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# *In situ* comparison of diffusivities for hydrogen and deuterium in palladium

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An electrochemical permeation method was employed to study the diffusion behaviour of hydrogen and deuterium in palladium. Solutions of 0.1 M LiOD (in $D_2O$) and 0.1 M LiOH (in $H_2O$) and their mixtures were used as the catholytes. More than one hundred diffusivity data from 20 palladium membranes were collected. Statistical analysis of these data was made to examine the validity of the reversed isotope dependence for hydrogen diffusion in palladium. It was concluded that the effective diffusivities increased with the concentration of deuterium in the electrolyte. In addition, an *in situ* experiment was also performed by adding to the cathodic cell an equivalent amount of LiOD solution to the original LiOH solution, or vice versa. Graphical comparison of the corresponding permeation transients showed that the permeation rate increased when deuterium was added to the solution of $H_2O$, and the rate decreased when hydrogen was added to the solution of $D_2O$. This constitutes direct evidence for the higher diffusivity of deuterium than that of hydrogen in palladium.

## 1. Introduction

Classical rate theory predicts that light isotopes diffuse faster than the heavier ones in metals [1, 2]. This is generally observed for the diffusion of heavy isotopes [3, 4]. For light isotopes such as hydrogen and deuterium, their effective diffusivities in iron and austenitic stainless steel indicate an isotope effect close to the classical ratio, 1.41 [5, 6]. Higher diffusivity of hydrogen has also been observed in vanadium, niobium and tantalum [7]. It is interesting, however, that a reversed isotope dependence is associated with palladium over a broad temperature range from about −60 to 200° C [8–10]. This inversion has been attributed to a larger activation energy for hydrogen diffusion [10, 11]. In most tests, the values of diffusivity for deuterium and hydrogen in palladium were measured from different membranes and different runs. Sometimes the difference between the diffusivities of deuterium and hydrogen could be smaller than the scattering range within a group of data for an individual isotope. To improve the reliability of the experimental results, more specimens under a broad range of conditions should be tested. A statistical analysis of a larger data pool would give a more convincing conclusion for the reversed isotope dependence. An even more desirable experiment would be to directly compare the diffusivities of the two isotopes in one single test.

In this study, the individual rates of permeation of hydrogen and deuterium through Pd were measured first by an electrochemical method. The corresponding diffusivities were calculated. Two mixed solutions with different ratios of deuterium to hydrogen in the electrolyte were then tested. Sufficient experimental data from a number of specimens were collected for statistical analysis.

In a second part of the work, a further experiment was designed to study the *in situ* change of permeation flux due to the change of concentrations of the diffusible species (hydrogen and deuterium) on the cathodic side of the palladium membrane. The change in the permeation transient gives a direct measure of the difference between hydrogen and deuterium. This allows comparison between the diffusivities of deuterium and hydrogen with the same palladium membrane in a single run.

## 2. Experimental details

### 2.1. *Measurement of effective diffusivities*

The rates of permeation and the corresponding diffusivities of hydrogen isotopes through palladium were measured by an electrochemical method developed by Devanathan and Stachurski [12]. The apparatus has been described elsewhere [13, 14]. A palladium membrane (99.9% purity, 0.32 mm thickness, Yamanaka), which had been annealed at 830° C for 2 h in vacuum, was positioned between two cell compartments. This membrane, with an exposed area of $1.33\,cm^2$, acted as the working electrode for both cells. The counter and reference electrodes on each side of the membrane were a platinum sheet (99.9%, Tanaka) and a saturated calomel electrode (SCE), respectively. A potentiostat (Sycopel Microstat) was employed to supply a constant current on the cathodic side of the membrane. On the other side the potential was kept at a relatively positive potential against the SCE via another potentiostat (Pine RDE) so that the concentration of the adsorbed hydrogen isotopes was essentially zero. Thus, the atomic hydrogen isotopes formed on the cathodic side of the membrane diffused through it and were immediately consumed on the anodic side. In practice, a series of replicate permeations were done at increased or decreased step-wise charging current densities (2.3 to 9.0, 9.0 to 45.0, 45.0 to 9.0 and 9.0 to 2.3 $\mu A\,cm^{-2}$). When the charging current started to increase or decrease on the cathodic side, the permeation current on the anodic side was immediately monitored by a recorder (Yokogawa 3025) until a new steady state value was attained. The calculation of diffusivity from the permeation transient is illustrated in the following section. During the measurement, high purity argon was continuously bubbled through the solution.

