

MATERIALS/SURFACE ASPECTS OF HYDROGEN/ DEUTERIUM LOADING INTO Pd CATHODE

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ABSTRACT

Electrolytic hydrogen and deuterium loading into Pd and Pd-Rh alloys have been investigated applying various modes of surface modification: thiourea on Pd and Pd-Rh, Pd black on Pd and Pd-Rh and Pd-Rh deposit on Pd. From these systematic data role of the bulk and surface properties of the cathode in determining the maximum loading has been discussed. The cathode loading is improved for Pd and Pd-Rh with a surface modified by thiourea and Pd modified by Pd-Rh deposit, while reduction of the cathode loading was observed when the surface of the Pd-Rh alloy cathode was modified by Pd-black. These results show clearly importance of controlling the surface catalytic property of the cathode in controlling and improving the maximum cathode loading. It has been found that $\bar{D}/Pd \geq 0.95$ can be achieved reproducibly in electrolyte solutions containing thiourea at high concentrations. However, electrolysis in solutions containing thiourea can be conducted successfully only when the anode and cathode are separated by an ion exchange membrane in order to avoid the consumption of thiourea by anodic oxidation at the anode.

Application of partial deload/reload cycles to a Pd cathode in 1M-LiOD has led to improvement of cathode loading to the value between 0.9 and 0.95, but implication of such effects is not well understood yet in terms of the bulk and the surface properties of the cathode.

INTRODUCTION

Despite the well referred importance of attaining and maintaining high cathode loading in the generation of excess heat in the Pd/LiOD systems, no reproducible ways to achieve $D/Pd > 0.95$ has been known to date. It has been believed that there are some good Pd materials, the nature of which is unknown, which would guarantee such high loading under certain electrolysis conditions. While nature of such materials are scarcely understood, optimization of electrolysis conditions which leads to the highest loading for a given Pd material has been a target in the investigations of certain research groups. The effects of ordinary electrolysis conditions such as current density, cathode overvoltage and temperature, the difference between the acidic and alkaline solutions, isotope effect observed between the light water and the heavy water systems, cation effect observed in LiOH, NaOH, KOH and $(CH_3)_4NOH$, and surface modification by catalytic poison such as thiourea at its low concentrations have been fairly well understood [1].

Optimization of such ordinary electrolysis conditions, however, has been still unsatisfactory in achieving cathode loading higher than 0.95. The cathode material and its preparation as well as pretreatment is probably a key area to achieve successful loading. The issue is closely related to a fundamental question: "Is the successful loading determined by the bulk property of the palladium or the surface characteristics?" The well known pretreatment of palladium samples by vacuum annealing followed by chemical etching in aqua regia has been successful in achieving cathode loading higher than 0.9 [2, 3, 4, 5]. But such combined pretreatment may change both the bulk as well as the surface properties of the palladium sample, and it is difficult to elucidate the role of the surface and bulk properties separately.

The purpose of the present report is to give some answer to the above question as to the respective role of the surface and the bulk property of the palladium in determining the high cathode loading. For this purpose we have conducted experiments to determine cathode loading of palladium and palladium-rhodium alloy in either 1M-LiOD or 2.8M- H_2SO_4 and 2.8M- D_2SO_4 by modifying their surfaces in various ways. The surface of the cathode was modified by thiourea, Pd/Pd deposited film and Pd-Rh deposited alloy film and their effect on the cathode loading was monitored. The results were interpreted in terms of the respective roles of the surface and the bulk properties on the cathode loading.

EXPERIMENTAL

Measurements of the cathode loading were conducted either in fuel cell type closed cells by monitoring the gas (D_2) pressure as described elsewhere [6] or in open cells by monitoring the electrical resistance change of the Pd cathode. The resistance change is defined as ratio R/R_0 where R and R_0 are the cathode resistance with and without absorbed hydrogen or deuterium respectively, and they were measured by AC four terminals method using a NF or HP milli-Ohm meter with 1kHz AC probe current of 1mA amplitude. The relation between R/R_0 and H/Pd or D/Pd to convert the measured resistance change to cathode loading were determined in a series of experiments in fuel cell type closed cells measuring simultaneously the cathode loading from gas pressure and the resistance change.

The surface modification by thiourea was possible in the limited concentration range only below 0.6 mM in fuel cell type closed cells due to its poisoning action on the fuel cell anode at higher concentrations [1]. In open cells, however, thiourea in the electrolyte is electrochemically oxidized at the platinum anode and its bulk concentration is reduced during electrolysis. The effect of surface modification is no longer maintained under such conditions. We have developed electrolysis method to separate the anode and the cathode compartments by an ion-exchange membrane which is practically impermeable to thiourea during a certain electrolysis period. It has been found that the cation exchange membrane Nafion can be successfully applied for such purposes in acidic electrolytes. We have conducted H(D)/Pd measurements of a Pd foil, $5\text{mm} \times 20\text{mm} \times 50 \mu\text{m}$, in 2.8M- H_2SO_4 and D_2SO_4 with up to 1M-thiourea in a Pyrex glass cell separated to two compartments by a Nafion membrane which is held on a glass flange as shown in Fig. 1. The Pd foil was annealed in vacuum at 850°C for 2 hours and then etched in freshly prepared H_2SO_4/HNO_3 mixture for ten minutes.

The surface of the Pd rod electrode was modified in two ways either by electrodepositing Pd-black or by forming a thin film of Pd-Rh alloy in order to see the effect of surface catalytic properties of Pd on the cathode loading. A thin film of Pd-Rh alloy was formed on the Pd surface by electrodepositing rhodium followed by alloying the surface region for 4 hours at 800°C in a vacuum oven. The Pd-Rh alloy was selected because of its high electrolytic loading of deuterium at the rhodium concentration between 5-10%. It was thought that the results of electrolytic loading into such Pd cathode with a modified surface will answer to two questions: Is the good loading of the bulk Pd-Rh alloy due to its bulk property or the surface property? Can we improve the

loading characteristics of Pd by adding a new surface with better catalytic properties? The answers to such questions would be very useful in establishing the respective roles of the surface and the bulk of the cathode.

Modifying the cathode surface by Pd-black would be also useful in knowing the role of the catalytic property of the surface for the cathode loading. The deposition of Pd-black was conducted in 1M-HCl containing PdCl₂. A relatively smooth surface and rough one were prepared by controlling concentration of PdCl₂, and the surface area of the deposits were measured by conducting cyclic voltammetry between 0.4 V and 1.5 V(RHE).

RESULTS AND DISCUSSION

1. Cathode loading and the resistance change

Figures 2 and 3 show the relation between resistance ratio, R/R_0 , and the cathode loading, H/Pd and D/Pd, measured for a ϕ 2mm \times 50mm Pd rod(99.99% up, Johnson Matthey) in fuel cell type closed cells in 1M-LiOH and LiOD containing 0.6mM-thiourea. The low cathode loading region was investigated potentiostatically allowing the loading process to reach steady state in order to avoid building up of non-steady state distribution of hydrogen/deuterium which affects the measured resistance of the cathode. The high cathode loading region was investigated either galvanostatically in 1M-LiOH or potentiostatically in 1M-LiOD after the potentiostatic measurements in the lower cathode loading region. Figure 4 presents a set of data recorded in 1M-LiOD with 0.6mM-thiourea to show the sequence of the applied overvoltage, current response, resistance ratio R/R_0 and D/Pd measured from the gas (D₂) pressure in the course of an entire measurement which took for this case over 5 months. The Pd electrode was set at 800mV/RHE to avoid deuterium absorption as well as electrochemical oxidation of thiourea at the palladium electrode before onset of deuterium loading which was initiated at 200mV/RHE for 10 days. The overvoltage was lowered to 100mV, 50mV and 0V spending 40, 20 and 30 days at each value to allow the absorption to reach equilibrium. As seen in Fig. 4, however, the absorption equilibrium was not reached in these time span at the positive overvoltages, but only at 0 mV the resistance ratio and the D/Pd reached steady value of 0.75 which is indicative of absorption equilibrium at the reversible hydrogen electrode potential under D₂ gas of ca 6atm. In the negative overvoltage region, however, the resistance ratio as well as D/Pd reached their respective steady value, and decrease of the resistance ratio accompanied by increase of D/Pd was observed up to the current density of 120mA/cm². Although the absorption equilibrium was not

established at positive overvoltages, we can assume that there is little concentration gradient of absorbed deuterium inside the Pd electrode in view of the electrode diameter, 2mm, and the time span spent during the measurement. This is an important point as such concentration gradient (decrease) from the Pd surface to its interior could give rise to a lower resistance than the value corresponding to homogeneous deuterium distribution in the Pd electrode [7].

The present results thus obtained spending 5 months are almost in agreement with the previous data reported by various groups [8, 9, 10, 11] as shown in Figs. 2 and 3. Because the data of the cathode loading was available up to H/Pd and D/Pd around 0.9 in the present study, curve fitting was applied by using a fifth order polynomial to obtain the relation between R/R_0 and the cathode loading between 0.9 and 1.0. The extrapolated curves are almost consistent with the data reported by Baranovsky et al [10] at under high pressure of hydrogen and deuterium. It is important to mention the difference between the R/R_0 vs D/Pd relation to be employed in our study and the similar relation frequently employed by the group at SRI [12, 13, 20]. Figure 5 compares the three curves to show the R/R_0 vs D/Pd relation, which show that all the three curves almost coincide at D/Pd=0.9, below which our curve gives higher D/Pd than other two curves reported by SRI, while lower D/Pd by a few percent would be obtained above D/Pd=0.9. It is confusing a little bit for different groups to apply different calibration curves in the calculation of D/Pd from the measured R/R_0 , and it is necessary to keep this in mind when interpreting cathode loading data obtained by resistance measurements.

