Pd-Ni layer is lower than that in the second Pd layer, indicating that hydrogen transport through the Pd-Ni layer is retarded by the OH$^-$-H$^+$ bonds in the passivating $Ni(OH)_2$ film.
2. The value of the charge transfer resistance R_{ct} of the Pd-Ni/Pd bilayer electrode is greater than that of the Pd single layer electrode, which means that the hydrogen overpotential on the Pd-Ni layer surface is raised by the impediment of the Volmer reaction on the passivating $Ni(OH)_2$ film formed on the layer surface.
3. From the greater value of the equilibrium absorption constant K_{eq} for the Pd-Ni/Pd bilayer electrode than

that for the Pd single layer electrode, it is suggested that the concentration of the absorbed hydrogen in the Pd-Ni/Pd bilayer electrode surface is markedly raised by the large hydrogen solubility in the passivating $Ni(OH)_2$ film as compared to that in the Pd single layer electrode surface.

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