NHE Session

STUDY OF MATERIAL PROCESSING AND TREATMENT FOR HIGH DEUTERIUM-LOADING

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ABSTRACT

The electrochemical deuterium loading behavior of Pd cathodes in $LiOD/D_2O$ system has been studied experimentally using a resistance measurement method. The material conditions of Pd cathodes significantly affect the attainable D/Pd loading ratio. In addition, the D/Pd is affected by the applied current density profile, pattern of increasing current and anodic treatments.

As a result of the experiments, it was concluded that higher annealing temperatures (~1000 °C) result in higher D/Pd. In addition, etching in aqua regia proved to be a better surface treatment than polishing. It was confirmed that using the pre-electrolysis treatments resulted in higher D/Pd. The electrolysis current pattern and anodic treatment cycles likewise affected the D/Pd.

On the other hand the electrochemical hydrogen loading behavior of Pd cathode in $LiOH/H_2O$ system has been studied by a volume/weight measurement method. This shows analogous effects due to annealing as loading experiments with deuterium.

1. Introduction

Many results have been reported regarding the D/Pd reached during electrolysis, but the maximum D/Pd is dependent upon on the manufacturing history of the electrodes and the conditions of electrolysis. It has been pointed out by several observers that attaining a deuterium loading ratio greater than 0.85 is a prerequisite for observing excess heat generation phenomena [1].

A resistance measurement method was used in order to establish a procedure for selecting electrodes which can be expected to give a high D/Pd. In this study relationships were found for the D/Pd and the following parameters: heat treatment of the electrodes, current pattern, cycle of electrolysis, and surface treatment of electrodes.

On the other hand, the H/Pd was studied by a volume/weight measurement system in order to compare the H/Pd of several kinds of Pd.

2. Experimental

2-1. D/Pd by resistance measurement

All samples for cathode were made of Pd (2 mm in diameter and 50 mm in length) with a purity of more than 99.99%. The standard protocol for these Pd samples includes melting and casting in

vacuum and cold working at room temperature. These samples were used to study the effect of heat treatment (see section 3-1.a below), current density effect (3-1.b.) and the effect of multiple repetition of current cycles (3-1.c.). The Pd cathodes were subjected to various pre-electrolysis treatments, such as (1) a vacuum annealing to release the stress, to recrystallise and to clean the surface by thermal etching, and (2) a surface treatment to remove surface defects and to clean the surface. The D/Pd loading ratio is affected by the current density profile, current increasing pattern and anodic treatments.

Figure 1 shows the schematic figure of electrolysis cell and system for a resistance measurement method. D/Pd values were estimated from the resistance of the Pd measured by 4-point probe measurements with an AC signal (1mA, 1kHz) during electrolysis, using a milli-ohmmeter made by NF Electronic Instruments. D/Pd was calculated as a function of R/R_0 using an empirical method by McKubre [1] (see Fig. 2). Five Pt wires (2 current leads, 2 potential leads and one electrolysis lead) were spot welded on a Pd electrode. This electrode was positioned at the center of a spiral Pt anode in an open electrolysis cell filled with 1M LiOD. The cell is made by Teflon, is cold in water bath at 20 °C. Electrolysis was performed with stepwise current density patterns and repetition of cycles. A reverse potential of 0.75V was applied after each cycle of electrolysis.

2-2. H/Pd by volume/weight measurement

Fig. 3 shows the cells for the volume/weight measurement system. The cell was made entirely of Pt. Pd electrodes were immersed in 0.1M LiOH solution. Electrolysis was performed with a current density of 100 mA/cm^2. After electrolysis the gaseous volume of hydrogen discharged from Pd electrode was measured using a measuring cylinder and then the weight of the Pd electrode was weighed in order to measure the increased weight due to the absorption of hydrogen. The H/Pd of the Pd electrode was calculated using the gas volume and the weight increase.

Table 1 and 2 describe the experimental results and conditions of each experiment. Table 1 shows the comparative effects of purity, heat treatment and the presence or lack of an upper electrode. Table 2 describes the effects of etching, heat treatment (temperature, time and environment),exposure times of sample in air after heat treatment and degassing (deoxygenating) in a 0.1M LiOH solution through which a reducing or inert gas was bubbled. The effects of various heat treatments is likewise extracted from there results.