2. Effect of surface modification by thiourea

Figure 6 shows a series of R/R_0 data for a Pd foil in 2.8M- D_2SO_4 containing thiourea, $(NH_2)_2C=S$, of 0, 0.3mM, 3mM, 30mM, 300mM and 1M measured at 20°C for a series of applied electrolysis current density up to 500mA/cm². Upon addition of thiourea the initial peak of R/R_0 becomes more prominent with its increasing concentration and the R/R_0 value becomes lower for a given current density. Magnification of the initial change of the R/R_0 for the series of concentrations at 30mA/cm² shown in Fig. 7 demonstrates the marked effect of surface modification by thiourea. Figure 8 shows dependence of D/Pd on current density for a series of 2.8M- D_2SO_4 containing up to 1M-thiourea, and it demonstrates marked effect of thiourea to give D/Pd of 0.96 at 500mA/cm² in a solution containing 1M-thiourea. Dependence of the cathode loading on the concentration of thiourea at a constant current density, 500mA/cm², is shown in Fig. 9 both for H_2SO_4 and

D₂SO₄ solutions, which shows a systematic effect of surface modification by thiourea on the cathode loading, and H/Pd of 0.99 can be achieved according to this data. The current dependence of H/Pd is shown in Fig. 10, which again demonstrates marked improvement of the cathode loading upon addition of thiourea in 2.8M-sulfuric acid.

The data presented in Figs. 6-10 to show the marked effect of the surface modification by thiourea strongly suggests that the cathode loading can be controlled primarily by modifying the surface property of the cathode. Although we do not know the microscopic mechanism of the surface modification, deactivation of the Tafel step to recombine two adsorbed deuterium atoms to form a molecule is certainly what happens upon addition of thiourea. This is understood in terms of the overvoltage of the Tafel step, η_2 , which is related to the chemical potential of absorbed hydrogen atoms according to the relation;

$$\mu_{\text{H(ads.)}} = \mu_{\text{H}_2} - 2F \eta_2.$$

Existence of the second term in the right hand side of the above equation demonstrates advantage of the electrolytic cathode loading compared to the gas phase loading for which we have the first term, chemical potential of the hydrogen gas, only. The advantage can be interpreted in terms of effective pressure or fugacity of the hypothetical hydrogen gas which is in equilibrium with the absorbed hydrogen to have the chemical potential given by the above equation [14].

$$P_{\text{H}_2^*} / P_{\text{H}_2} = \exp(-2F \eta_2 / RT),$$

where P_{H_2} and $P_{\text{H}_2^*}$ are the actual pressure of the hydrogen gas in the electrolytic cell and the effective pressure operating under cathodic polarization.

It should be mentioned that thiourea acts as a catalytic poison of the Tafel step by adsorbing on the cathode surface, and the adsorption appears to be reversible, i.e., not chemisorption upon which adsorbed molecules usually decomposes to form a strongly adsorbed species. This is inferred from the fact that effect of thiourea cannot be maintained if the anode and the cathode compartments are not separated by the ion-exchange membrane. The Fig. 11 shows a typical example to show the gradual loss of the effect of thiourea during electrolysis in a cell which has the anode and the cathode in the same compartment. The decrease of the resistance ratio R/R_0 after passing through the maximum upon applying electrolysis current, 50mA/cm², is followed by the gradual increase due to desorption of absorbed hydrogen, which is more prominent in the sulfuric acid containing thiourea at lower

concentrations. Thiourea is electrochemically oxidized at the platinum anode leading to deterioration of the bulk concentration which causes desorption of the adsorbed thiourea molecules and simultaneously desorption of adsorbed hydrogen atoms.

3. Surface modification of Pd-Rh alloy cathode by Pd-black

Pd-Rh alloy has better electrolytic hydrogen/deuterium loading characteristics than palladium as we reported at ICCF4. We have tried to find if the better cathode loading of the alloy is controlled by its bulk or the surface property. For this purpose we have conducted experiments applying surface modification by Pd-black to see if the cathode loading of the alloy could be maintained with a thin layer of the Pd-black on its surface. Measurements were conducted in a fuel cell type closed cells as described elsewhere. Pd-Rh(10atm.%) was selected for the experiments in view of its highest cathode loading characteristics of all the Pd-Rh alloy cathodes investigated up to 30atm% Rh [15]. A thin layer of the Pd-black was deposited in either 0.1wt% or 2 wt% PdCl₂ in 0.1M-HCl at 12.5mA/cm² for 15 min., the former being for obtaining high surface area and the latter smooth Pd-black deposited layer. In fact surface area of 429.2 cm² and 6.4 cm² were obtained in this manner for the geometrical surface area of 2.7 cm²(ϕ 4mm \times 20mm), which were determined by conducting cyclic voltammetry between 0.4 V and 1.5 V in 0.5M-H₂SO₄. After loading experiments, however, these surface area changed to 150cm² and 12cm², respectively, i.e., the rougher surface became a little bit smoother and the smooth surface rougher.

Figure 12 compares the dependence of D/M(Pd+Rh) on overvoltage for Pd, Pd-Rh(10atm%), Pd-Rh(10atm%)/Pd(150cm²) and Pd-Rh(10atm%)/Pd(12cm²). Addition of the Pd-black layer on the surface degrades the loading characteristics of the alloy cathode according to these data, and D/M of the alloy with modified surface lies between Pd-Rh(10atm%) and Pd. The difference in the surface roughness of the Pd-black on the alloy surface has not caused significant change in the loading characteristics. It is interesting to note that dependence of the cathode loading on overvoltage presented in Fig. 12 show tendency to saturate at high overvoltage, i.e., higher than ca -800 mV. In other words, the increase of the total cathode overvoltage in this region is not contributing to increase in the cathode loading. This is interpreted in terms of the constituent overvoltage of the Tafel step which is almost invariant at high current densities despite the rapid increase of the total cathode overvoltage. The Tafel lines recorded for these cathodes simultaneously with the cathode loading are shown in Fig. 13, and indeed the slope of them become steeper at high current densities. The steep increase of the cathode

overvoltage is caused not by the increase of the overvoltage of the Tafel step but of the discharge step of the hydrogen evolution reaction in the alkaline solutions, which is discharge of water molecules combined with discharge of Li^+ ions according to the post-surface analysis of the Pd electrode as described later.

The data presented in Fig. 12 suggests clearly that the cathode loading is strongly influenced by the surface property of the cathode but at the same time the bulk property is still a key factor to determine the cathode loading.

4. Surface modification of Pd by Pd-Rh alloy film

We then tried to add a thin film of Pd-Rh alloy on a Pd surface to see if the loading characteristics of the Pd could be improved by modifying its surface with a Pd-Rh alloy film, which was formed by depositing Rh on the Pd surface in 0.5M- H_2SO_4 containing 1mM- $\text{Rh}_2(\text{SO}_4)_3$ at 12.5mA/cm² for 15 min. followed by annealing /alloying at 850°C for 2 hours in vacuum. Figure 14 shows the Auger depth profile of Pd and Rh before (A) and after (B) the annealing treatment. Sputtering rate is 6 nm/min and 13 nm/min before and after 300 min, respectively. According to the depth profile the thickness of the Rh deposit is ca 600 nm, while alloying extends into the Pd substrate up to 3.1 μm after the annealing treatment with continuous change of Rh concentration from ca 30% near the surface to several % in this region. Figure 15 shows dependence of D/M on overvoltage for this Pd electrode with the modified surface, and we can see that the loading characteristics is greatly improved at high cathode overvoltage compared to Pd electrode, but is not as good as Pd-Rh(10atm%). The data presented in Fig. 15 again demonstrates importance of the surface catalytic property as well as bulk property of the cathode substrate to accommodate absorbed deuterium.

5. Surface modification of the cathode by electrolysis products in LiOD

It has been frequently recognized that the cathode surface is subjected to *in-situ* modification or contamination by electrolysis products such as Li or platinum deposits during electrolysis in LiOD. In many experiments conducted in cells made of pyrex glass the dissolution of the glass components inevitably leads to accumulation of such materials on the cathode and the anode surfaces. Effect of these *in-situ* modification of the cathode surface has not been understood to any satisfactory extent due to absence of systematic studies.

We have conducted a series of XPS and SIMS analysis of the surface and near surface region of Pd samples which have been

subjected to a long term loading experiments in 1M-LiOD in quartz cells at 20 °C, D/Pd having been monitored by resistance measurements, and tried to relate the cathode loading data and the results of these surface analyses. Figure 16 presents a set of XPS spectra for a Pd sample taken after various sputtering times by Ar⁺: 0, 60 and 300 sec, respectively, which shows almost no sign of Pd but strong Pt bands for the unsputtered sample. But as sputtering proceeds the Pt bands intensity decrease drastically with development of Pd bands dominating the entire spectrum. The ratio Pt/Pd on the surface was determined from the narrow spectra of Pt and Pd for six Pd samples, O-1 to O-6, and is summarized in Table 1. The ratio varies from sample to sample, the largest and the smallest values being 50.4 and 0.6, respectively. The data indicates that the surface of the Pd cathodes are heavily contaminated by platinum, the origin of which being most likely the platinum anode or the four Pt leads welded to the Pd cathode for the resistance measurements. It is possible to relate the large variation of the surface Pt/Pd ratio of the samples to their electrolysis history if we classify the samples to two groups: one having the Pt/Pd ratio smaller than 1 and the other with the ratio larger than 10. All the samples were initially subjected to cathodic polarization at 300mA/cm², but the following electrolysis history was quite different between the two groups of samples with the large and the small Pt/Pd ratio. Figure 17 presents typical electrolysis history of the two groups as represented by the change of cathode resistance ratio with the applied current density during electrolysis which lasted for nearly fifty days. The group of the samples with the large Pt/Pd ratio was subjected to repeated load/deload cycles as shown by A while the other group of Pd samples underwent an unexpected resistance increase around 25th days which is indicative of deloading and did not experience the repeated load/deload cycles as shown by B. Dissolution of platinum from the Pt anode would depend on the total length of time of electrolysis at 300mA/cm², which is in fact almost the same for the electrolysis histories A and B as shown in Fig. 17. This suggests that dissolution of platinum from the Pt anode cannot explain the large difference of the surface Pt/Pd ratio, while dissolution of platinum from the Pt leads welded to the Pd cathode during the repeated deloading conducted by applying +1.5 V to the cathode is more likely responsible to the larger surface Pt/Pd ratio.

Figures 18 and 19 show the depth profile of Li and Pt respectively observed by SIMS for the six Pd samples described above. Comparison of the depth profile of the Pd sample before electrolysis, O-7, with the others, O-1 to O-6, clearly demonstrates that these depth profiles of Li and Pt deposits have been developed near the surface during electrolysis, although the quantitative difference of these depth profiles among the six samples is not well

interpreted in terms of their electrolysis history. We can note that both Li and Pt concentration drops sharply within 20-30 nm from the surface and that their depth profiles are closely related to each other if we take samples O-1 and O-7 for example. The quantitatively close relation, however, is not well understood at the moment. The apparent presence of a maximum in the Li depth profile near the surface around 10-20 nm is probably either an artifact in the SIMS analysis due to adsorbed oxygen, as the primary ion being O_2^+ , or due to loss of the surface Li upon washing by water after the electrolysis.