Two solutions for the cathodic compartment were used for the diffusivity measurement. Solution A was prepared by the addition of lithium hydroxide (purity, 98%) to deionized $H_2O$ (resistivity, 18.3 MΩ). Solution B was prepared by the addition of lithium deuteroxide (purity 99%) to $D_2O$ (Isotec, purity 99.9%). The concentration of both solutions was 0.1 M. Two more solutions were prepared by mixing these two solutions with the ratios of A : B = 1 : 1 and 3 : 1. On the anodic side, solution A was used for all experiments.

The mathematical analysis for hydrogen diffusion in metals was first developed by McBreen *et al.* [15]. The diffusivity of hydrogen or deuterium is calculated as follows:

$$D = 0.138L^2/t_{1/2} \qquad (1)$$

where $D$ is diffusivity, $L$ is the specimen thickness, and $t_{1/2}$ is the half-rise time (i.e. the time required for the permeation transient to reach one half of the steady state value). Both buildup and decay transients were studied.

### 2.2. *In situ comparison of diffusivities of hydrogen and deuterium*

An experiment was designed for *in situ* comparison of diffusivities of hydrogen and deuterium. During the permeation test, a different solution in equal amount was added to the initial solution on the cathodic side at the time of about one half of $t_{1/2}$. In practice, the experiments were conducted by adding solution A ($H_2O$) to the initial solution B ($D_2O$), or vice versa. The buildup or decay permeation transient was continuously monitored. The value of $t_{1/2}$ was estimated based on the diffusivity of the hydrogen isotope in the initial solution, as measured in the previous section. There are two reasons for choosing that period for addition. First, it was important to ensure that the permeation transient of the early stage from the initial solution was reproducible. Second, if there was a change in the effective diffusivity due to the addition of a second solution, there would be sufficient time to reveal the difference in the permeation curve.

Prior to this *in situ* experiment, some blank tests were also performed to examine the feasibility of this design. An equal amount of the same solution was added at one half of $t_{1/2}$ during the permeation measurement. By comparing with the blank test, any change in the buildup or decay transient due to the addition of a different solution would provide direct evidence indicating the difference in diffusivities between the two isotopes.

## 3. Results and discussion

### 3.1. *Statistical analysis of diffusivities of hydrogen and deuterium*

Since scattering of diffusivities under the same experimental condition has always been observed for pure hydrogen and deuterium, more replicate permeations with successively increased or decreased charging current densities in solutions with various ratios of

*Table 1. Summary of diffusivity data for hydrogen/deuterium in palladium at 22 ± 1° C*

| *Stepwise charging current density/* $\mu A\,cm^{-2}$ | *Electrolyte (unit:* $10^{-7}\,cm^2\,s^{-1}$*)* | | | |
|---|---|---|---|---|
| | $H_2O$ | $H_2O/D_2O = 3$ | $H_2O/D_2O = 1$ | $D_2O$ |
| 2.3 to 9.0 | 1.10 | 1.17 | 1.18 | 1.42 |
| | 1.18 | 1.18 | 1.23 | 1.44 |
| | 1.22 | 1.19 | 1.27 | 1.46 |
| | 1.23 | 1.27 | 1.28 | 1.47 |
| | 1.24 | 1.47 | 1.29 | 1.53 |
| | 1.25 | 1.57 | 1.32 | 1.54 |
| | 1.26 | | 1.46 | 1.56 |
| | 1.27 | | 1.47 | 1.57 |
| 9.0 to 2.3 | 1.17 | 1.18 | 1.18 | 1.35 |
| | 1.18 | 1.21 | 1.21 | 1.44 |
| | 1.21 | 1.22 | 1.24 | 1.47 |
| | 1.26 | 1.23 | 1.26 | 1.49 |
| | 1.27 | 1.25 | 1.28 | 1.56 |
| | 1.28 | 1.26 | 1.30 | 1.57 |
| | | | 1.31 | 1.58 |
| | | | 1.37 | 1.59 |
| 9.0 to 45.0 | 1.11 | 1.13 | 1.19 | 1.39 |
| | 1.13 | 1.17 | 1.21 | 1.40 |
| | 1.16 | 1.18 | 1.22 | 1.47 |
| | 1.21 | 1.23 | 1.23 | 1.48 |
| | 1.23 | 1.30 | 1.24 | 1.57 |
| | 1.25 | 1.31 | 1.26 | 1.61 |
| | 1.27 | | 1.31 | 1.62 |
| | 1.31 | | 1.47 | 1.65 |
| 45.0 to 9.0 | 1.15 | 1.18 | 1.21 | 1.43 |
| | 1.16 | 1.23 | 1.22 | 1.45 |
| | 1.17 | 1.25 | 1.23 | 1.54 |
| | 1.18 | 1.26 | 1.24 | 1.58 |
| | 1.20 | 1.27 | 1.25 | 1.60 |
| | 1.21 | 1.29 | 1.31 | 1.61 |
| | 1.24 | | 1.33 | 1.64 |
| | | | 1.42 | |

