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An investigation of the electrochemical kinetics of deuterium insertion into a Pd membrane electrode in 0.1 M LiOD solution by the a.c. impedance technique

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Abstract

The absorption and diffusion of deuterium into and through a palladium membrane electrode respectively in 0.1 M LiOD solution have been studied by means of an a.c. impedance technique in combination with an electrochemical permeation cell. A.c. impedances of the electrode were measured in the overpotential range from -0.07 to 0.23 V (*vs.* a reversible hydrogen electrode) applied to the cathodic side of the palladium membrane after the deuterium permeation current had achieved a steady state. The measured impedance spectra were analysed using a complex non-linear least-squares (CNLS) fitting method based upon a faradaic admittance equation derived previously for a model of diffusion-controlled indirect hydrogen absorption into the palladium membrane via an adsorbed phase. Assuming tridimensional adsorption of deuterium in the interfacial region, the steady state current and deuterium coverage were theoretically calculated as a function of overpotential with the kinetic rate constants of Volmer adsorption, deuterium absorption reaction and deuterium diffusivity in palladium best fitted to the measured impedance spectra. The value of forward rate constant of Volmer adsorption and the ratio of bulk concentration of absorbed deuterium to surface concentration of adsorbed deuterium were determined to be 2.16×10^{-9} mol cm^{-2} s^{-1} and 4.88×10^{2} cm^{-1} respectively, smaller by one order of magnitude than those of hydrogen (1.26×10^{-8} mol cm^{-2} s^{-1} and 2.35×10^{3} cm^{-1} respectively), whereas the value of backward rate constant was 1.74×10^{-9} mol cm^{-2} s^{-1}, similar to that of hydrogen (3.85×10^{-9} mol cm^{-2} s^{-1}). The diffusivity of deuterium in palladium was found to be $(5.10\pm1.04)\times10^{-7}$ cm^{2} s^{-1}, slightly higher than that of hydrogen ($(3.49\pm0.69)\times10^{-7}$ cm^{2} s^{-1}), representing the reverse isotope effect.

1. Introduction

The recently claimed observations of cold fusion [1, 2] in the palladium–hydrogen system when charged with deuterium have generated great interest. Many investigators have attempted to verify these claims. Even now, discussions are controversial. The chance to realize nuclear fusion will depend on the concentration of deuterium in the bulk [1] or surface layer [2]. Hence electrochemical investigations of the mechanism and kinetics of deuterium absorption are fundamentally needed.

Deuterium can actually be treated like hydrogen. The mechanism of hydrogen evolution in aqueous solution [3] involves the formation of an adsorbed hydrogen atom intermediate (Volmer reaction), an electrochemical desorption of hydrogen into solution (Heyrovsky reaction) and a chemical desorption by the combination of two adatoms (Tafel reaction). Additionally, hydrogen enters into the metal through two pathways [4–7]. One involves hydrogen entering into the metal through an adsorbed state [4, 5] and the other involves hydrogen entering directly into the metal without passing through the adsorbed state [6, 7].

In previous work [8] we have noticed a circuit component of Warburg impedance associated with the diffusion process of adsorbed hydrogen from the equivalent circuit analysis of impedance spectra for the hydrogen evolution reaction on a palladium-deposited copper electrode in 0.1 M NaOH solution. However, detailed analysis of the Warburg impedance was not made owing partly to the lack of impedance data in the low frequency range and partly to complicated diffusion boundary condition. Using Armstrong's kinetic approach to faradaic impedance [9], we have recently derived faradaic admittances involving the hydrogen

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absorption reaction (HAR) into a metal membrane electrode under a permeable boundary condition [10] and confirmed their validity by measuring a.c. impedances from a permeation double cell with a palladium membrane in 0.1 M LiOH solution [11].

The present work is aimed at investigating the absorption and diffusion of deuterium into and through a palladium membrane electrode respectively in 0.1 M LiOD solution by measuring the electrode impedance from a permeation double cell and by analysing the data based upon the derived faradaic admittance involving the deuterium absorption reaction (DAR). The results of deuterium behaviour into and through the palladium electrode are compared with those of hydrogen behaviour obtained in 0.1 M LiOH solution [11].

2. Experimental details

The chemical composition of the as-received pure Pd foil specimens (Aldrich Chemical Company) was 100 ppm Pt, 40 ppm Fe, 30 ppm Si, 15 ppm Al (by weight) and the balance Pd. The foil specimens were annealed under high vacuum (10^{-5} Pa) at 650 °C for 2 h, followed by furnace cooling, mechanically ground with 1200 grit silicon carbide paper to eliminate surface oxide film on the specimen and then chemically etched in concentrated nitric acid for 30 s. The final thickness of the foil specimen was about 50 μm. The roughness factor of the specimen, $f_w = S_w/S_g$ (where S_w is the permeation (real) surface area and S_g is the geometrical (apparent) surface area of the membrane specimen), was estimated in previous work [11] to be about 2.74 by means of the usual linear sweep voltammetry [12–14].

