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Approach to Obtain Higher Deuterium Loading Ratios of Palladium Cathodes

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Abstract

Deuterium loading ratios in the electrolytic palladium cathodes are measured by the electric resistance method. Many kinds of palladium rod are prepared and their loading ratios are determined during our standard electrolysis procedure. Some palladium cathodes are provided with additional treatments to change surface conditions. As the results, it is found that the deuterium loading ratio is very sensitive to palladium surface conditions. For example, when a palladium sample of which surface is modified by aqua regia, the loading ratio as high as D/Pd ≈ 0.95 is obtained at 200 mA/cm^2 of electrolytic currents, which can hardly be achieved with an ordinary palladium cathode rod.

1. Introduction

Since the announcement of cold fusion in 1989 [1], a number of attempts have been made to address the reproducibility of excess heat production. M. McKubre and coworkers of SRI [2] reported that a correlation existed between an excess heat reproducibility and D/Pd loading ratios and suggested that the loading ratio should exceed 0.85 to generate excess heat. They also showed that the amount of excess heat increased exponentially or to the square, with the difference of the loading ratio above the threshold, D/Pd=0.85. Furthermore, they claimed that if the loading ratio is attained to D/Pd ≧ 1, excess heat would be observed with a 100 % reproducibility.

It is known, however, very difficult to attain such a high loading ratio as to exceed 0.90. The present paper reports on studies on some relationship between material properties and the loading ratios to achieve higher loading ratios of deuterium in the palladium.

2. Experimental

2.1 Preparation of Palladium Cathodes

A typical process of producing palladium cathode rods used mostly in our loading experiments, is shown in Figure 1. Palladium lumps from Tanaka Kikinzoku Kogyo (99.95 % Pd) were melted and cast into a rod (50 mm in diameter) in the air. Calcium-

boride (CaB_6) powder was added into the molten palladium to remove dissolved oxygens. The rod was homogenized at 750 ℃ for 2 hours under the vacuum ($<5 \times 10^{-4}$ Torr), and then swaged into a wire of 2 mm in diameter. The wire was cut to pieces of 50 mm in length and they were annealed at 850℃ for 4 hours in the vacuum ($<5 \times 10^{-4}$ Torr). After the rods were cooled down to the room temperature in the vacuum, they were polished with diamond slurry (0.5 μm in diameter) for 30 minutes.

Impurity content of the palladium rods are shown in Table 1, which was detected by Inductively Coupled Plasma Spectrometry (ICP). The content of 200-250 ppm boron by weight, is due to CaB_6 addition.

The palladium rods produced by the above-mentioned process are described as "Standard palladium cathodes" hereafter. With respect to the deuterium loading, those standard cathodes were compared with other palladium cathodes processed by a different method from the standard procedure.

2.2 The Experimental System

The deuterium loading into palladium rods was performed by the electrolysis method, and in-situ measurements of the loading ratios were made with the resistance method.

The electrolytic cell used in the present loading experiments is shown in Figure 2, where the casing of the cell is made of tetrafluoroethylene (FEP) not to be corroded by the electrolyte of 1M LiOD solution. The anode is made of platinum mesh (99.9 % Pt), 20 mm in diameter. and 60 mm in length, and palladium rods (99.9 % Pd), 2 mm in diameter, and 50 mm in length, were used as the cathodes. Five nickel leads 0.5 mm in diameter were spot welded to the cathode. Two of the leads were welded to each end-face of the rod, which served to deliver currents along the rod to measure its electric resistance. Other two leads were welded to the rod at the positions ca. 3 mm from each end of the cathode, to measure the voltage drop along the palladium cathode. The last lead was welded to the position ca. 1.5mm from the upper end of the cathode to derive electrolytic currents.

Loading experiments were performed in an electrolyte of 1.0 M LiOD produced by dissolving a lithium metal piece (Aldrich, 99.9 % Li) in the heavy water, D_2O (ISOTEC, 99.9 %). Throughout the loading experiments, the electrolytic cell was immersed in a water bath maintaining a constant temperature at 25 ± 1 ℃. Electrolyte temperatures were measured with a thermocouple (K type).