3. Results and discussion

3-1. D/Pd by resistance measurement

a. *Heat treatment of electrodes.* Figure 4 shows the resulting D/Pd for electrodes with different heat treatments. There were a vacuum annealing to release the stress, to recrystallise and to clean the surface by thermal etching. Pd electrodes heat treated at 200 °C for 3 hours (dehydrogenation treatment), 850 °C for 3 hours, and 1000 °C for 3 hours after manufacturing were used in this study. The results show that electrodes heat treated at higher temperatures yielded a higher D/Pd.

b. *Current density of electrolysis.* Figure 5 shows the resulting D/Pd obtained from four electrolysis current density patterns during two cycles. A current pattern which starts from a lower current density (20 mA/cm^2) gives a higher D/Pd (D/Pd =0.90) and a current pattern with a higher starting current density (200mA/cm^2) gives a lower D/Pd (D/Pd = 0.83). This tendency can be observed more clearly in the second cycle. A tentative hypothesis has been formed to explain this behavior. Deuterium entering at 20 mA/cm^2 due to its slow loading, may be able to diffuse inward. However, deuterium at 200 mA/cm^2 is more rapidly absorbed near the surface, possibly creating PdD near the surface and straining the lattice. This may have interfered with the ability to absorb deuterium later on.

c. *Repetition of current cycles.* Figure 6 shows how the D/Pd changed as the cycle was repeated. This result shows that the maximum D/Pd reached in the first cycle (D/Pd = 0.86) was lower than those reached in the second (D/Pd = 0.90) and the third cycle (D/Pd = 0.95). With each repetition of electrolytic cycles, the maximum D/Pd was larger than the D/Pd reached in the previous cycle. This likewise resulted in improved D/Pd. By this reverse potential, deuterium absorbed on the surface layer was desorbed. Thus density of deuterium was decreased in the surface layer. As a result in the next cycle more deuterium was easily absorbed. However, there is still a limiting value of the D/Pd value for reasons which are not entirely clear.

d. *Surface treatment of electrodes.* We also studied the effect of surface treatments of Pd electrodes. Heat treatment of NHE standard material results in changing the grain size difference between the inner and near surface regions. Figure 7 illustrates the manufacturing process of Pd electrodes which we used in this study. Special treatments include forging, homogenizing and modification of grain size. The resultant grain size is 50 μ to 100 μ, which is referred to as small grain. Figure 8 shows the D/Pd for electrodes with different surface treatments; i.e. polishing with diamond grit and etching with aqua regia. Electrodes etched with aqua regia showed higher D/Pd (D/Pd = 0.95) than electrodes polished with diamond grit (D/Pd = 0.92). For example, etching the cathode in aqua regia resulted in higher loading than polishing with diamond grit. Also, short etching time appears to be better than etching for longer time.

3-2. H/Pd by volume/weight measurement

a. *Heat treatment.* The 850 °C treatment samples achieved a higher loading ratio than the untreated samples and the 200 °C samples as shown in Table 1. It appears that the H/Pd was slightly higher when samples were annealed at 1000 °C than at 850 °C ones as show in Table 2. Heat treatment times of 1000 C are affected to H/Pd.

b. *Other effects.* Aqua regia etching also affected H/Pd. In addition, there may be small effects due to other variable which have not yet been clearly identified. At any rate there is considerable variability in the process, as shown in Tables 1 and 2.

4. Conclusions

The electrochemical deuterium loading behavior of Pd cathodes in $LiOD/D_2O$ system has been studied experimentally using a resistance measurement method. The material conditions of Pd cathodes significantly affect the attainable D/Pd loading ratio. In addition, the D/Pd is affected by the applied current density profile, pattern of increasing current and anodic treatments.

On the other hand the electrochemical hydrogen loading behavior of Pd cathode in $LiOH/H_2O$ system has been studied by a volume/weight measurement method.

The following conclusions follow from the experimental results.

(1) Pd electrodes heat treated at higher temperatures yield a higher D/Pd. The same results for H/Pd were obtained by a volume/weight measurement system. A heat treatment of 1000 C was more effective than 850 C, which in turn was more effective than 200 C.