An electrochemical double cell [15] which allows electrochemical deuterium charging on the cathodic side of the membrane specimen and electrochemical detection on the anodic side was used in this study. The Pd membrane specimen separated the two electrochemical compartments and was in contact with 0.1 M LiOD solution prepared by dissolving lithium metal in D_2O (99.9 at.%, Aldrich Chemical Company). The solution was deaerated by bubbling with nitrogen gas before and during the experiments. The geometrical surface area S_g of the membrane specimen exposed to electrolyte was 3.14 cm^2 on both sides. In each compartment a platinum wire and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode respectively. The counter electrode was separated from each compartment by a glass frit. The potential of a reversible hydrogen electrode (RHE) was measured to be about −0.980 V(SCE) in 0.1 M LiOH solution. All potentials quoted are referred to the value of the potential of the RHE.

The electrochemical permeation double cell is composed of cathodic and anodic compartments separated by the palladium membrane specimen. A cathodic potential was applied to the entry side of the membrane specimen using a Solartron 1286 ECI under the remote control of an IBM-compatible personal computer. The deuterium absorbed into the entry side of the membrane specimen diffuses towards the exit side subject to a constant anodic potential of 0.94 V(RHE) produced via a Wenking LT 78 potentiostat, which allows any deuterium coming through the membrane to be oxidized to D^+.

When the steady state deuterium permeation had been attained, the electrode impedance measurement was initiated at the cathodic compartment using a Solartron 1255 FRA in conjunction with the Solartron 1286 ECI by superimposing an a.c. voltage of 5 mV amplitude on a d.c. potential from −0.07 to 0.23 V(RHE) over a frequency ranging from 5 mHz to 20 kHz. The experimental frequency was scanned from high to low values. To avoid grounding problems, the Solartron 1286 ECI was operated in the main grounded mode and the Wenking potentiostat in the floating mode. All experiments were carried out at room temperature.

3. Analysis of impedance data

For the discharge of deuterium from alkaline solutions of heavy water, one considers the reaction steps similar to Volmer adsorption and Tafel chemical desorption respectively as

$$D_2O + M + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MD_{ads} + OD^- \qquad (\text{rate } \nu_1) \tag{1}$$

$$2MD_{ads} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2M + D_2 \qquad (\text{rate } \nu_2) \tag{2}$$

where ν_1 and ν_2 are the rates of Volmer adsorption and Tafel chemical desorption respectively, k_1 and k_{-1} are the forward and backward rate constants of the Volmer adsorption reaction respectively and k_2 and k_{-2} are the forward and backward rate constants of the Tafel chemical desorption reaction respectively.

In addition to these reactions, the adsorbed deuterium passes on into the absorbed state by jumping into the interstitial sites beneath the first atomic layer [4, 5] owing to the difference in deuterium activity. The absorbed deuterium subsequently diffuses towards the exit side of the Pd membrane, since the activity of deuterium at the exit side of the Pd membrane is almost zero under the permeable condition:

$$\begin{array}{ll} D_{ads} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} D_{abs}(x=0) & (\text{rate } v_3) \\ \qquad\quad J_p \Big\downarrow \text{bulk diffusion} & \\ \qquad\quad D_{abs}(x=L) & \end{array} \tag{3}$$

where k_3 and k_{-3} are the rate constants of deuterium transfer from the surface to the bulk and from the bulk to the surface respectively, J_p is the flux of deuterium diffusing away from the entry side of the Pd membrane and L is the thickness of the Pd membrane. Under the permeable condition J_p at steady state is given by Fick's first law. Assuming low deuterium coverages and low degrees of saturation of deuterium within the Pd electrode, the rate of the DAR is given like the rate of the HAR [4, 5] by

$$\nu_3 = k_3\theta - k_{-3}C_s \tag{4}$$

where θ is the deuterium coverage on the entry side of the membrane and C_s is the concentration of deuterium at $x=0$.

When k_3 and k_{-3} are sufficiently fast such that the diffusion-controlled absorption condition is satisfied, the faradaic admittance Y_f for the reaction scheme consisting of Volmer adsorption (1), Tafel desorption (2) and deuterium absorption (3) reaction, has been derived in previous work [10] as

$$Y_f = \frac{1}{R_{ct}} \times \left(1 - \frac{B'}{j\omega l_{eq} + B' + C' + (j\omega D_D)^{1/2} \coth[(j\omega/D_D)^{1/2}L]}\right) \tag{5}$$

where

$$R_{ct} = -\frac{1}{F\,\partial\nu_1/\partial E}, \qquad B' = -l_{eq}\frac{\partial\nu_1}{\partial\Gamma}$$

$$C' = 2l_{eq}\frac{\partial\nu_2}{\partial\Gamma}, \qquad \frac{1}{l_{eq}} = -\frac{\partial\nu_3/\partial\Gamma}{\partial\nu_3/\partial C_s}$$

D_D is the deuterium diffusivity in Pd and Γ (mol cm^{-2}) is the surface concentration of adsorbed deuterium.