All the data shown in Figs. 16 and 19 and in Table 1 are indicative of heavy contamination of the surface region of the Pd cathode by Li and Pt deposits as previously reported by other groups [16, 17, 18], but interpretation of the loading data in terms of the surface contamination is not straightforward.

In the case of Li, however, comparison of the cathode loading data in 1M-LiOH and 1M- $(CH_3)_4NOH$, which is alkali metal free alkaline solution, clearly demonstrates, as shown in Fig. 20, however, that presence of the lithium deposit in the surface layer is not contributing to improving the cathode loading since the data observed in the lithium-free system is as good as or even better than the cathode loading in LiOH [1].

The platinum deposit which accumulates on the cathode surface during electrolysis has been considered to reduce the cathode loading since it would catalyze the Tafel step to enhance hydrogen desorption out of the palladium cathode. Comparison of the loading data observed in the open cells with an Pt anode and fuel cell type closed cells is interesting in discussing the role of the surface contamination by Pt since in the latter cells the surface Pt/Pd ratio is much smaller than in open cells as shown in Table 2. Figure 21 shows results of such comparison of the cathode loading data for the JM Pd(99.99%up) pretreated by the same procedure: mechanical polishing, degassing in vacuum at 200°C for 3 hours, and chemical etching in freshly prepared HNO_3/H_2SO_4 mixture for 10 min. The results show, however, that D/Pd in open cells is a few % higher than in the fuel cell type closed cells, i.e., the less contaminated system by platinum gave rise to lower cathode loading. We can conclude that the surface contamination by platinum is not playing a key role in the series of present loading experiments. Presumably there is some other unknown factors which are playing more important role in suppressing the maximum loading level than the surface contamination by platinum.

6. Improvement of the cathode loading by load/deload cycles

Improvement of cathode loading by repeated load/partial deload cycles was reported recently for Pd wires with palladized surface which were subjected to preloading in gas phase before electrolytic loading [19]. But because determination of the cathode loading was conducted volumetrically by using water filled manometer, two possible sources of error are envisaged: firstly, the apparent increase of cathode loading detected volumetrically may be due to hydrogen or deuterium trapped in internal voids or micro cracks created by the load/deload cycles, secondly contamination by H₂O from the manometer the rate of which was estimated as 0.13% a day could contribute to the apparent D/Pd increase during the load/deload cycles which lasted for 1-2 weeks.

The effect of repeated deload/reload cycles was also indicated for a Pd rod of 3 mm diameter with a smooth surface more recently by applying resistance measurements [20], although the details of the study was not reported.

We have conducted similar measurements to see the effect of applying load/deload cycles on the cathode loading in open cells made of quartz glass. In order to avoid the problems described above, however, the cathode loading was monitored by resistance measurements which would not be affected by increase of absorbed hydrogen or deuterium trapped in the internal voids or micro cracks, while the cell was kept purged by dry boil-off nitrogen above the electrolyte solution to avoid H₂O contamination the level of which was determined by NMR before and after the loading experiments.

Figure 22 presents a typical example to show the resistance change of the JM Pd(99.99%up) cathode and electrolysis current during the entire period of experiment to see the effect of load/deload cycles. The current density was increased in a step wise manner up to 1 A/cm² and then decreased to zero at which deloading proceeded for 5 days until D/Pd decreased down to 0.572, and then reloading was conducted at 0.3 A/cm². By this first deload/reload cycle the D/Pd at 0.3 A/cm² reached 0.919 while it was 0.893 before applying such cycle. The cycle was repeated for several times as shown in Fig. 22 and further improvement of the cathode loading was recorded. Figure 23 presents result of such deload/reload procedure for two samples, which shows that the effect of such deload/reload cycles observed for the two samples almost saturated after applying two cycles. The effect of the deload/reload cycles and the tendency for the effect to saturate was commonly observed for other Pd materials with different purities ranging from 99%up to 99.99%up and with different heat treatment, i.e., either cold worked or annealed at 850°C, from other sources, and the maximum D/Pd achieved after applying the deload/reload cycles lies between 0.90 and 0.95 which varies from sample to sample. The fact that the effect of deload/reload cycles is

commonly observed for Pd materials with different bulk properties especially with different heat treatments suggests that the cycle is giving rise to some change in the surface catalytic property to control the desorption of absorbed deuterium.

Because this was confirmed by the resistance change of the cathode the observed improvement of the cathode loading is not caused by trapping of hydrogen/deuterium in the internal voids or micro cracks possibly created in the cathode upon applying deload/reload cycles.

The deloading in the above experiments was conducted simply by switching off the electrolysis current for a few days, during which period the D/Pd decreased to around 0.6. We then tried to find effect of degree of deloading on the improvement of the cathode loading after reloading at 300 mA/cm². The degree of deloading was adjusted either by controlling the time at zero current before the reloading or by applying anodic current to the Pd cathode for a given time to enhance deloading. Figure 24 presents a set of data obtained for ten JM Pd samples which shows the relation between the D/Pd before reloading and the D/Pd after reloading at 300 mA/cm². The data suggests that it is necessary to deload the Pd cathode below D/Pd=0.6~0.7 for the effect of deload/reload cycle to develop and that the effect appears to increase as the cathode is more deloaded until D/Pd=0.40~0.6 is reached. What these findings mean is not clear at the moment, but it looks as if it were necessary for the cathode to go into the $\alpha \rightarrow \beta$ transition region during the deloading process for the effect of deload/reload cycle to start developing.

There is a problem in interpreting the data corresponding to complete or near complete deloading in Fig. 24 that Pd cathodes sometimes undergo irreversible change in its size when it is subjected to such heavy deloading. The estimation of D/Pd from the resistance measurements is no longer reliable when such change in the cathode size is accompanied with the deloading process. We checked actual size change of the cathode as a function of the cathode loading by measuring the change in the cathode length during the load/deload processes. Figure 25 presents a pair of data of two experiments using JM Pd rods (ϕ 2mm \times 40mm, 99.99%up) to show % change in cathode length with respect to the original one during the load and deload processes. We can note that the cathodes become longer as loading increases with different rates for a unit increase of D/Pd below and above D/Pd = 0.58 : 1% and 3.8%, respectively, while the cathode length is reduced almost linearly during the deloading process at the same rate, 3.8%, until the complete deloading. There is a marked hysteresis in the size change below D/Pd=0.58 and this would give rise to irreversible resistance change of the cathode if the cathode is deloaded below this level. In view of this results all the data presented in Fig. 24

for D/Pd before reloading below 0.2 would be suffering from the irreversible size change and the D/Pd after reloading for this region would be actually lower than plotted by at least ca 1.6 %.

The region above D/Pd=0.58 corresponds to the so-called β phase, in which the change of the cathode length is completely reversible as demonstrated in Fig. 26 for the three consecutive load/deload cycles above D/Pd=0.6. Apart from the reversible change it is interesting to note that the cathode becomes longer accompanied by increase of D/Pd as the cycle is repeated. This is an independent proof obtained by the monitoring of the cathode length to confirm the effect of deload/reload cycles on the loading. The rate of the length change in the β phase region is 3.8 % with respect to an unit increase of D/Pd, and this is close to the rate 4.4% predicted from the lattice constant data [21] assuming a uniform lattice expansion in the Pd cathode, as shown in Fig. 25, while the rate experimentally observed during the loading process below β phase region which is considerably smaller than the rate in the β phase suggests strongly that the cathode expands originally much more along the radial direction than the direction along the rod axis.

Finally NMR analysis of the 1M-LiOD used in the above experiments was conducted to see the level of contamination by light water which might affect the long term resistance measurements in the electrolytic cells as increase of H/D in the cathode would contribute to lowering its resistance, which will be interpreted misleadingly in terms of apparently higher cathode loading. Figure 27 shows a set of data to show the NMR analysis of 1M-LiOD before pre-electrolysis, after pre-electrolysis, after electrolysis in open cells, and after electrolysis in fuel cell type closed cells. The atomic ratio H/D in the electrolyte becomes slightly smaller after pre-electrolysis, but is markedly reduced after prolonged electrolysis in open cells, while no such reduction in H/D was not observed in the fuel cell type closed cells. These results confirm effectiveness of pre-electrolysis and electrolysis in open cells in reducing the light water level in the electrolyte due to the preferential hydrogen evolution at the Pd cathode, while in the fuel cell type closed cells no such reduction is to be expected as the evolved hydrogen goes back to the electrolyte by electrochemical oxidation at the fuel cell anode. In conclusion the improvement of the cathode loading by applying the deload/reload cycles is not an artifact caused by light water contamination during the long term electrolysis.

Practically it is very important to maintain the improved cathode loading at high current densities as the high D/Pd at high current densities is the necessary condition for the excess heat generation according to the previous data of various groups [13, 22, 23]. Figure 28 presents an example to show the dependence of

D/Pd on current density before and after the improvement of the cathode loading by applying the deload/reload cycles. The improved cathode loading is maintained at high current densities giving rise to a new dependence of D/Pd on current density. Addition of 100 ppm Al appears to improve the cathode loading at higher current densities as reported before [20].

In conclusion the improvement of the cathode loading by applying the deload/reload cycles could be an effective way to establish the necessary condition for excess heat generation.

7. Cathode loading in 1M-LiOH

We conducted H/Pd measurements in 1M-LiOH in order to understand the problem encountered in achieving the high cathode loading in 1M-LiOD is really specific to the heavy water system. Two experiments were run for this purpose in similar cells made of quartz glass using JM Pd(ϕ 2mm \times 40mm, 99.99% up) cathodes which were mechanically polished, cleaned, chemically etched, and degassed in the same procedure as described already. Figure 29 presents a pair of data to show change of the cathode resistance ratio with the applied current density. Electrolysis was initiated at 30 mA/cm², upon which the resistance ratio goes through a sharp maximum as predicted from Fig. 2 and becomes a steady value around 1.5. With further increase of the current density the ratio goes down continuously, which is indicative of further increase of the cathode loading. Figure 30 presents dependence of H/Pd on current density determined from the data in Fig. 29. H/Pd of 0.97 is achieved at 500 mA/cm², and it is very likely that higher loading would be achieved at higher current densities as there is little tendency for H/Pd to saturate.