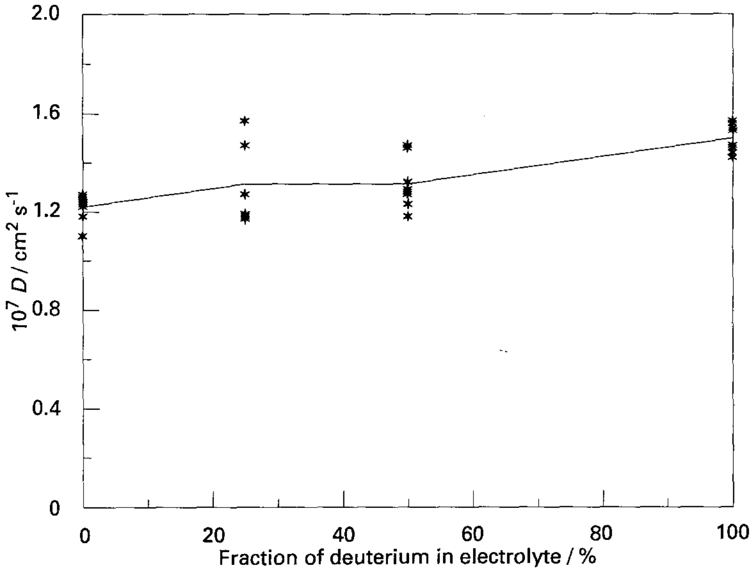

Fig. 1. Effective diffusivities of hydrogen/deuterium in Pd at 22 ± 1° C at increasing stepwise charging current density from 2.3 to 9.0 $\mu$A cm$^{-2}$ for various solutions.

A/B are needed. In Table 1 more than one hundred diffusivity data measured from 20 palladium specimens at 22 ± 1° C are given in order of magnitude. The data obtained in the present work are in fairly good agreement with previously reported diffusivities of hydrogen and deuterium using similar experimental technique [8–12]. These data can be plotted for various stepwise charging current intervals as shown in Figs 1 to 4. Figures 1 and 2 show the diffusivities calculated from the buildup transients at increased stepwise charging current densities from 2.3 to 9.0 $\mu$A cm$^{-2}$ and from 9.0 to 45.0 $\mu$A cm$^{-2}$, respectively. Figures 3 and 4 show the diffusivities from the decay transients at decreased current densities from 45.0 to 9.0 $\mu$A cm$^{-2}$ and from 9.0 to 2.3 $\mu$A cm$^{-2}$, respectively. Although some scatter is present, useful information about the variation of effective diffusivities due to different ratios of hydrogen to deuterium in the solutions can be recognized. For example, in these four figures the average values of diffusivity for various solutions were connected by a solid line. A gradual increase in the diffusivities with increase in the content of deuterium is observed for all test sequences. Furthermore, the diffusivities measured from solution B ($D_2O$) are always higher than those from solution A ($H_2O$), no matter how large the scattering ranges are for both solutions. It can be concluded that the diffusivity of deuterium is indeed about 25% higher than that of hydrogen.