The slowest step in hydrogen permeation through a Pd membrane is known to be the diffusion step through the membrane [15, 16]. In the case of diffusion-controlled absorption the DAR (3) can be considered to be in equilibrium and therefore the equilibrium absorption constant K_{eq} of the DAR (3), *i.e.* the ratio of concentration of absorbed deuterium, C_s, to surface concentration of adsorbed deuterium, Γ [16], is defined by

$$K_{eq} = \frac{C_s}{\Gamma} = \frac{C_s}{\Gamma_{max}\theta} = \frac{k_3}{\Gamma_{max}k_{-3}} = \frac{k_3'}{k_{-3}} = \frac{1}{l_{eq}} \tag{6}$$

where Γ_{max} is the maximum surface concentration of adsorbed deuterium required to complete the coverage and $k_3' = k_3/\Gamma_{max}$.

Impedance spectra measured on solid electrodes often show deviations from the ideal semicircle. In this case the double-layer impedance $Z_{dl} = 1/j\omega C_{dl}$ is represented by the constant-phase element (CPE) [17, 18] defined as

$$\hat{Z}_{CPE} = \frac{1}{T(j\omega)^{\phi}} \tag{7}$$

where T is a constant with dimensions of F cm^{-2} s$^{-(1-\phi)}$ and ϕ is the fractional parameter representing the degree of depression of the semicircle. Thus the total impedance Z_t is given by

$$Z_t = R_s + \frac{1}{T(j\omega)^{\phi} + Y_f} \tag{8}$$

where R_s is the solution resistance.

The real and imaginary components Z' and Z'' obtained at each d.c. potential were analysed using the complex non-linear least-squares (CNLS) fitting method written by Macdonald *et al.* [19] and modified in our laboratory [20] to accurately determine the parameters in the faradaic admittance equation derived from kinetic considerations. Calculations were performed on an IBM 486 personal computer. Modulus weighting (MWT) was selected as a weighting factor for each experimental point. A curve-fitting error representing the goodness of curve fit was calculated from

$$\mathrm{Err} = \left(\frac{1}{n}\sum_{i=1}^{n}\frac{(a_i - A_i)^2 + (b_i - B_i)^2}{a_i^2 + b_i^2}\right)^{1/2} \tag{9}$$

where a_i and b_i are the real and imaginary components of experimental impedance data respectively, A_i and B_i are the real and imaginary components of curve-fitted impedance data at the same frequency as a_i and b_i respectively and n is the number of experimental data points.

4. Results and discussion

Figure 1 shows the plot of deuterium permeation current density *vs.* deuterium charging current density obtained from the Pd membrane electrode of thickness 50 μm in 0.1 M LiOD solution using the galvanostatic charging technique. In view of the small amount of deuterium leaving the membrane through the edges [16], it is reasonable to assume that almost all deuterium produced on the surface of the Pd membrane enters into its interior without evolution of deuterium, *i.e.* $\partial\nu_2/\partial\Gamma = 0$.

Figure 2 shows the complex plane impedance spectra obtained from the Pd membrane electrode of thickness 50 μm in 0.1 M LiOD solution at 0.23, 0.2 and 0.18 V(RHE). It is noted that oscillation around the steady state deuterium permeation current was clearly observed at the exit side during the impedance measurement. The parameters involved in eqn. (8) combined with

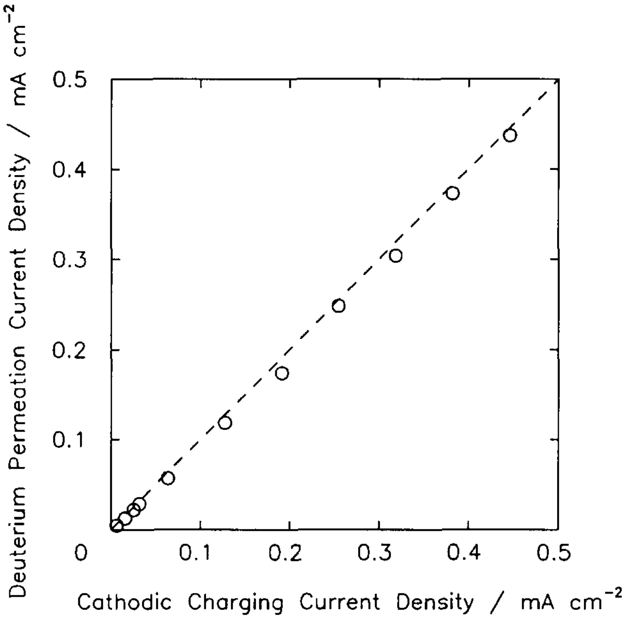

Fig. 1. Deuterium permeation current density *vs*. cathodic charging current density obtained from Pd membrane electrode in 0.1 M LiOD solution by using galvanostatic charging technique: ○, experimental data; – – –, reference line with unit slope.