The data in 1M-LiOH strongly suggests that the difficulty encountered in the cathode loading in LiOD is really specific to the heavy water system as reported before [3].

8. Conclusion

There are still unknown factors related to the bulk and/or surface properties of the cathode to control its maximum loading by deuterium. We have found out at least two systems which guarantee the cathode loading higher than 0.95, the one being Pd-Rh alloys containing 5-10 atm% rhodium and the other Pd in 2.8M-D₂SO₄ containing 1M-thiourea. The deload/reload cycles certainly improves the cathode loading to get it higher than 0.9 but less than 0.95.

The results reported in the present study strongly indicate that the surface property of the palladium cathodes essentially controls

the maximum loading level apart from modifying the bulk property by alloying with rhodium. The detailed picture of such surface to enhance the cathode loading, however, is not clear yet at the molecular level.

References

1. H. Akita, Y. Tsuchida, T. Nakata, A. Kubota, M. Kobayashi, Y. Yamamoto, N. Hasegawa, N. Hayakawa and K. Kunimatsu, Proceedings of ICCF4, vol. 1 p 21-1, Electric Power Res. Inst. Palo Alto California, 1994.
2. T. A. Green and T. I. Quickenden, *J. Electroanal. Chem.*, 368(1994)121.
3. T. A. Green and T. I. Quickenden, *J. Electroanal. Chem.*, 389(1995)91.
4. M. C. H. McKutre, R. Rocha-Filho, S. I. Smedley, F. Tanzella, S. Crouch-Baker, T. O. Passell and J. Santucci. Proceedings of ICCF2 "The Science of cold fusion" p 419, T. Bressani, E. Del Guidice and G. Preparata (Eds.) SIF Bologna, 1991.
5. H. Okamoto, T. Sano, Y. Oyabe, T. Terazawa and T. Ohi, ICCF5 Book of abstracts p 505, Monte-Carlo, Monaco 1995.
6. K. Kunimatsu, N. Hasegawa, A. Kubota, N. Imai, M. Ishikawa, H. Akita, and Y. Tsuchida, Proceedings of ICCF3 "Frontiers of Cold Fusion" Ed. by H. Ikegami, Universal Academy press Inc. 1993, p 31.
7. T. Nakata, A. Kubota and K. Kunimatsu, Abstracts of '93 Fall meeting of the Japanese Electrochem. Soc., Fukuoka p 255. Abstracts of the 61st annual meeting of the Japanese Electrochem. Soc., Sendai, p 309.
8. T. B. Flanagan and F. A. Lewis, *Z. Physik. Chem.*, 27(1961)104.
9. J. C. Barton, F. A. Lewis and I. Woodward, *Trans. Faraday Soc.*, 59(1963)1201.
10. B. Baranowski, F. A. Lewis, W. D. Mcfall, S. Filipek and T. C. Witherspoon, *Proc. Royal Soc. London A* 386(1983)309.
11. A. W. Szafranski and B. Baranowski, *Phis. Stat. Sol.* (a) 9(1972)435.
12. M. C. H. Mckubre, R. C. Rocha-filho, J. Chao, B. Chexal, T. Passel and J. Santucci, *Proc. of the 1st Ann. Conf. on Cold Fusion* 1991 p 20.
13. M. C. H. McKbre, S. Crouch-Baker, R. C. Rocha-Filho, S. I. Smedley and F. L. Tanzella, T. O. Passel. and J. Santucci, *J. Electroanal. Chem.*, 368(1994)55.
14. T. Maoka and M. Enyo, *Electrochim. Acta*, 26(1981)607.
15. Y. Yamamoto, N. Hayakawa and K. Kunimatsu, Abstracts of '94 Fall meeting of the Japanese Electrochem. Soc., Yokohama, p 183.
16. O. Yamazaki, H. Yoshitake, N. Kamiya and K. Ota,

- J. Electroanal. Chem., 390(1995)127.
17. M. Nakada, T. Kusunoki, M. Okamoto and O. Odawara, Proc. of the ICCF3 "Frontiers of Cold Fusion" Ed. by H. Ikegami, Univ. Acad. Press Inc. 1993 p 581.
 18. D. R. Coupland, M. L. Doyle, J. W. Jenkins, J. H. F. Notton, R. J. Potter and D. T. Thompson, Proc. of ICCF1 p 299.
 19. F. G. Will, K. Cedzynska and D. C. Linton, J. Electroanal. Chem., 360(1993)161.
 20. M. C. H. McKubre, B. Bush, S. Crouch-Baker, A. Hauser, N. Jevtic, S. Smedley, M. Srinivasan, F. Tanzella, M. Williams, and S. Wing, Proc. of ICCF4 vol. 1 5-1.
 21. J. E. Schirber and B. Morosin, Phys. Lett. B 12(1975)117.
 22. M. C. H. Mckubre, S. Crouch-Baker, A. M. Riley, S. I. Smedley and F. L. Tanzella, Proc. of ICCF3 "Frontiers of Cold Fusion" Ed. By H. Ikegami Univ. Acad. Press Inc. 1993 p 5.
 23. N. Hasegawa, N. Hayakawa, Y. Tsuchida, Y. Yamamoto and K. Kunimatsu, Proc. of ICCF4 p 3-1.

Table 1 Surface Pt/Pd ratio determined from the XPS narrow spectra of Pd cathodes(JM 99.99% up, ϕ 2mm \times 40mm) after prolonged electrolysis in 1M LiOD in open cells made of quartz glass.

| | O-1 | O-2 | O-3 | O-4 | O-5 | O-6 |
|-------|------|------|-----|------|------|-----|
| Pt/Pd | 50.4 | 11.6 | 0.8 | 11.0 | 12.7 | 0.6 |

Table 2 Surface Pt/Pd ratio determined from the XPS narrow spectra of Pd cathodes after long term electrolysis in 1M LiOD in fuel cell type closed cells.

| | F-1(white spot) | F-1(black spot) | F-2(white spot) | F-2(black spot) |
|-------|-----------------|-----------------|-----------------|-----------------|
| Pt/Pd | 0.27 | 0.05 | 0.19 | 0.02 |

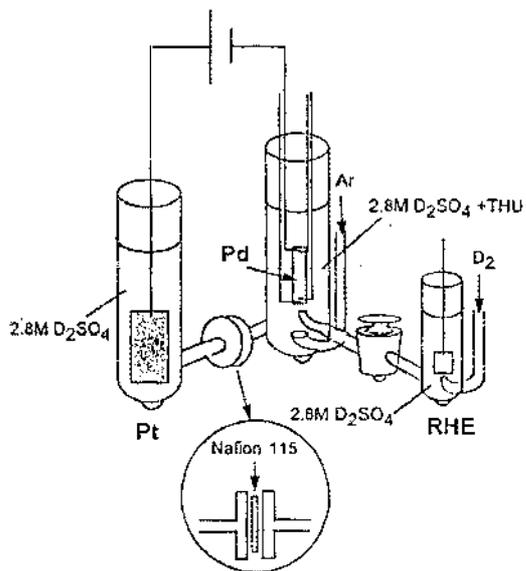


Fig.1 Electrolysis cell to separate the cathode and the anode compartments by cation exchange membrane Nafion 115.

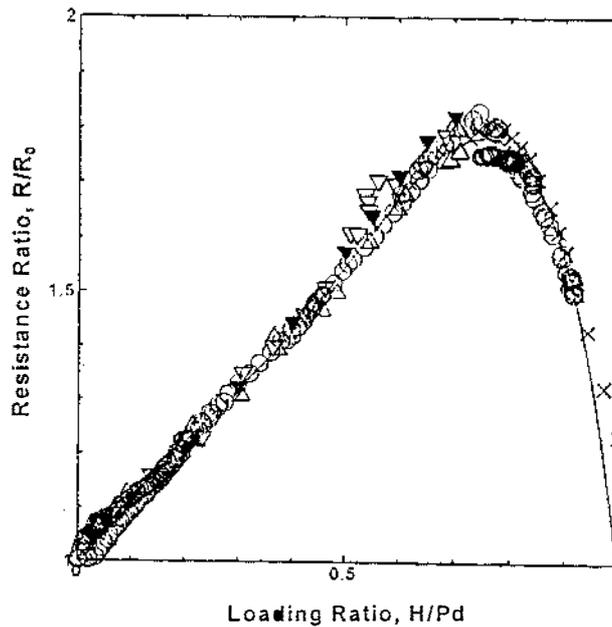


Fig.2 Cathode resistance ratio vs. H/Pd relationship obtained in the present study in 1M-LiOH at 20° C (○), Lewis et al., 25° C (△▽▽), Baranowski et al., 25° C (×).

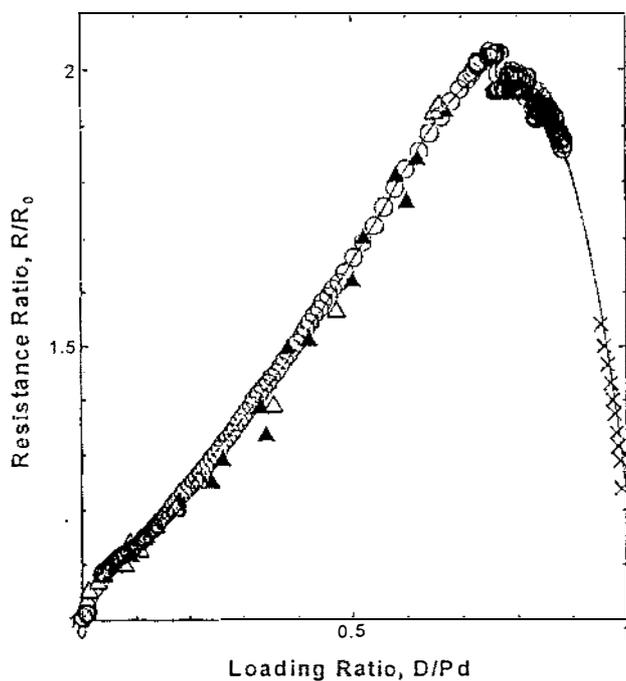


Fig.3 Cathode resistance ratio vs. D/Pd relationship obtained in the present study in 1M-LiOD containing 0.6mM thiourea at 20° C (○), Sieverts & Danz, 25° C (▲), Flanagan & Lewis, 25° C (△), Baranowski et al., 25° C (×).