From Figs 1 to 4, the increase in the effective diffusivities from a solution of pure A to solutions of A/B = 3 : 1 and 1 : 1 is small, while a bigger increase is observed when the solution is changed from A/B = 1 : 1 to pure solution of B. This indicates that the diffusion behaviour in palladium was dominated by hydrogen when the hydrogen and deuterium were simultaneously present in the mixed solution. This phenomenon is caused by the formation of adsorbed hydrogen in preference to that of deuterium on the palladium surface, and the detailed explanation is as follows. When the effective diffusivities of hydrogen and deuterium from mixed solutions are measured, different adsorption characteristics for hydrogen and deuterium should be taken into account. The actual ratio of hydrogen/deuterium adsorbed on the Pd surface should be different from the original

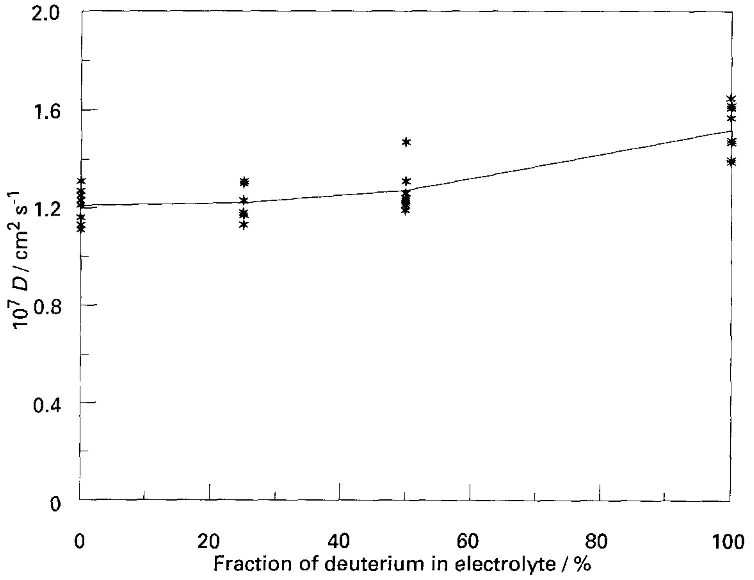

Fig. 2. Effective diffusivities of hydrogen/deuterium in Pd at 22 ± 1° C at increasing stepwise charging current density from 9.0 to 45.0 $\mu$A cm$^{-2}$ for various solutions.

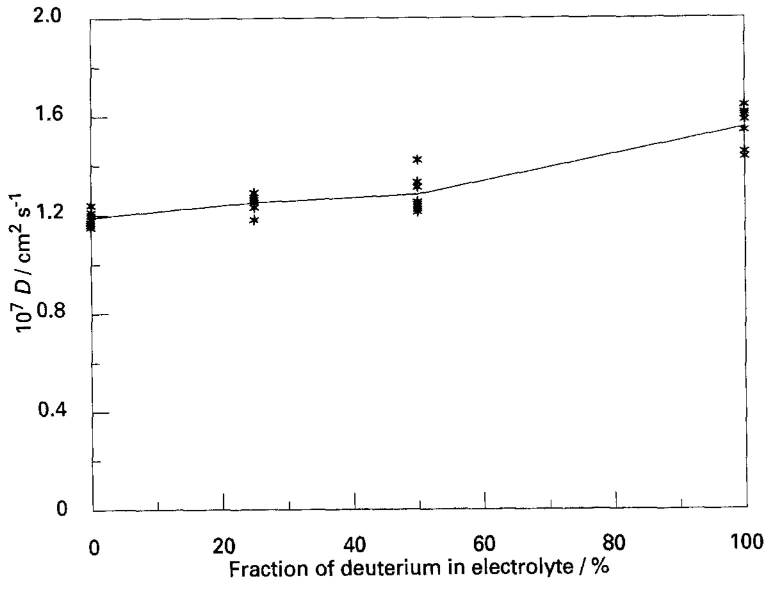

Fig. 3. Effective diffusivities of hydrogen/deuterium in Pd at 22 ± 1° C at decreasing stepwise charging current density from 45.0 to 9.0 $\mu$A cm$^{-2}$ for various solutions.