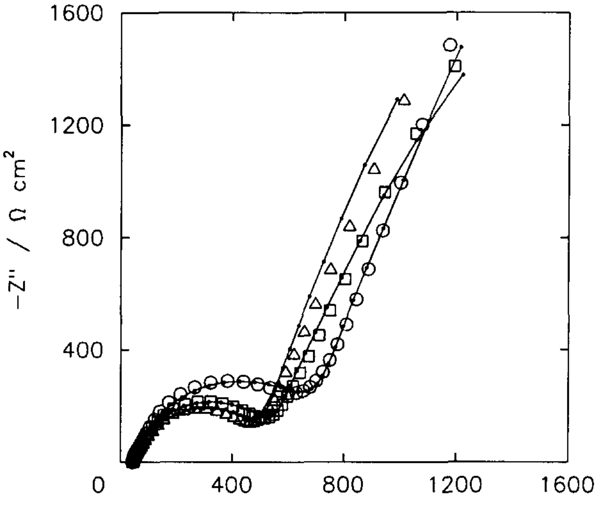

Fig. 2. Complex plane impedance spectra for DAR into Pd membrane electrode in 0.1 M LiOD solution at various overpotentials η: ○, 0.23; □, 0.20; △, 0.18 V(RHE). Solid curves represent the theoretical curves calculated by using optimum fit parameters on the basis of eqn. (5).

eqn. (5) were determined using the CNLS fitting method under the condition of $C'=0$. The values of the resulting fit parameters are summarized in Table 1. The solid curves in Fig. 2 represent the theoretical Nyquist curves calculated from the optimum fit parameters at the corresponding overpotentials.

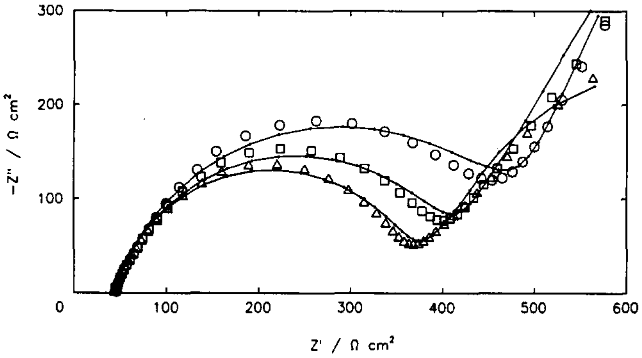

Fig. 3. Complex plane impedance spectra for DAR into Pd membrane electrode in 0.1 M LiOD solution at various overpotentials η: ○, 0.16; □, 0.13; △, 0.10 V(RHE). Solid curves represent the theoretical curves calculated by using optimum fit parameters on the basis of eqn. (5).

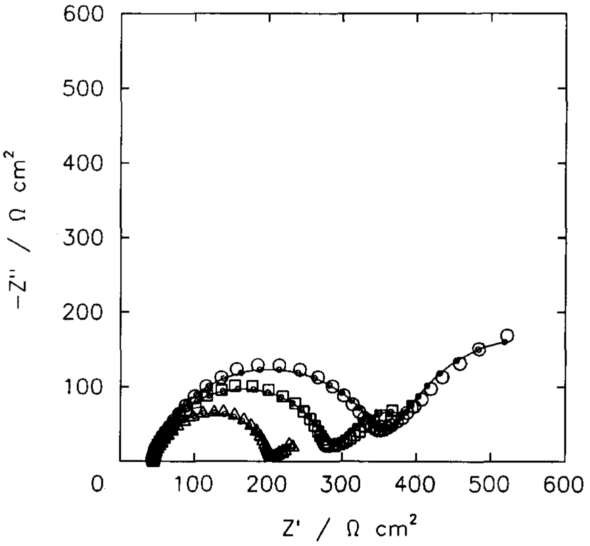

Fig. 4. Complex plane impedance spectra for DAR into Pd membrane electrode in 0.1 M LiOD solution at various overpotentials η: ○, 0.08; □, 0.03; △, -0.07 V(RHE). Solid curves represent the theoretical curves calculated by using optimum fit parameters on the basis of eqn. (5).