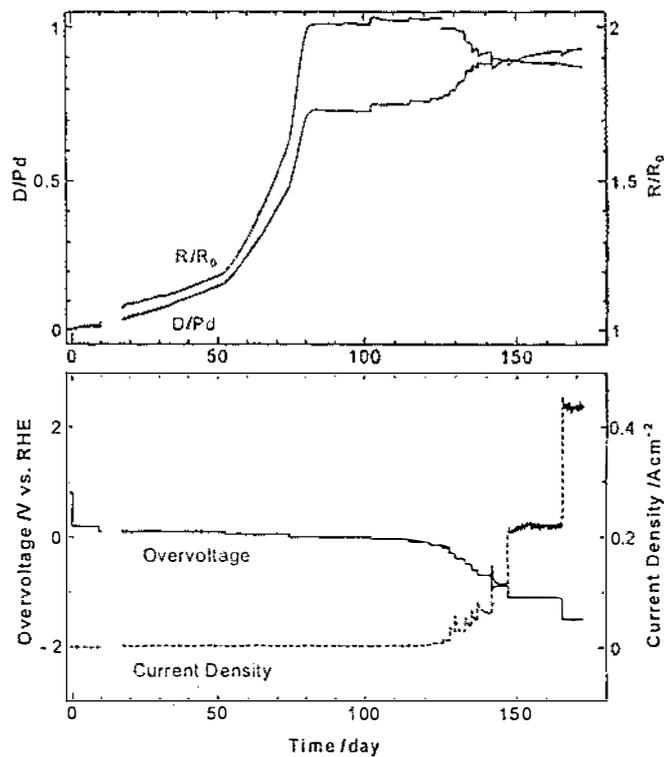


Fig.4 Change of R/R_0 , D/Pd , cathode overvoltage and current density during the long term electrolysis using a Pd cathode ($\phi 2\text{mm} \times 50\text{mm}$, 99.99% up) in 1M-LiOD containing 0.6mM thiourea.

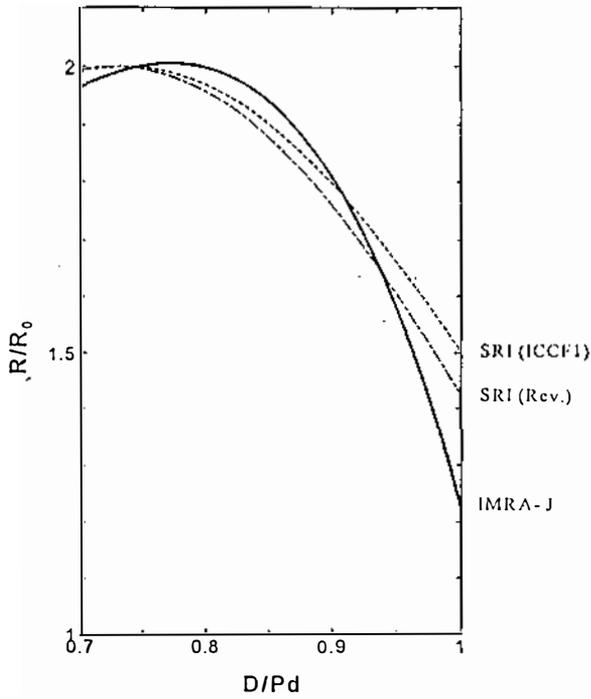


Fig. 5 Cathode resistance ratio, R/R_0 , vs. D/Pd for the cathode loading higher than 0.7: SRI (ICCF1), SRI (Revised) and IMRA Japan curves.

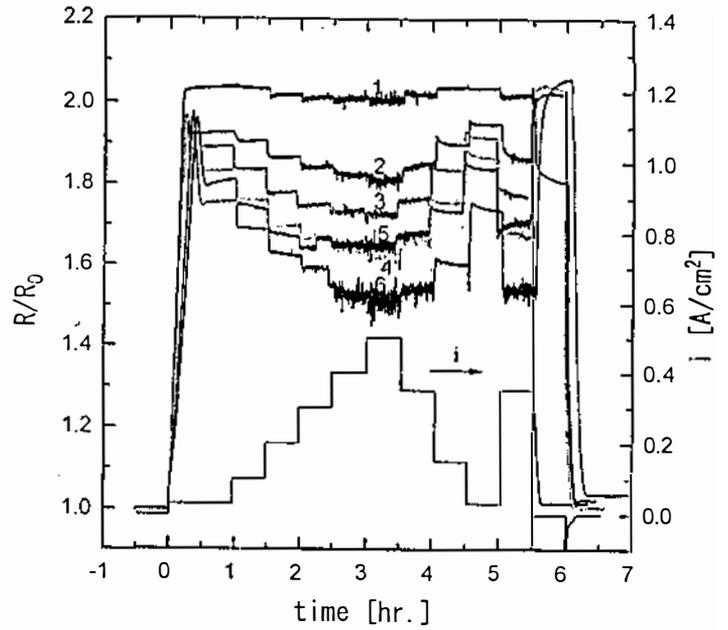


Fig. 6 Change of resistance ratio of a Pd foil cathode ($5\text{mm} \times 20\text{mm} \times 50\ \mu\text{m}$) with applied current density in $2.8\text{M-D}_2\text{SO}_4$ containing thiourea at 20°C . Concentration of thiourea: 0 (1), 0.3mM (2), 3mM (3), 30mM (4), 300mM (5), 1M (6).

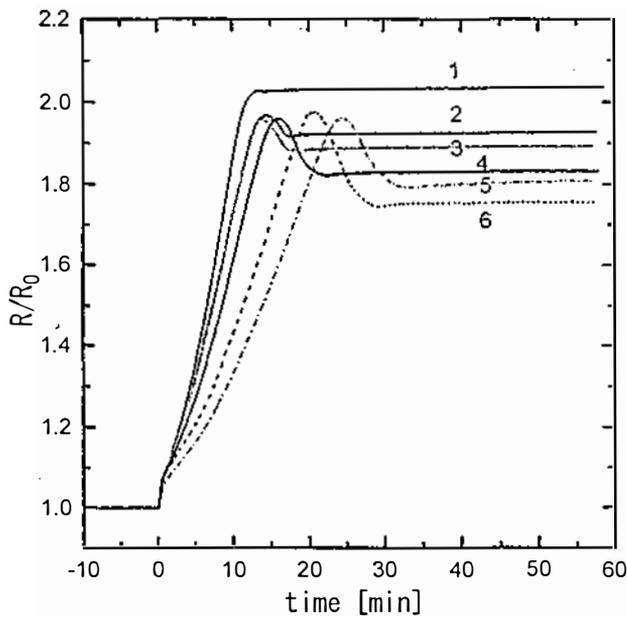


Fig. 7 Initial stage of Fig. 6 to show change of resistance ratio with time at 30mA/cm^2 .

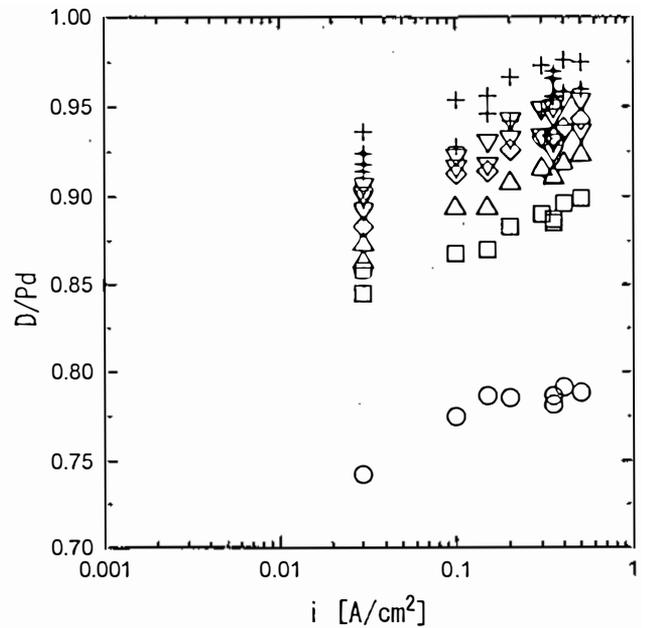


Fig. 8 Dependence of D/Pd on current density for the Pd foil cathode in $2.8\text{M-D}_2\text{SO}_4$ containing thiourea. Concentration of thiourea: 0mM (○), 0.3mM (□), 3mM (△), 30mM (◇), 300mM (▽), 1M (+). The D/Pd in pure D_2SO_4 was determined electrochemically by integrating the anodic dissolution current.

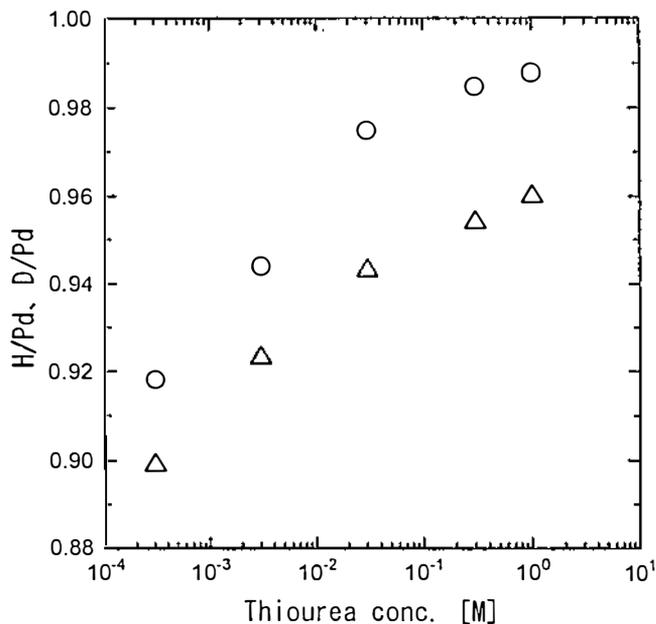


Fig. 9 Dependence of H/Pd and D/Pd on thiourea concentration for the Pd foil cathode at 20°C and 0.5 A/cm² in 2.8M-H₂SO₄ (○) and D₂SO₄ (△).