(2) The D/Pd attained higher values for an initial current density of $20mA/cm^2$ than for an initial current density of $200mA/cm^2$

(3) The repetition of electrolytic cycles resulted in a larger D/Pd than in the previous cycle.

(4) Etching by aqua regia was more effective than polishing for D/Pd.

5. Acknowledgment

NHE Session

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Reference:

[1] M. C. H. McKubre et al., *First Annual Conf. on Cold Fusion Proceedings*, p.20 (1990).

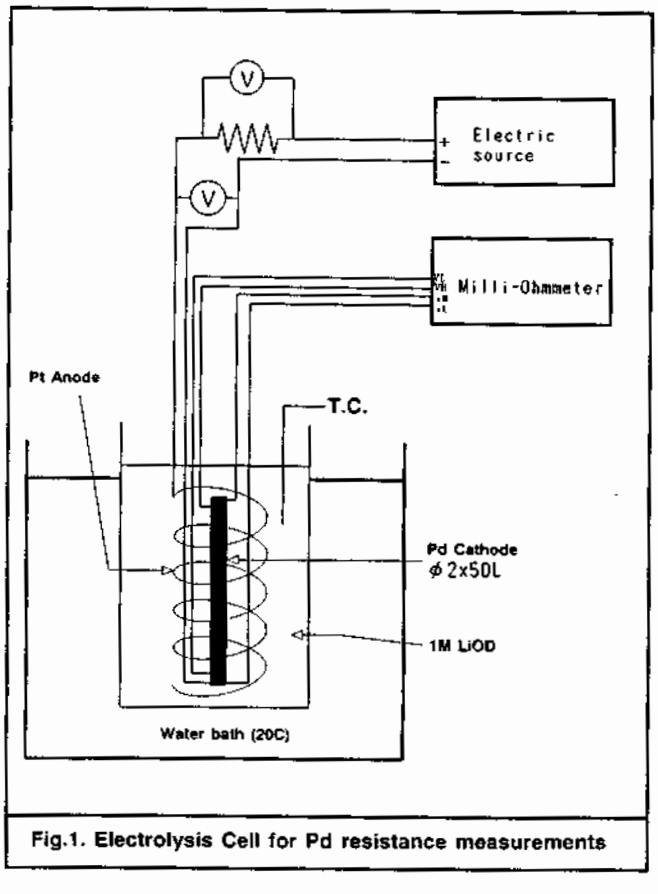

Fig.1. Electrolysis Cell for Pd resistance measurements

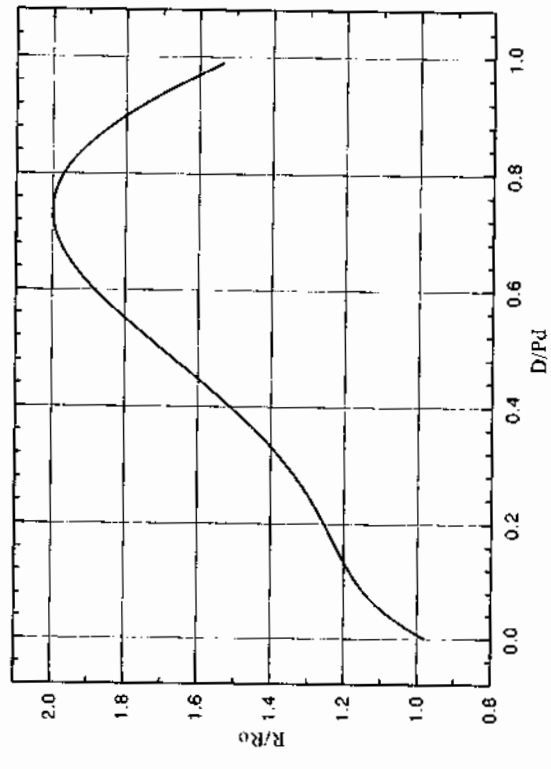

Fig. 2. Correlation Between D/Pd and R/Ro.[1]