The complex plane impedance spectra involving the DAR into the Pd membrane electrode obtained in 0.1 M LiOD solution at various overpotentials are presented in Figs. 3 and 4. As the overpotential was lowered, the Warburg impedance originating from the finite length diffusion process clearly appeared in the Nyquist plot. However, at overpotentials below 0.03 V(RHE) the Warburg impedance appeared ambiguously in the Nyquist plot. In Table 1 the deuterium diffusivity through Pd was determined to be $(5.10 \pm 1.04) \times 10^{-7}$ cm^2 s^{-1} from the impedance spectra in the overpotential range from 0.03 to 0.23 V(RHE), which is comparable with the value of 4.8×10^{-7} cm^2 s^{-1} reported by Bucur [21]. On the other hand, the hydrogen diffusivity was determined to be $(3.49 \pm 0.69) \times 10^{-7}$ cm^2 s^{-1} [11] from the impedance spectra in the overpotential range from 0 to 0.28 V(RHE), *i.e.* slightly lower than the deuterium

TABLE 1. Optimum fit parameters involved in eqn. (8) combined with eqn. (5) obtained from impedance spectra for DAR into Pd membrane electrode in 0.1 M LiOD solution at various overpotentials

η (V *vs.* RHE)	$T\times10^4$ (F cm^{-2} s$^{-(1-\phi)}$)	$\phi\times10$	R_{ct} (Ω cm^2)	$B'\times10^4$ (cm s^{-1})	$l_{eq}\times10^3$ (cm)	$D_D\times10^7$ (cm^2 s^{-1})	Err (%)
0.23	2.25	7.98	777.6	9.04	2.53	3.65	9.48
0.20	2.14	8.03	572.6	7.02	1.98	4.20	9.31
0.18	2.49	7.71	539.2	10.04	2.74	4.49	4.29
0.16	2.56	7.69	499.1	6.27	2.05	4.45	5.17
0.13	2.46	7.76	406.1	3.62	1.63	5.10	4.91
0.10	1.87	8.39	339.1	1.89	0.98	6.36	4.37
0.08	1.86	8.46	317.1	1.25	0.82	5.57	4.10
0.06	1.84	8.49	288.6	1.07	0.96	6.85	4.13
0.03	1.75	8.71	244.5	0.64	0.64	5.27	2.91
−0.02	1.82	8.79	223.1	0.56	0.75	5.68	2.77
−0.07	2.14	8.55	223.6	0.86	1.61	10.81	2.44

diffusivity value. It has been shown that the reverse isotope effect prevails in the diffusion of hydrogen isotopes in Pd below 500 K [22, 23].

The equilibrium constant K_{eq} for the DAR into the Pd membrane electrode determined from the impedance spectra in 0.1 M LiOD solution is shown in Fig. 5 as a function of overpotential. To enable a comparison, the overpotential dependence of K_{eq} for the HAR into the Pd membrane in 0.1 M LiOH solution [11] is also depicted in Fig. 5. At all overpotentials investigated, K_{eq} for the DAR was smaller than that for the HAR into the Pd membrane.

Figure 6 shows the overpotential dependence of the charge transfer resistance R_{ct} for the Volmer adsorption reaction (1) on the Pd electrode in 0.1 M LiOD solution.

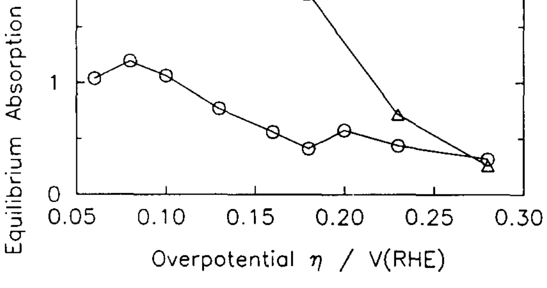

Fig. 5. Equilibrium absorption constant K_{eq} as a function of overpotential η determined from impedance spectra of Pd membrane electrode in two different solutions: ○, 0.1 M LiOD solution; △, 0.1 M LiOH solution (data taken from ref. 11).

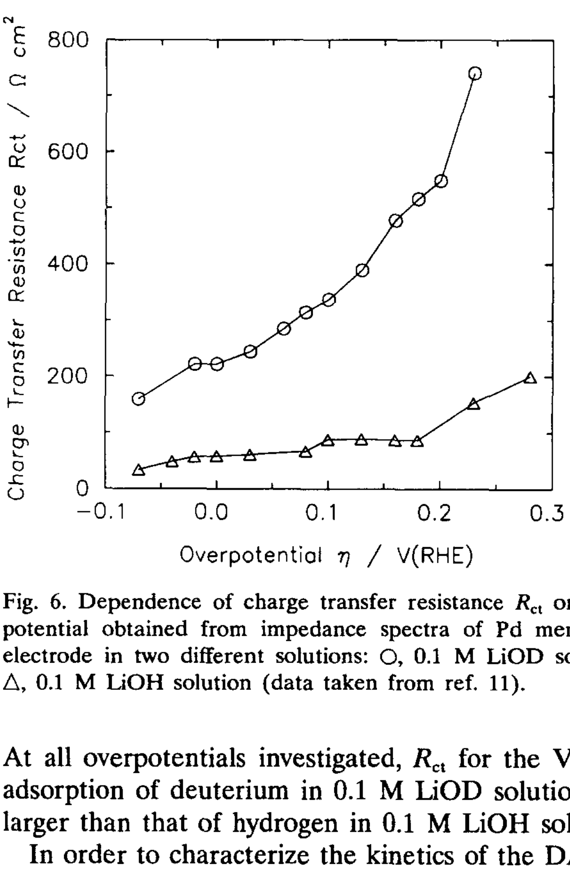

Fig. 6. Dependence of charge transfer resistance R_{ct} on overpotential obtained from impedance spectra of Pd membrane electrode in two different solutions: ○, 0.1 M LiOD solution; △, 0.1 M LiOH solution (data taken from ref. 11).