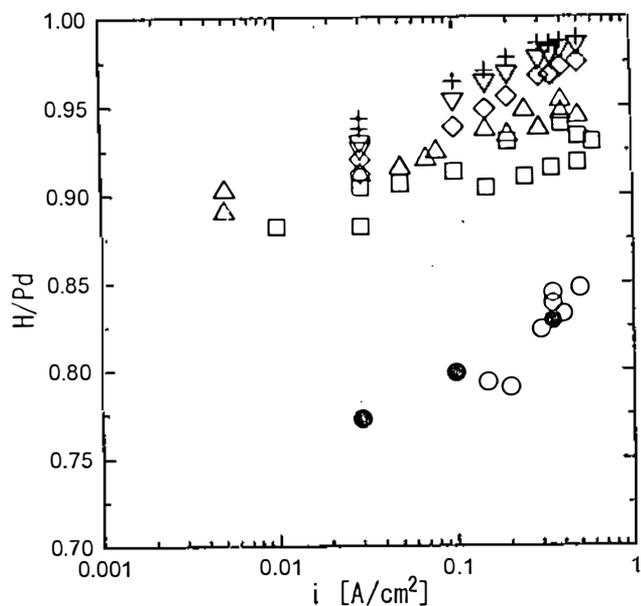


Fig. 10 Dependence of H/Pd on current density for the Pd foil cathode at 20°C in 2.8M-H₂SO₄ containing thiourea. Concentration of thiourea: 0 (○, ●), 0.3mM (□), 3mM (△), 30mM (◇), 300mM (▽), 1M (+). The data points ● were determined electrochemically by anodic oxidation of the absorbed hydrogen.

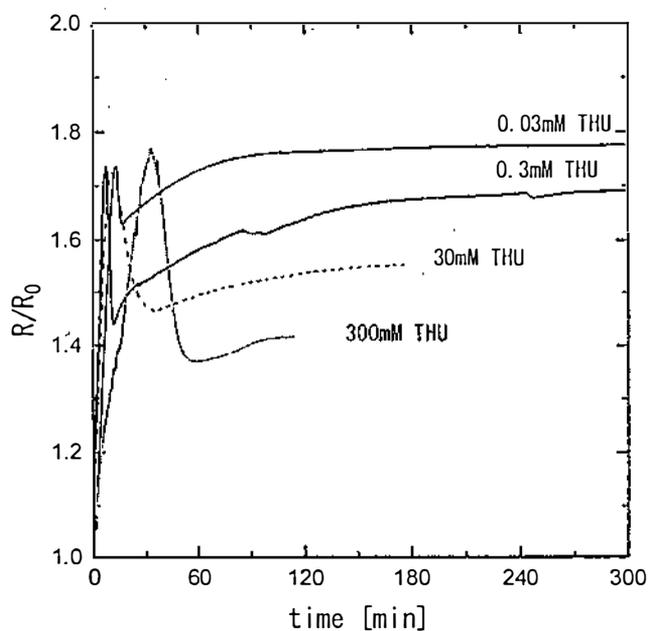


Fig. 11 Change of resistance ratio with time for the Pd foil cathode in 0.5M-H₂SO₄ containing thiourea observed at 20°C in a electrolysis cell with the Pd cathode and Pt anode in the same compartment.

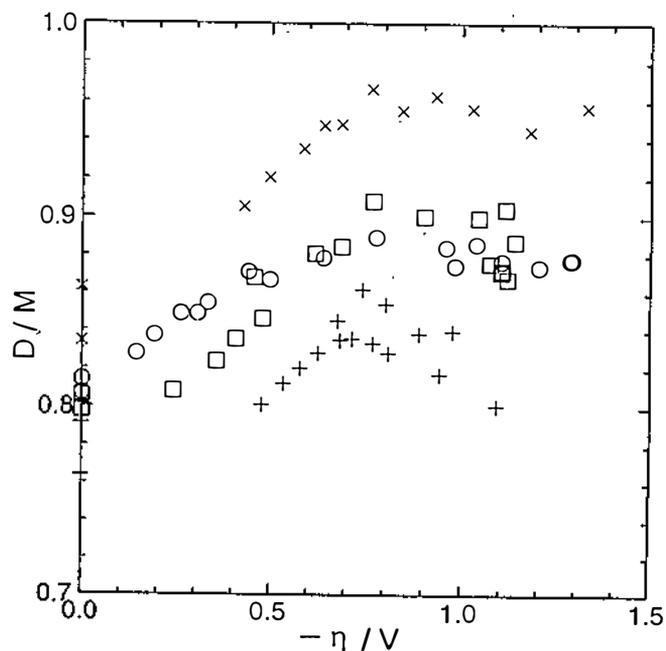


Fig. 12 Dependence of D/M on cathode overvoltage observed at 10°C in 1M-LiOD for ϕ 4mm Pd(+), Pd-Rh(10at%)(x), Pd-Rh(10at%)/Pd(150 cm²)(O), Pd-Rh(10at%)/Pd(12cm²)(□).

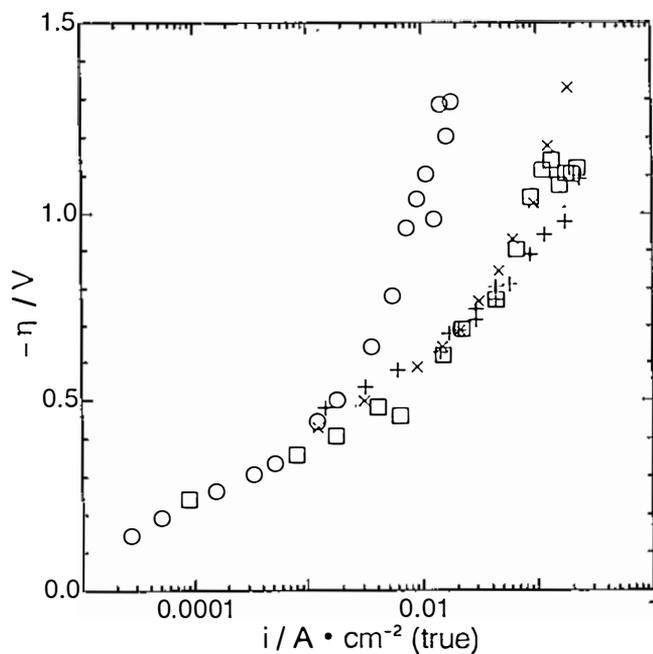


Fig. 13 Tafel lines observed in 1M-LiOD at 10°C for ϕ 4mm Pd, Pd-Rh and Pd-Rh/Pd alloys. The notations are the same as Fig. 12.

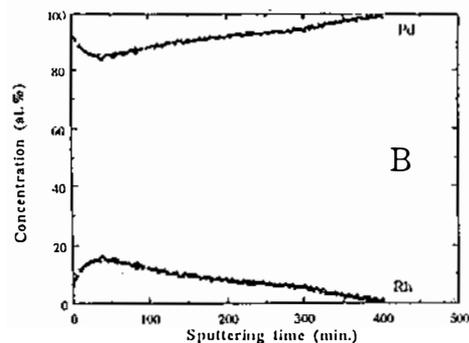
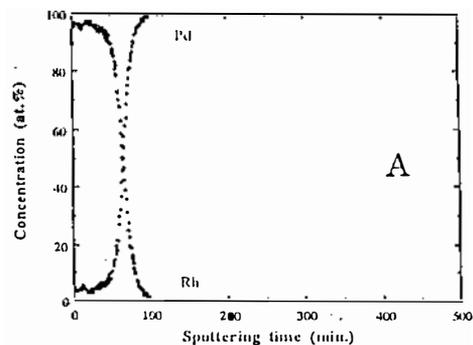


Fig. 14 Auger depth profile of Pd and Rh of the Pd cathode with an electrodeposited Rh film before (A) and after (B) annealing at 850°C for 2 hours in vacuum.

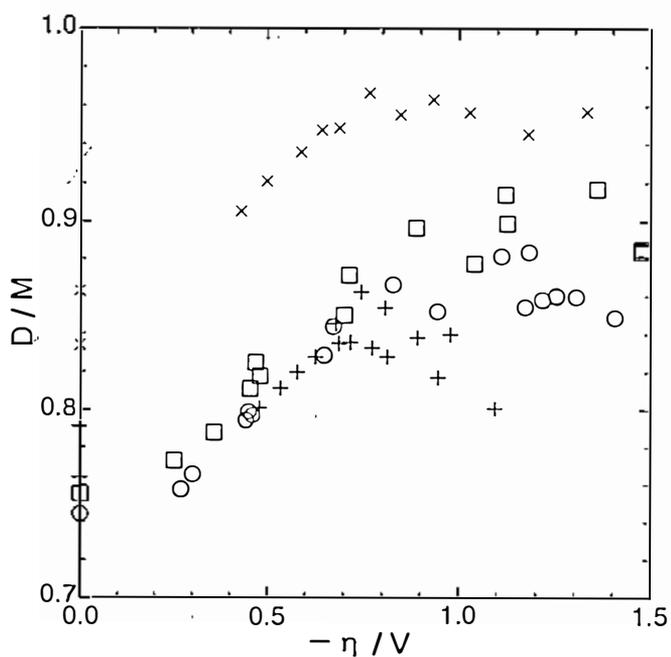


Fig. 15 Dependence of D/M on cathode overvoltage observed in 1M-LiOD at 10°C for ϕ 4mm Pd(+), Pd-Rh(10 at%)(x), Pd/Pd-Rh(O, □).

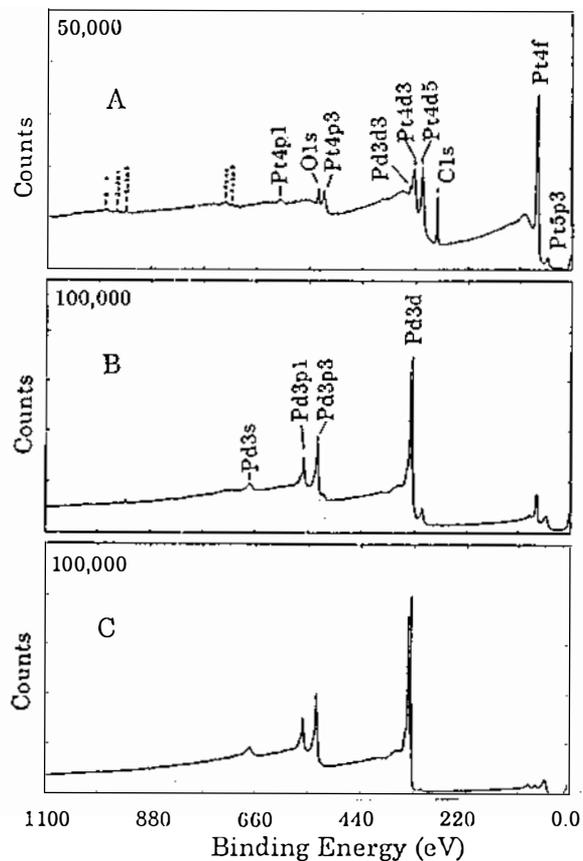


Fig. 16 Change of XPS spectra of a Pd cathode surface with sputtering time: 0 (A), 60 sec (B), 300 sec (C). The Pd cathode was subjected to a long term electrolysis in 1M-LiOD in an open cell with a Pt anode.