*Table 2. Permeation current densities in palladium at 22 ± 1° C*

| *Electrolyte* | *Charging current density/$\mu$A cm$^{-2}$* | | |
|---|---|---|---|
| | *2.3* | *9.0* | *45.0* |
| $H_2O$ | 1.9 ± 0.2 | 8.0 ± 0.5 | 37.6 ± 1.5 |
| $H_2O/D_2O = 3$ | 1.8 ± 0.2 | 7.7 ± 0.8 | 38.3 ± 1.7 |
| $H_2O/D_2O = 1$ | 1.8 ± 0.3 | 7.7 ± 0.6 | 37.0 ± 1.5 |
| $D_2O$ | 1.8 ± 0.2 | 7.7 ± 0.6 | 38.0 ± 1.5 |

ratio in the mixed solution. It has been reported by Czerwinski *et al.* [16] that the adsorption of hydrogen on palladium occurred at a potential of about 0.1 V more positive than the corresponding potential for deuterium on the cyclic voltammogram. In other words, the formation of adsorbed hydrogen on palladium occurs more easily than that of deuterium. Hence it is expected that the exact ratios of hydrogen/deuterium on palladium is higher than those in the mixed solution, and this selectivity effect on the palladium surface should have a significant influence on the diffusion behaviour in the palladium lattice. A similar result was also found by Storms *et al.* [17] for a (H + D)/Pd ratio of 0.66. The above explanation is also applicable to their case.

Table 2 summarizes the average permeation currents from different charging currents for various solutions. The steady-state permeation currents are always very consistent. The relative deviations for systems under the same experimental conditions are quite small. For all charging currents, the permeation currents are consistently 15–20% lower than the charging currents. This indicates that most hydrogen/deuterium formed on the cathodic side has permeated through the membrane. Table 2 also shows that the steady-state permeation currents for all solutions under the same charging currents are essentially the same. Since the permeation flux comes from the multiplication of diffusivity and solubility, this implies that under the same charging current, the solubility of deuterium in palladium is lower than that of hydrogen. This result (in $\alpha$-phase Pd) is consistent with Flanagan's [18] finding.

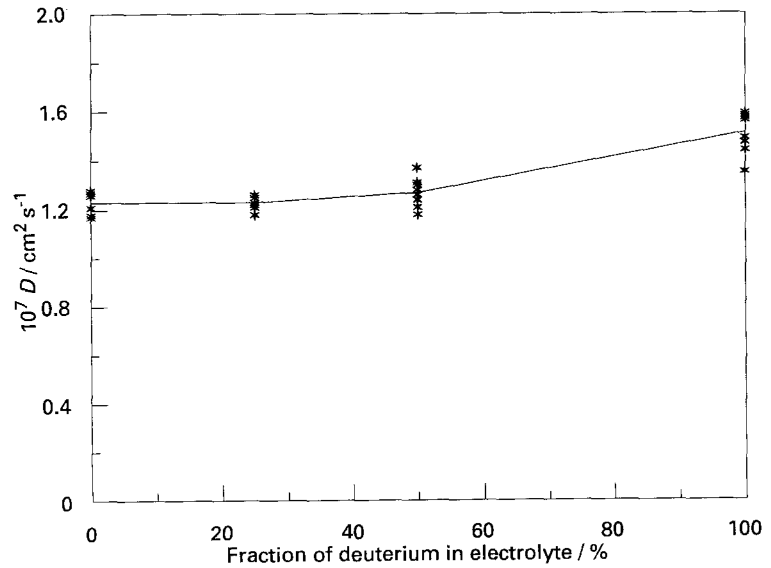

Fig. 4. Effective diffusivities of hydrogen/deuterium in Pd at 22 ± 1° C at decreasing stepwise charging current density from 9.0 to 2.3 $\mu$A cm$^{-2}$ for various solutions.