At all overpotentials investigated, R_{ct} for the Volmer adsorption of deuterium in 0.1 M LiOD solution was larger than that of hydrogen in 0.1 M LiOH solution.

In order to characterize the kinetics of the DAR in the D–Pd system, we introduce the appropriate kinetic rate equations. Assuming that (i) the adsorption reaction of deuterium obeys a Langmuir isotherm [3, 24] and (ii) the rates of electrochemical reactions are exponentially potential dependent (Tafel's law) [3, 24], the rates of the Volmer adsorption and Tafel desorption reactions are given by

$$\nu_1 = k_1'(1-\theta) - k_{-1}'\theta \tag{10}$$

and

$$\nu_2 = k_2\theta^2 - k_{-2}(1-\theta)^2 P_{D_2} \tag{11}$$

respectively, where $k_1'=k_1\exp(-\alpha F\eta/RT)$, $k_{-1}'=k_{-1}\exp[(1-\alpha)F\eta/RT]$, α is the transfer coefficient, F is the Faraday constant, T is the absolute temperature and P_{D_2} is the partial pressure of gaseous deuterium, D_2. The rate eqn. (4) of the DAR is additionally assumed to be valid. From the kinetic equations described above, one can find the partial derivatives included in the faradaic admittance eqn. (5) in terms of kinetic rate constants.

For the simulation of impedance spectra with kinetic rate constants, we need further to know the values of the transfer coefficient α, the maximum surface concentration of adsorbed deuterium, Γ_{max}, and the steady state deuterium coverage θ_{ss}. The transfer coefficient was taken to be 0.2 from the plot of steady state current *vs.* overpotential (see below). Assuming a charge density of 255 μC cm^{-2} [11] required to complete the coverage of deuterium ($\theta=1$), Γ_{max} is calculated to be about 7.25×10^{-9} mol cm^{-2} from the roughness factor of the specimen ($f_w=2.74$).

Under the negligible evolution of deuterium, the steady state deuterium coverage θ_{ss} can be calculated from the mass balance between the rate of the Volmer adsorption step, ν_1, and the steady state flux of deuterium diffusing away from the entry side of the membrane, J_p^{ss}, as

$$\theta_{ss}=\frac{k_1'}{k_1'+k_{-1}'+(D_D/L)\Gamma_{max}/l_{eq}} \qquad (12)$$

Using eqn. (8) combined with eqn. (5) and the partial derivatives included in eqn. (5) under the conditions of $\Gamma_{max}=7.25\times10^{-9}$ mol cm^{-2} and $C'=0$, we conducted the simulation of the impedance spectra measured at 0.16 V(RHE). Actually, the value of Γ_{max} was too low to fit to the measured impedance spectra.

Exceptionally large values of the surface concentration of hydrogen in the H–Pd system have often been found [12, 16, 25] and were discussed by Bucur and Bota [25]. According to their suggestion, one of the reasons for the excessive surface concentration could be the large density of defects located in the thin surface layer of Pd and on the surface area induced by mechanical or electrochemical treatment of the Pd surface. They reported that the effective correlation between the roughness factor and the equivalent thickness of the surface layer can be expressed by

$$f_w=5.38\times10^4\lambda^{5/6} \qquad (13)$$

where λ is the thickness of the surface layer. This relationship may hold for deuterium absorption into the Pd membrane. The thickness of the surface layer in our specimen was calculated to be about 7×10^{-6} cm from the roughness factor $f_w=2.74$.