In-situ measurements of the cathode resistance were made by using the standard four-probe technique, as already described. The measurement was automated to take data at every 2 minute interval with Milliohmmeter (Yokogawa-Hewlett-Packard, Ltd. HP 4338), which delivered alternative currents (1kHz, typically 10 mA) through the cathode rod . The electrolysis was operated with a galvanostat.

The value of measured resistance was adjusted to the value of the resistance at

25.0 ℃ and the resistance ratio ,R/R_0, was calculated, where R_0 was the resistance of the palladium cathode without hydrogen loadings. The relative resistance ratio ,R/R_0, was plotted versus loading ratios, D/Pd, at 298 K . The calibration curve was the one employed by M. McKubre and coworkers[2].

3. Results and Discussion

A. Effect of the current patterns

It has been often suggested that an electrolytic current pattern of the electrolysis would play a crucial role in the phenomenon of "cold fusion" [3,4], and that this current pattern would also affect the deuterium loading in the palladium cathodes.
M. McKubre et al. [5] reported that they achieved high loading ratios by step-up electrolysis and periodic stripping of a cathode surface with a reversed polarity for deloading.

As the first step in the construction of our palladium rods evaluation system, we had to decide the electrolytic current pattern to obtain higher loading ratios. A step-up electrolytic current pattern included an anodic stripping; started with a low constant current, then stepped-up to a higher current and reversed the current polarity for a short time at a low current, was employed in the present experiments. Furthermore, a constant electrolytic current pattern (at 200 mA/cm^2) was examind.

Figure 3 shows a different behavior of deuterium loading into a palladium cathode. "Standard palladium cathodes" were used in this case.

In the step-up electrolysis, at the initial stage of the constant current electrolysis ($20mA/cm^2$), the R/R_0 value increased to near 2.0 and then began to decrease. It means that the deuterium loading ratios went beyond 0.75 and the further decrease of R/R_0 values indicated the increase of deuterium loading ratios. The maximum loading ratio increased as the electrolytic currents were increased, finally, attained to 0.91

In the high constant current electrolysis, at the beginning of the constant current electrolysis of $200mA/cm^2$, the R/R_0 value started to decreased through the first peak ($R/R_0=2$) as well as the step-up electrolysis. The decrease stopped to the 1.9 of R/R_0 and the further decrease was not observed and eventually the maximum deuterium loading ratio attained to 0.85 at most.

From these results, we had selected the step-up electrolytic current pattern for evaluating our palladium rods.

In addition, the alternating polarity method was also examined in the present experiments. And, it was found that the loading ratios after such anodic stripping of some palladium cathodes were observed to get higher than those before the anodic stripping. Typical results of the anodic stripping are shown in Figure 4, which are not always reproducible even under the same electrolytic condition. It is uncontrollable for us at present. Accordingly the palladium cathodes are electrolyzed by the step-up current pattern included an anodic stripping and evaluated with the maximum loading

ratio before the anodic stripping.

The maximum loading ratio of many "Standard" palladium cathodes were measured to exhibit D/Pd= 0.90 ± 0.01 before the anodic stripping which was still not good enough according to the SRI criterion for the better excess heat generation.

B. Effect of Processing on Deuterium Loading Ratio

Effects of unidentified characteristics of those processed palladium rods on the deuterium loading ratios were investigated from the following two points of view.

One is that a certain processing to a palladium rod surface seems to influence its bulk properties. Another is that the processing will change and control only some surface conditions.

The maximum deuterium loading ratio of each palladium rod before the anodic stripping was considered to be governed by its bulk properties.

Experimental results are summarized in Table 2. When the purity of palladium rods, or some processing such as casting and annealing, which might change their bulk properties, were modified, their maximum deuterium loading ratios were observed still not to exceed that of Standard.

Further treatments were added, such as polishing, etching by aqua regia, heating to a high temperature, etc. to a standard palladium rod with an expectation of some effect on the deuterium loading ratio. These results are summarized in Table 3.