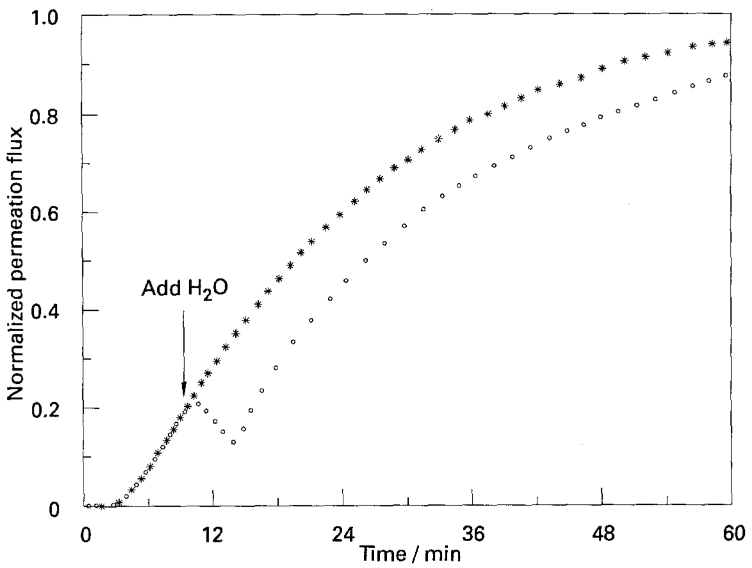

Fig. 5. Change of the buildup transient curve due to the addition of aerated solution of $H_2O$. (∗—∗) Addition of deaerated $H_2O$; (○—○) addition of aerated $H_2O$.

### 3.2. *In situ comparison of diffusivities of hydrogen and deuterium*

Some blank experiments were conducted before the *in situ* experiments to study the feasibility of these experiments. For the blank experiments, identical solution was added to the initial solution at one half of $t_{1/2}$. The effect of the addition on the diffusion behaviour of hydrogen/deuterium and the corresponding change in the transient curve were examined. In principle, the transient curve should not be affected by the addition of the same solution. This was indeed observed. In all blank experiments for solutions A, B and the mixed solutions, the transient curves did not change at all. However, the solution to be added should be subjected to some pretreatment before the addition. The pretreatment included a 1 h purge with argon and rigorous temperature control of the added solution. The temperature difference between the initial solution and the added solution and the dissolved oxygen may greatly influence the electrochemical permeation kinetics. In some tests, some solutions were used without prepurging with argon. The permeation transient was substantially disturbed, and the transient kinetics were delayed, as illustrated in Fig. 5 for solution A. Presumably part of the current was consumed by the dissolved oxygen.

For the *in situ* experiments, a series of normalized buildup transients at 22 ± 1° C are shown in Fig. 6. The influence of the *in situ* addition of a different solution on the diffusion behaviour of hydrogen/deuterium can be measured from the distortion of the buildup transient curve. Curves (a) and (d) are the buildup transients obtained for permeation of pure deuterium and hydrogen (i.e. from solutions B and A), respectively. Curves (b) and (c) are the transients obtained from the *in situ* experiments. For curve (b), the experiment was operated initially with solution B on the same palladium membrane as that for curve (a), so that their behaviours were essentially the same in the early stages of the transients. After about eight minutes, an equal amount of solution A was added to solution B in the cathodic cell. It was

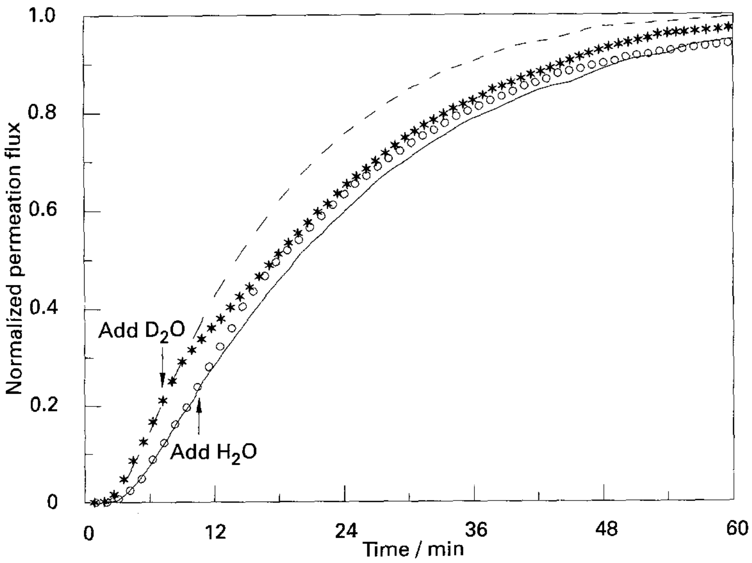

Fig. 6. Comparison of the buildup transients due to the *in situ* addition of different solutions at increasing charging current density from 9.0 to 45.0 $\mu A\,cm^{-2}$. Curves: (a) ----- $D_2O$; (b) ∗—∗ $D_2O$ (+$H_2O$); (c) ○—○ $H_2O$ (+$D_2O$); (d) —— $H_2O$.