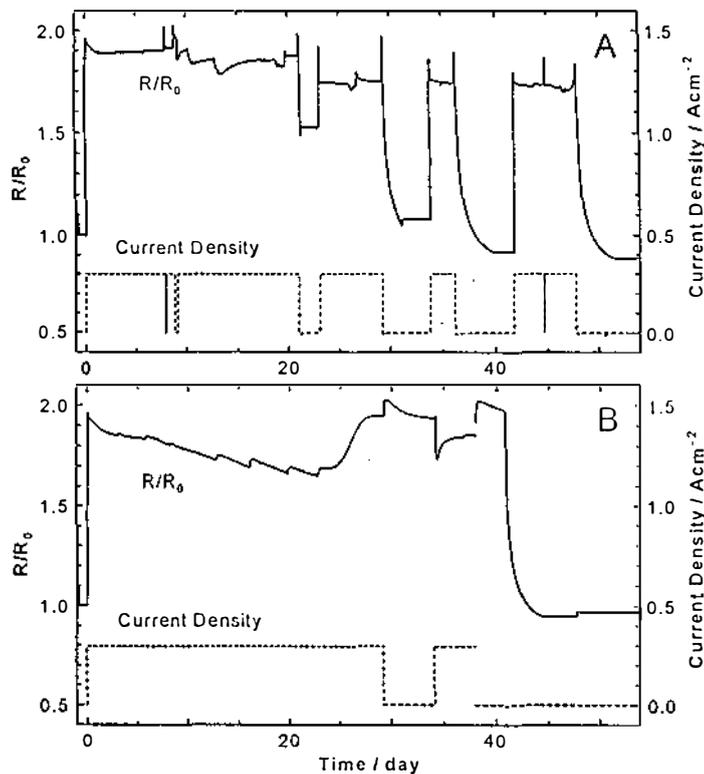


Fig.17 Change of resistance ratio of the Pd rod cathodes (JM, ϕ 2mm \times 40mm, 99.99% up) and current density during the electrolysis in 1M-LiOD at 20°C in open cells. A: Pd with surface Pt/Pd ratio higher than 10, and B: Pd with surface Pt/Pd ratio lower than 1.0

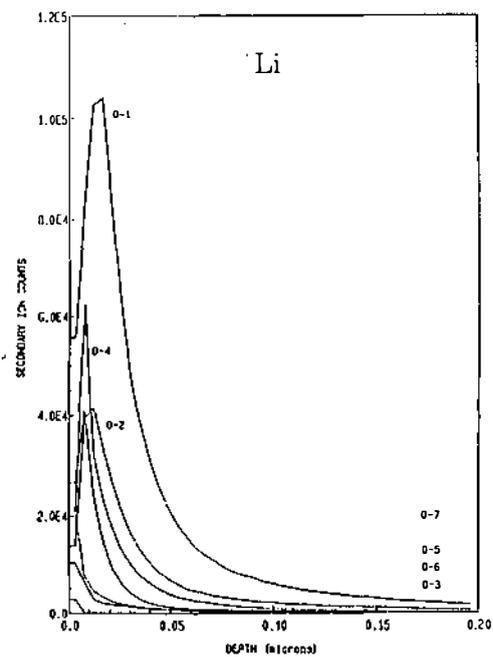


Fig. 18 SIMS depth profile of Li for Pd rods (JM, ϕ 2mm \times 40mm, 99.99%) before electrolysis (O-7) and subjected to long term electrolysis in 1M-LiOD in open cells (O-1—O-6).

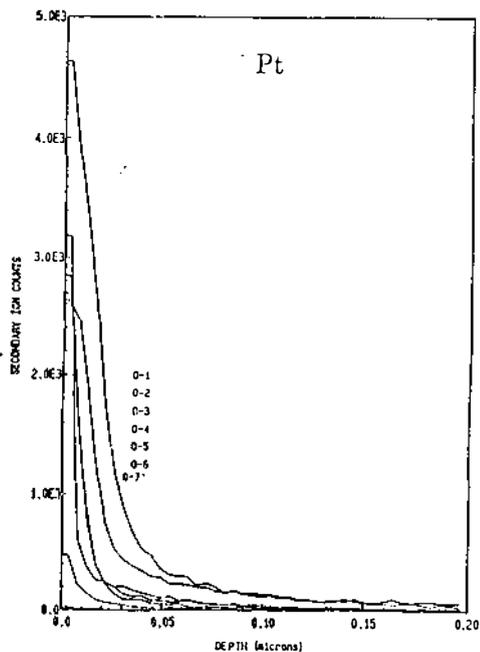


Fig. 19 SIMS depth profile of Pt for Pd rods. The notation is the same as Fig. 18.

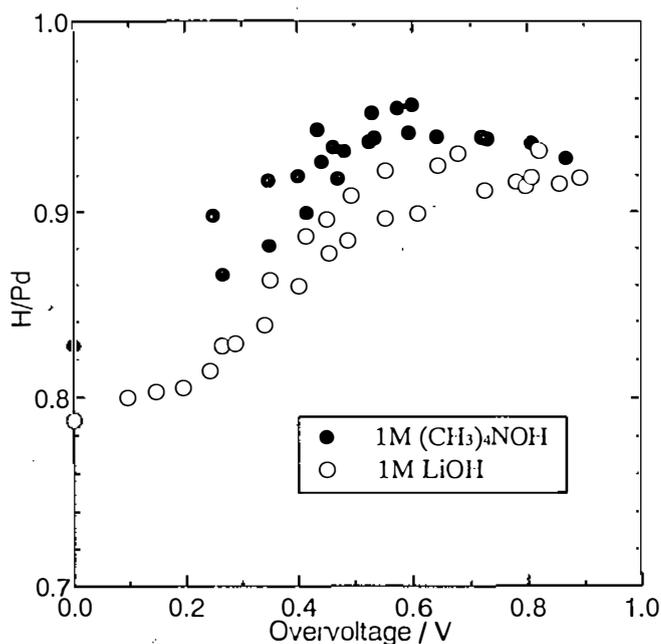


Fig.20 Comparison of overvoltage dependence of H/Pd for ϕ 4mm Pd(TNK, 99.9% up) observed in 1M-LiOH(O) and 1M-(CH₃)₄NOH(●) at 10°C.

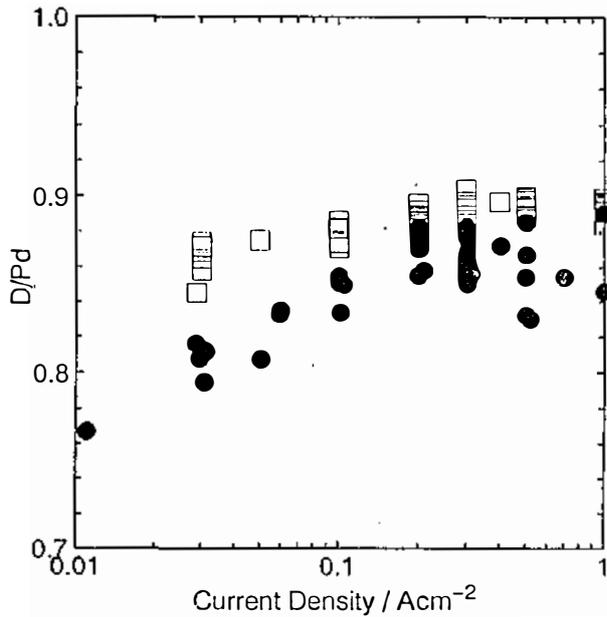


Fig.21 Comparison of D/Pd observed for 6 Pd cathodes in open cells(□) and 5 Pd cathodes in fuel cell type closed cells (●) in 1M-LiOD at 20°C. Pd rods: φ 2mm × 40mm, JM 99.99 %up

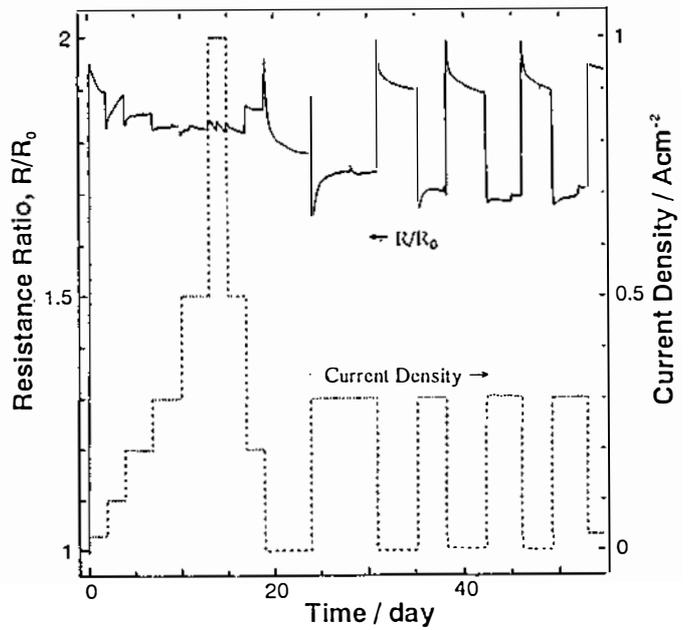


Fig.22 Change of cathode resistance ratio and current density during the electrolysis in 1M-LiOD at 20°C to see the effect of deload/reload cycles on the cathode loading

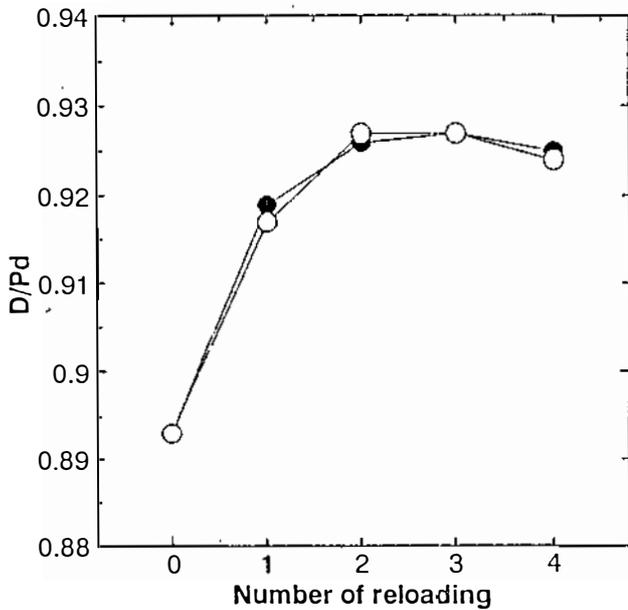


Fig.23 Dependence of D/Pd after reloading on the number of deload/reload cycles observed for two Pd cathodes in 1M LiOD at 20°C in open cells.