Eventually two effective surface treatments were identified to produce higher loading ratios than the standard palladium rods without treatment ; etching by aqua regia and high temperature annealing in the vacuum for a long time.

(i)Etching process by aqua regia

Aqua regia was prepared from HNO_3 (WAKO, highest grade, HNO_3 70 %) : HCl (WAKO, highest grade, HCl 30 %) = 1 : 4, volumetric ratio. The standard palladium rods were etched by aqua regia immediately after preparing the aqua regia for a definite time and rinsed by pure light water. To remove hydrogen gas absorbed in these samples during the etching, these samples were heated at 200 ℃ in a low vacuum condition (~10^{-2} Torr) for 24 hours.

Figure 5 shows the resistivity changes during electrolysis of the standard palladium rods etched for a different length of time. At the initial stage of the electrolysis, at 20 mA/cm^2, a rapid decrease of the resistivity was observed and followed by an increase. This is a peculiar feature to the palladium cathode etched by aqua regia and the cathode will indicate a rapid deuterium absorption and desorption at each change of electrolytic currents. The etched palladium rods were observed to attain higher loading ratios than the standard palladium rods, and the maximum deuterium loading ratios of the palladium rods etched by aqua regia for 10 minutes could attain to D/Pd = 0.95.

The chemical etching by aqua regia can be expressed as a chemical oxidization of palladium. From resistivity changes of electrochemically oxidized palladium rods, some additional studies were made on the effect of such chemical oxidation on the deuterium loading. Prior to the electrolysis, the standard palladium rod were oxidized by the anodic oxidation at the electrolytic current density of 20 mA/cm^2 for 20 hours, and the result is shown in Figure 6.

The palladium oxide formed on the surface by the anodic oxidation was found to reduce to show a metallic palladium surface as soon as the cathodic electrolysis is started. Apparently the color of the palladium rod was observed to turn into a dark black color with the anodic-cathodic polarization cycle, which may indicate a morphology change on the surface.

However, the maximum deuterium loading ratio of palladium with anodic oxidation was so small that the deuterium loading ratio was less than 0.75. From the result, we concluded that the anodic oxidation has no effect on the improvement of deuterium loading ratios such as shown by the chemical oxidation by aqua regia.

(ii)Heat treatment in vacuum at high temperature

Influence of heat treatments in the vacuum at high temperatures on the deuterium loading ratio was studied. The standard palladium rods were heated in a vacuum (5×10^{-5} Torr) at 1000 ℃ for 24 hours. (or 1200 ℃ for 24 hours) before the electrolysis.

Figure 7 shows the loading characteristics of those heat-treated palladium electrodes (1000 ℃ in the vacuum for 24 hours). Temporal changes of the resistivity of these palladium rods were gentle, that is to say, the deuterium absorption rate was rather slow, but the maximum deuterium loading ratio was attained to the value as high as 0.94.

It is conceived that the heat treatment can affect not only on surface properties, but also bulk properties. The heat-treated palladium rods were polished to remove surface layers, which might affect loading characteristics. Figure 8 shows loading characteristics of those of the heat-treated ones.

It will be conclusively important observation that resistivity changes of those heat-treated palladium rods are observed to show the same resistivity charactaeristics when their surface is polished. Thus we can conclude that the surface condition of palladium is a more crucial factor to control the deuterium loading than its bulk properties.

4. Conclusions

1) To achieve a higher deuterium loading ratio of palladium cathodes the step-up electrolysis must be adopted.

2) The deuterium loading characteristics is influenced and controlled the surface condition of palladium cathode rather than its bulk properties.

3) The deuterium loading ratios as high as 0.95 can be obtained by two simple treatments. They are etching by aqua regia and heating in vacuum at 1000 ℃ for 24hrs. With the above two treatment, each loading characteristics was observed not same with each other, but both treatments are observed to improve the maximum deuterium loading ratios in palladium cathodes, which were higher than that with the standard palladium rods.