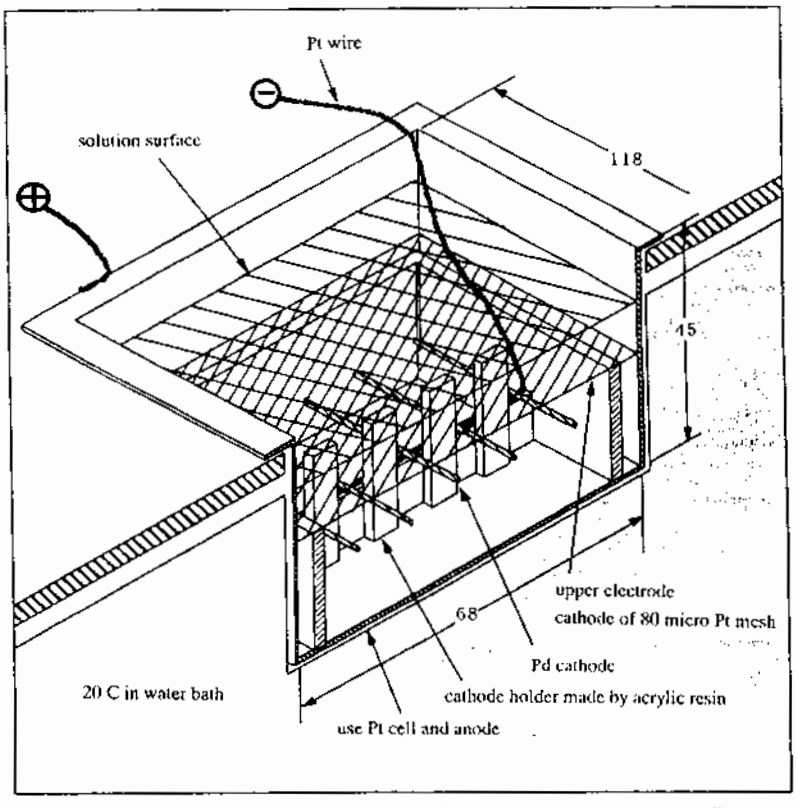

Fig 3. The schematic figure of "volume-weight method" electrolysis cell

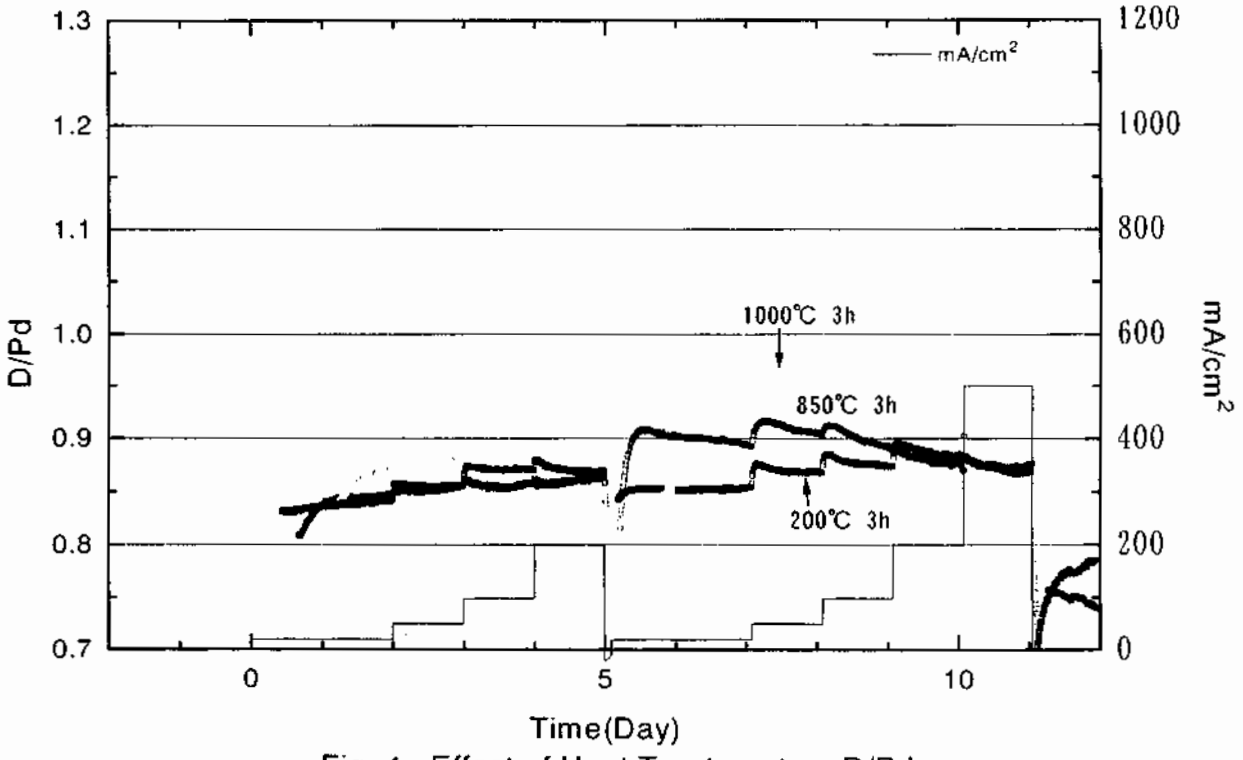

Fig. 4. Effect of Heat Treatment on D/Pd

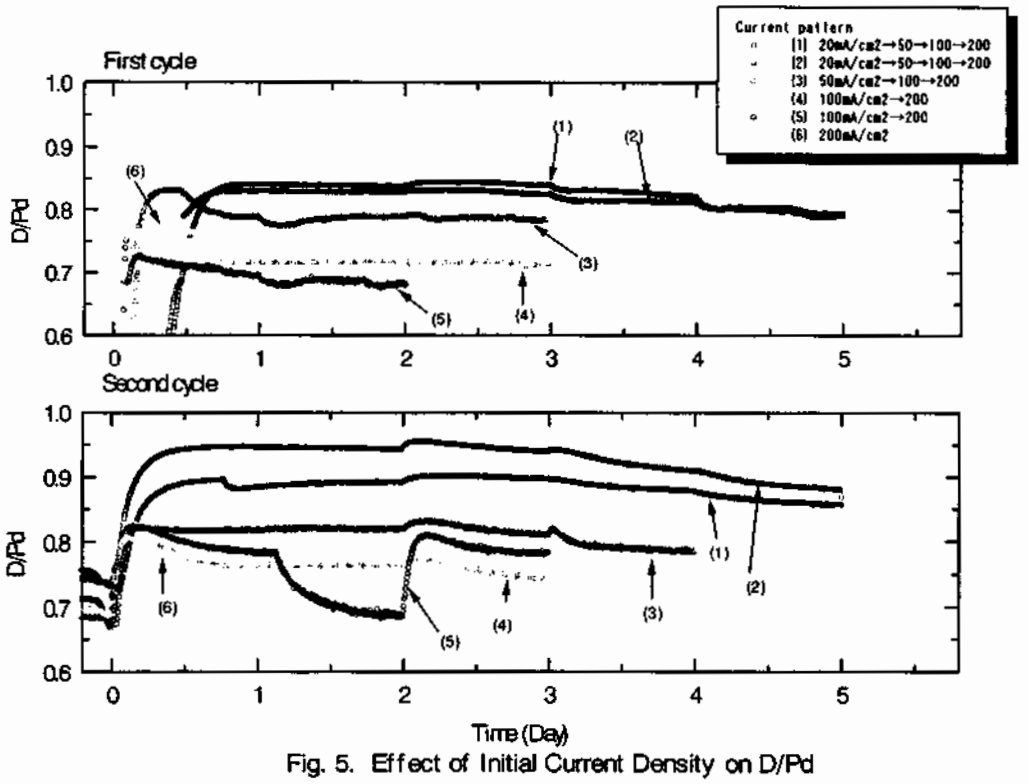

Fig. 5. Effect of Initial Current Density on D/Pd