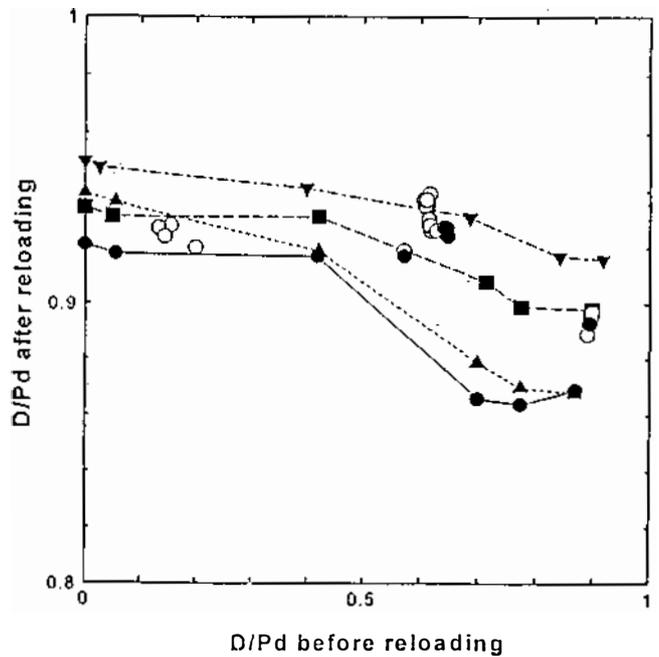


Fig.24 The effect of degree of deloading on D/Pd after reloading at 300mA/cm² of the ten JM Pd rods (φ2mm×40mm) in 1M-LiOD at 20°C.

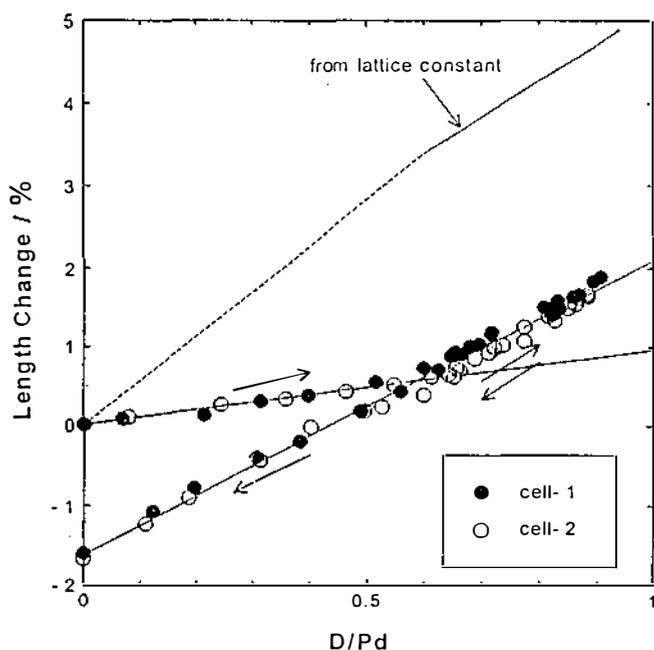


Fig.25 Dependence of change in cathode length on D/Pd observed for the two Pd rod cathodes (JM, $\phi 2\text{mm} \times 10\text{mm}$, 99.99% up) in 1M-LiOD and the change in length calculated from the lattice constant data assuming uniform expansion of the palladium lattice.

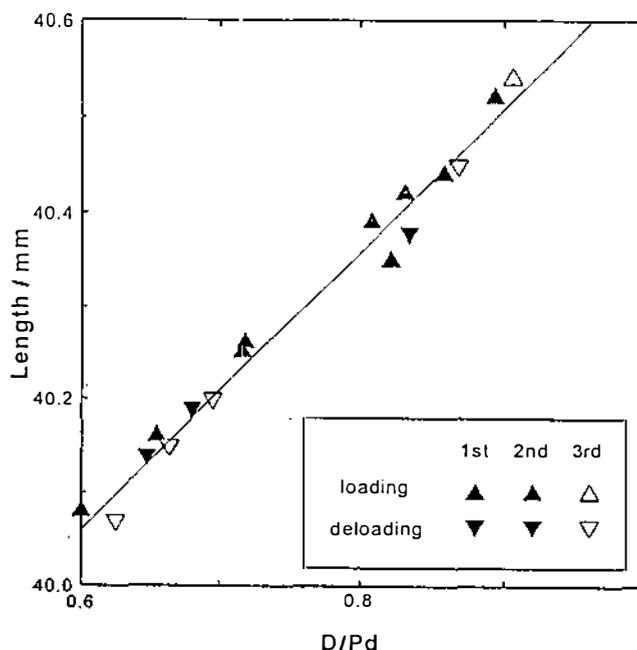


Fig.26 Change of the cathode length during the three consecutive load-de-load-load cycles in the β phase region.

| | Sample No | H/D at% | electorolysis time |
|-------------------------|-----------|-------------------------------|--------------------|
| | | 0.000 0.200 0.400 0.600 0.800 | |
| before pre-electrolysis | E-5 | 0.209 | |
| after pre-electrolysis | F-5 | 0.176 | pre-elec. 24hrs |
| | F-6 | 0.149 | pre-elec. 96hrs |
| Open cells | G-1 | 0.101 | 60days |
| | G-2 | 0.071 | ↑ |
| | G-3 | 0.086 | ↑ |
| | G-4 | 0.051 | ↑ |
| | G-5 | 0.062 | ↑ |
| | G-6 | 0.179 | ↑ |
| FC cells | D-3 | 0.620 | 90days |
| | D-9 | 0.386 | ↑ |
| | D-10 | 0.350 | 60days |

Fig.27 Results of the NMR analysis of H/D ratio in 1M LiOD before and after pre-electrolysis, after electrolysis in open cells for 60 days, and after electrolysis in fuel cell type closed cells for 60 and 90days.

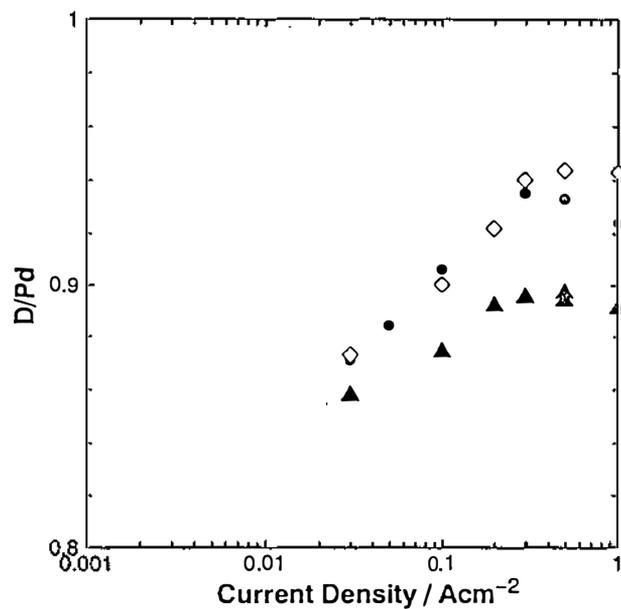


Fig.28 Dependence of D/Pd on current density before applying deload/reload cycles(▲), after the cycles(●) and with 100ppm Al after the cycles(◇) observed for a JM Pd rod (ϕ 2mm \times 40mm, 99.99 up) in 1M-LiOD at 20°C

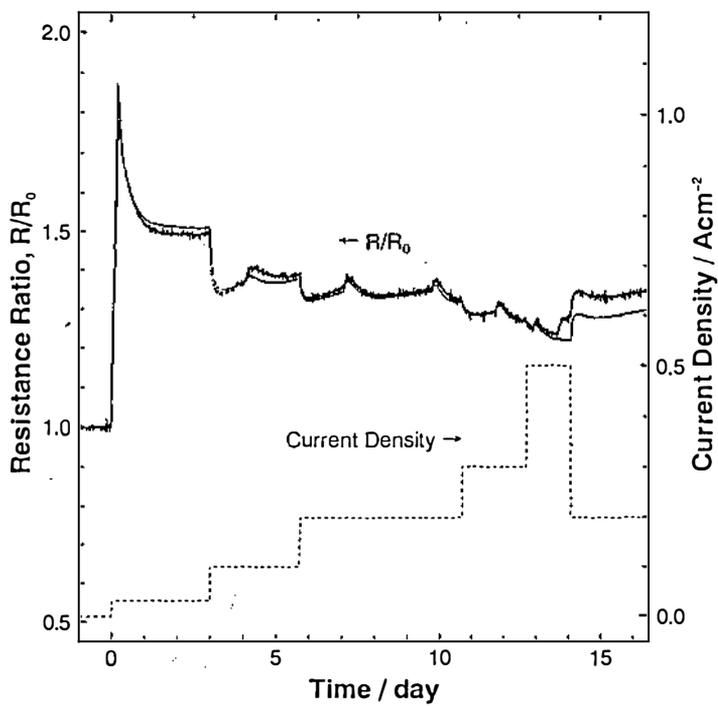


Fig.29 Change of the cathode resistance ratio and applied current density observed for JM Pd rods in 1M-LiOH at 20°C.