Provided that the maximum concentration of deuterium in this surface layer is identical with that of the bulk phase, *i.e.* $C_{max}=0.113$ mol cm^{-3}, the surface layer can be treated as a tridimensional network which can store hydrogen or deuterium in amounts up to 7.91×10^{-7} mol per unit geometrical surface area of the Pd membrane electrode. The impedance spectrum measured at 0.16 V(RHE) was simulated in terms of the kinetic constants k_1, k_{-1}, l_{eq} and D_D on the basis of eqn. (5) combined with the partial derivatives included in eqn. (5), a modified value of $\Gamma_{max}=7.91\times10^{-7}$ mol cm^{-2} and $C'=0$ by using the CNLS fitting method. With the kinetic constants $k_1=2.16\times10^{-9}$ mol cm^{-2} s^{-1}, $k_{-1}=1.74\times10^{-9}$ mol cm^{-2} s^{-1} and $l_{eq}=2.05\times10^{-3}$ cm and the deuterium diffusivity $D_D=4.45\times10^{-7}$ cm^2 s^{-1} we simulated quite well the impedance spectrum obtained in 0.1 M LiOD solution at 0.16 V(RHE). The measured and simulated impedance spectra are shown in Fig. 7. However, the impedance spectrum measured in 0.1 M LiOH solution at the same overpotential was best simulated with the kinetic constants $k_1=1.26\times10^{-8}$ mol cm^{-2} s^{-1}, $k_{-1}=3.85\times10^{-9}$ mol cm^{-2} s^{-1} and $l_{eq}=4.25\times10^{-4}$ cm and the hydrogen diffusivity $D_H=3.61\times10^{-7}$ cm^2 s^{-1} [11].

The steady state current density i_{ss} is given from the Volmer adsorption reaction by

$$i_{ss}=-F[k_1'(1-\theta_{ss})-k_{-1}'\theta_{ss}] \qquad (14)$$

We calculated the i_{ss} *vs.* η curve based upon eqns. (12) and (14) by using the kinetic constants best fitted to the measured impedance spectra in Fig. 7. The simulated steady state polarization curve is compared with the measured curve in Fig. 8. At overpotentials

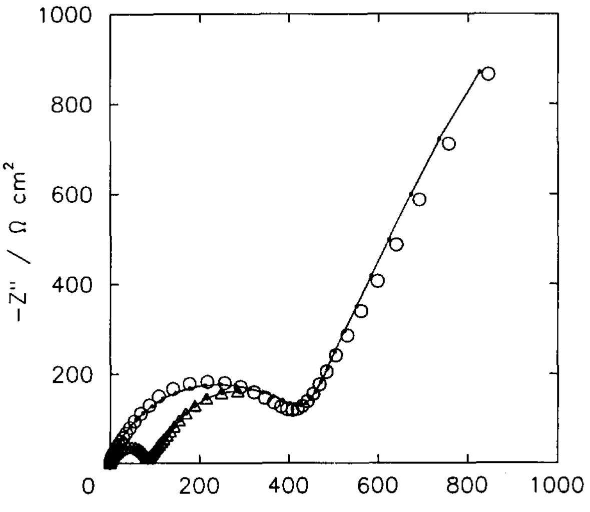

Fig. 7. Impedance spectra in Nyquist presentation for DAR and HAR into Pd membrane electrode at $\eta=0.16$ V(RHE): ○, experimental data in 0.1 M LiOD; ——, simulated curve; △, experimental data in 0.1 M LiOH (data taken from ref. 11); – – –, simulated curve. The values of kinetic constants used in the simulation are given in the text.

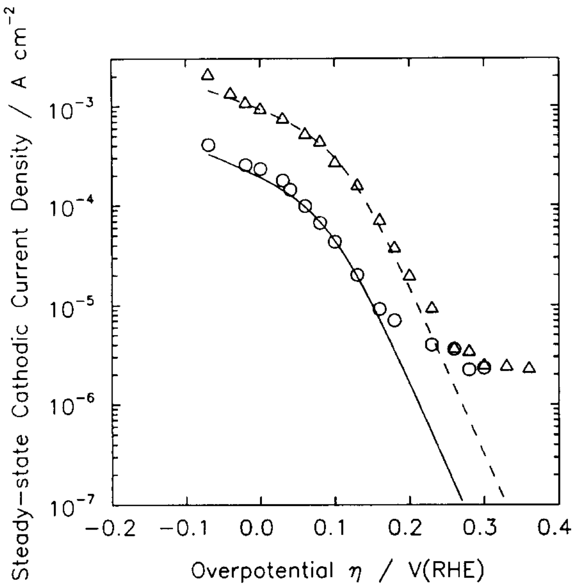

Fig. 8. Steady state cathodic current density i_{ss} *vs.* overpotential for DAR and HAR into Pd membrane electrode: ○, potentiostatically determined data in 0.1 M LiOD; ——, theoretical curve; △, potentiostatically determined data in 0.1 M LiOH; – – –, theoretical curve. The theoretical curves were calculated on the basis of eqns. (12) and (14) with the kinetic constants best fitted to the measured impedance spectra in Fig. 7.

above 0.20 V(RHE) the measured steady state current density showed nearly constant values due to the reduction of oxygen remaining slightly in solution.

From Fick's first law and eqn. (6) the steady state deuterium permeation current density i_p becomes

$$i_p = F\frac{D_D}{S_g L}\frac{\Gamma_{max}}{l_{eq}}\theta_{ss} \qquad (15)$$

The current density was calculated against the overpotential on the basis of eqns. (12) and (15) by using the kinetic constants best fitted to the measured impedance spectra and the result is presented in Fig. 9. The theoretically calculated curve was found to be in good agreement with the experimental data. The steady state cathodic current and correspondingly the permeation current of deuterium were smaller than those of hydrogen.