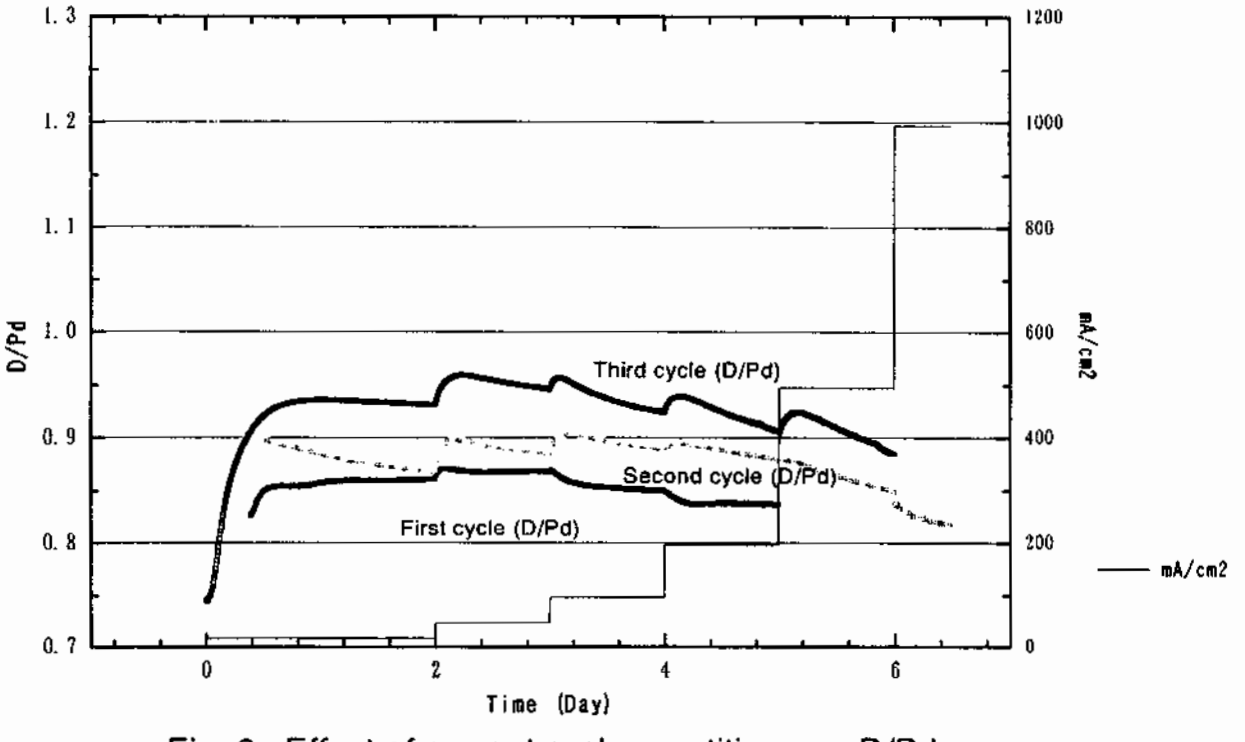

Fig. 6. Effect of current cycle repetitions on D/Pd
Treatment : 850 C 10 Hr Etched 10min

Modification of Grain size

	Process	Form
1	Raw material	Purity of Pd:99.99%up
2	Casting and melting in vacuum	30 □ mm
3	Machining	30 □ mm → 27 □ mm
4	Forging 900 ℃ × 1h in air	27 □ mm → 23 □ mm
5	Working	23 □ mm → 15 ϕ mm
6	Homogenizing	Annealed in N2 at 850 ℃ for 30 min
7	Working	15 ϕ mm → 2.0 ϕ mm
8	Cutting	Size 50mm length
9	Modification of grain size	Annealed in Ar at 850 ℃ for 30 min