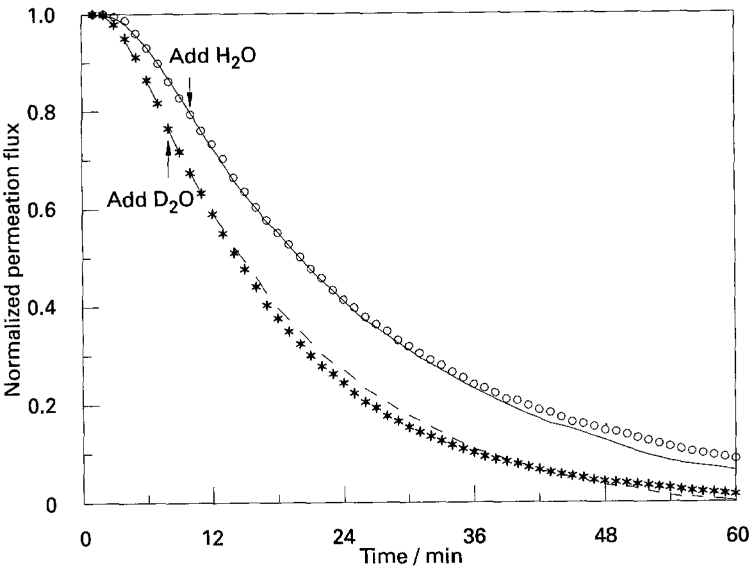

Fig. 7. Comparison of the decay transients due to the *in situ* addition of different solutions at decreasing charging current density from 45.0 to 9.0 $\mu A\,cm^{-2}$. Curves: (a) ----- $D_2O$; (b) $*$—$*$ $D_2O$ (+$H_2O$); (c) ○—○ $H_2O$ (+$D_2O$); (d) —— $H_2O$.

observed that two minutes later curve (b) started to depart from curve (a). This means that part of the palladium surface has been occupied by the adsorbed hydrogen on the cathodic side. Hydrogen then competed with deuterium in the permeation process. Accordingly, the corresponding transient curve was shifted. Since curve (b) lags behind curve (a), it is conceivable that the effective diffusivity decreases after the participation of hydrogen in the diffusion process. This *in situ* experiment offers direct evidence that hydrogen has a lower diffusivity than deuterium.

In Fig. 6, another group of buildup transients (curves (c) and (d)) can also be used to check the validity of the reversed isotope dependence for hydrogen diffusion. From curves (c) and (d), it can be seen that the effective diffusivity increases after the addition of deuterium (solution B) to the cathodic cell. Contribution of deuterium to the permeation process gradually moves the curve to the left. Thus, the reversed isotope dependence for hydrogen is again confirmed. It seems that the change between curves (c) and (d) is smaller than that between curves (a) and (b). This could be ascribed to the weaker adsorption of deuterium on the palladium surface than that of hydrogen, as mentioned in the previous Section.

When the *in situ* experiments were operated with the charging current decreased from 45.0 to 9.0 $\mu A\,cm^{-2}$, a different characteristic of the decay transients was observed as shown in Fig. 7. The sequences for these experiments were the same as those for the buildup transients shown in Fig. 6, except that the charging current was decreased. In contrast to the buildup mode, the change after the addition of a second solution is essentially negligible. In the decay mode, hydrogen/deuterium in the membrane is oversaturated and the permeation flux is controlled by the hydrogen isotope originally dissolved in the palladium membrane. Therefore, the newly produced isotope on the cathodic surface would have no effect on the kinetics of the decay transient, but only contribute to the final steady state flux value. That contribution should make no difference from that of the original species as shown in Table 2.

## 4. Conclusions

According to results from the statistical analysis of electrolytes with various ratios of hydrogen to deuterium, the effective diffusivities increase with the concentration of deuterium. The permeation fluxes are the same for all electrolytes.

In the *in situ* experiments, the buildup transients were shifted. This constitutes direct evidence for higher diffusivity of deuterium than that of hydrogen. No change in the decay transients was observed, because the permeation flux was controlled by the species originally dissolved in the membrane.

Formation of adsorbed hydrogen occurs more easily than that of deuterium. This selectivity effect, which occurs on the palladium surface, should affect the diffusion behaviour in the bulk palladium when hydrogen and deuterium are simultaneously present in the mixed solution.

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