Figure 10 shows the steady state deuterium coverage as a function of overpotential calculated theoretically from eqn. (12) with the kinetic constants best fitted to the measured impedance spectra in Fig. 7. The steady state coverage of deuterium was smaller than that of hydrogen on the Pd membrane electrode.

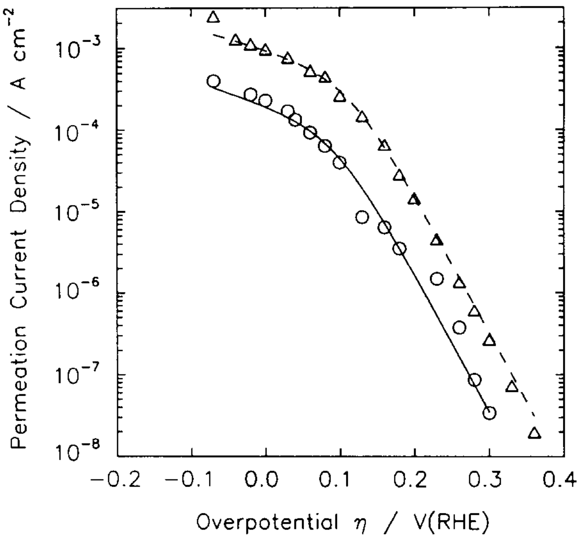

Fig. 9. Permeation current density i_p *vs.* overpotential for DAR and HAR into Pd membrane electrode: ○, potentiostatically determined data in 0.1 M LiOD; ——, theoretical curve; △, potentiostatically determined data in 0.1 M LiOH; – – –, theoretical curve. The theoretical curves were calculated on the basis of eqns. (12) and (15) with the kinetic constants best fitted to the measured impedance spectra in Fig. 7.

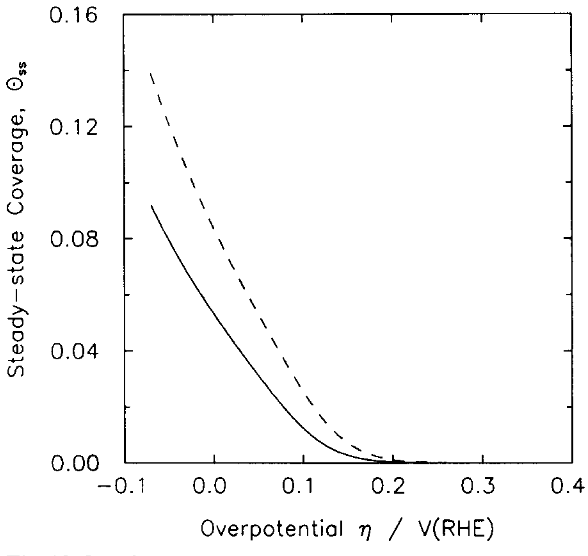

Fig. 10. Steady state coverage θ_{ss} of deuterium (——) and hydrogen (– – –) as a function of overpotential calculated theoretically on the basis of eqn. (12) with the kinetic constants best fitted to the measured impedance spectra in Fig. 7.

5. Conclusions

The absorption and diffusion of deuterium into and through a palladium membrane electrode respectively have been investigated in 0.1 M LiOD solution by using an a.c. impedance technique in combination with an electrochemical hydrogen permeation technique. The results are summarized as follows.

(1) Impedance spectra obtained in the overpotential range from −0.07 to 0.23 V(RHE) were satisfactorily analysed with the faradaic admittance derived from the model of the DAR in which deuterium enters into the palladium electrode through an adsorbed phase and

subsequently its diffusion through the membrane is the rate-determining step.

(2) Introducing a surface layer which can tridimensionally store deuterium, we simulated the complex plane impedance spectra in terms of the kinetic rate constant of Volmer adsorption, the equilibrium absorption constant and the deuterium diffusivity in palladium. The steady state current and coverage were theoretically calculated as a function of overpotential with the same kinetic constants as those best fitted to the measured impedance spectra.

(3) As a result, the value of forward rate constant of Volmer adsorption, 2.16×10^{-9} mol cm^{-2} s^{-1}, and the ratio of bulk concentration of absorbed deuterium to surface concentration of adsorbed deuterium, 4.88×10^{2} cm^{-1}, were one order of magnitude smaller than those of hydrogen, whereas the value of backward rate constant, 1.74×10^{-9} mol cm^{-2} s^{-1}, was similar to that of hydrogen. The diffusivity of deuterium in the Pd membrane, $(5.10 \pm 1.04) \times 10^{-7}$ cm^{2} s^{-1}, showed a slightly higher value than that of hydrogen owing to the reverse isotope effect.

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