Figure 7. Manufacturing procedure of Pd Electrode

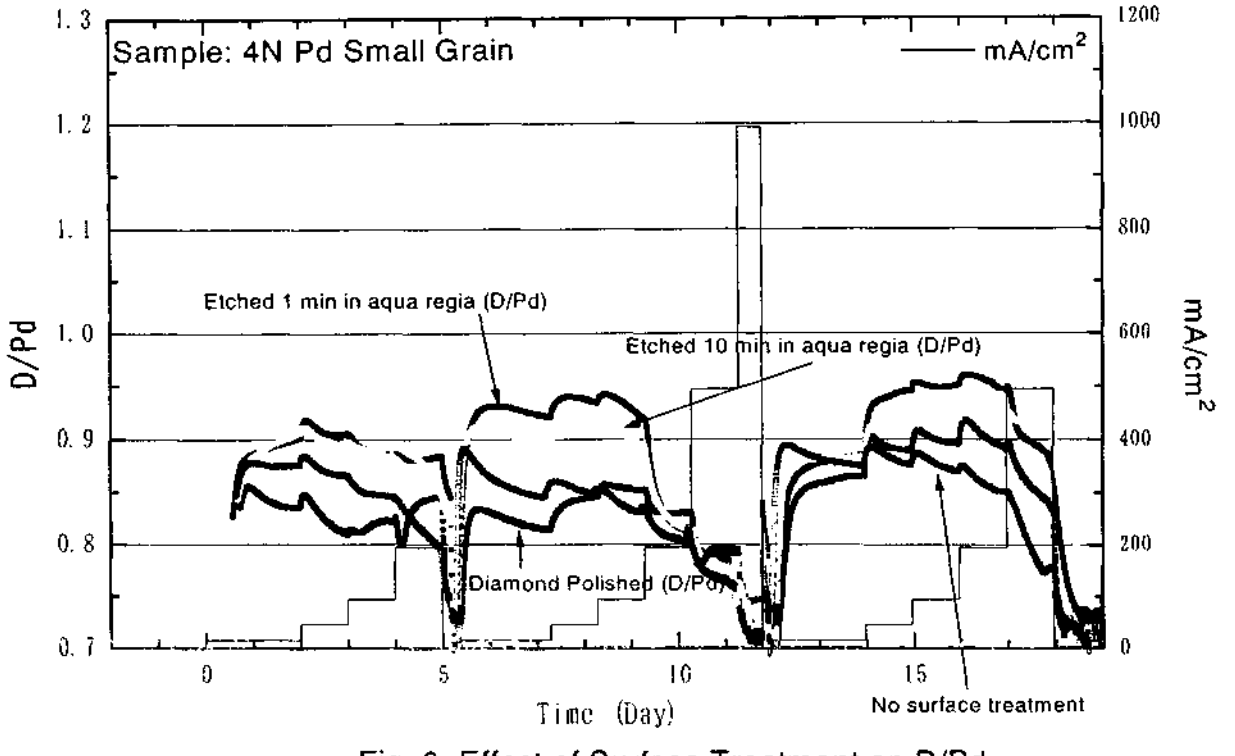

Fig. 8. Effect of Surface Treatment on D/Pd

Table. 1. Hydrogen Experimental Results -1

No	Purity	Homogeneous treatment	Heat treatment	H/Pd	Average
1	3N	—	—	0.809	X=0.811
8	4N	○	—	0.813	
2	3N	○	200 C (3hr)	0.821	X=0.816
7	4N	—	200 C (3hr)	0.810	
5	3N	—	850 C (3hr)	0.915	
6	3N	○	850 C (3hr)	0.925	X=0.914
4	4N	○	850 C (3hr)	0.904	
3	4N	—	850 C (3hr)	0.913	

Table. 2. Hydrogen Experimental Results -2

No.	Etched	Heat Treatment	Exposure	Degas	H/Pd	Average 1	Average 2
1	—	850 C (1hr)	1 min	—	0.925		
7	—	850 C (1hr)	2 days	Ar	0.920	X=0.926	
11	—	850 C (4hr)	2 days	H2	0.927		
13	—	850 C (4hr)	1 min	Vac.	0.930		X=0.926
2	○	850 C (4hr)	1 min	—	0.935		
8	○	850 C (4hr)	2 days	Ar	0.917	X=0.927	
12	○	850 C (4hr)	2 days	H2	0.927		
14	○	850 C (1hr)	1 min	Vac.	0.930		
3	—	1000 C (4hr)	2 days	—	0.934		
5	—	1000 C (4hr)	1 min	Ar	0.938	X=0.928	
9	—	1000 C (1hr)	1 min	H2	0.920		
15	—	1000 C (1hr)	2 days	Vac.	0.921		X=0.932
4	○	1000 C (1hr)	2 days	—	0.935		
6	○	1000 C (1hr)	1 min	Ar	0.939	X=0.936	
10	○	1000 C (4hr)	1 min	H2	0.937		
16	○	1000 C (4hr)	2 days	Vac.	0.932		

>99.99%Pd

Etched: Used aqua regia before heat treatment
Exposure: Exposure times of sample in air after heat treatment
Degas: deoxygenate in solution