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Table 1. Elemental analysis of standard Pd.

(ppm)

Element		Pt	Au	Ag	Al	B	Ca	Cd	Cr	Cu	Fe	Mg	Pb	Si	Ti
Raw material		<10	<10	7	-	-	3	-	-	6	<10	<1	-	<1	-
Casting Pd	Upper part	<10	<10	4	53	240	37	-	-	3	50	<1	-	1	<5
	Lower part	<10	<10	3	30	200	5	10	<1	5	10	<1	-	10	-

This analysis was carried out by ICP.

Table 2. Various Pd material and its maximum deuterium loading ratio before anodic stripping.

Parameters		Number of Samples	Average	Range of $(D/Pd)_{max}$ 0.85 0.90 0.95
Standard Pd		14	0.90	
Purity	99.99 %	2	0.89	
	99.5 %	2	0.88	
Casting	Melted in vacuum	4	0.89	
Annealing in vacuum	Unannealed	2	0.88	
	550 °C for 2 hr	3	0.86	
	1000 °C for 24 hr	3	0.89	

All Pd rods were polished by diamond slurry for 30 minutes to have same surface condition.

Table 3. Maximum deuterium loading ratio with Standard Pd before anodic stripping.

Parameters		Number of Samples	Average	Range of $(D/Pd)_{max}$ 0.85 0.90 0.95
Standard Pd		14	0.90	
Polishing	Unpolished	3	0.87	
	Polished for 4 hr	2	0.89	
	Polished by argon plasma	2	0.88	
Etching by aqua regia	Etched for 20 sec.	2	0.92	
	Etched for 3 min.	3	0.93	
	Etched for 10 min.	7	0.94	
Heat treatment in vac.	1000 °C for 24 hr	3	0.94	
	1200 °C for 24 hr	2	0.93	

Surface treatments were added on Standard Pd rods except for unpolished.

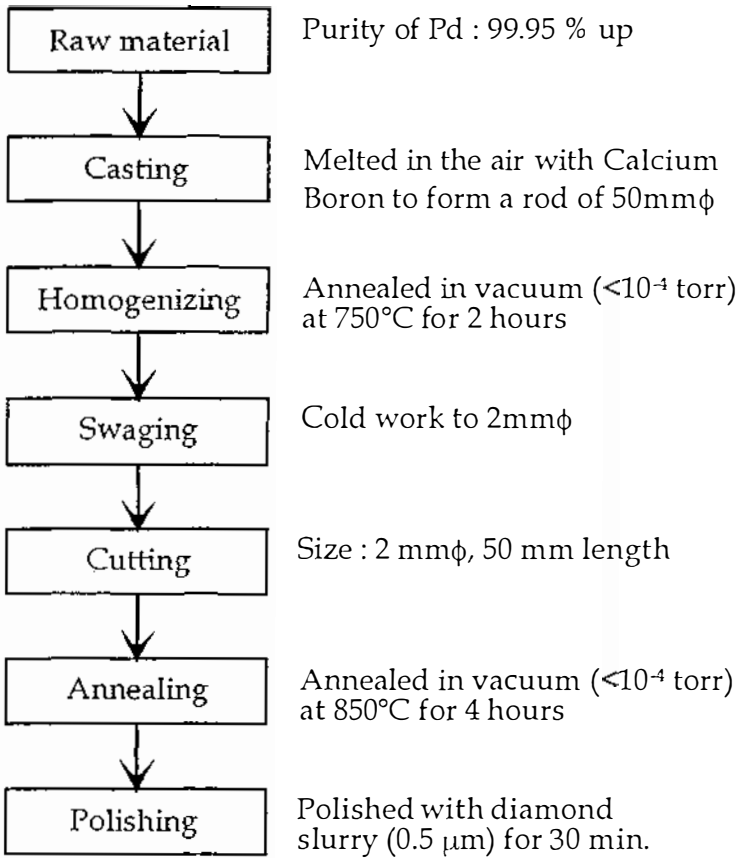

Figure 1. Process of Standard Pd electrode.

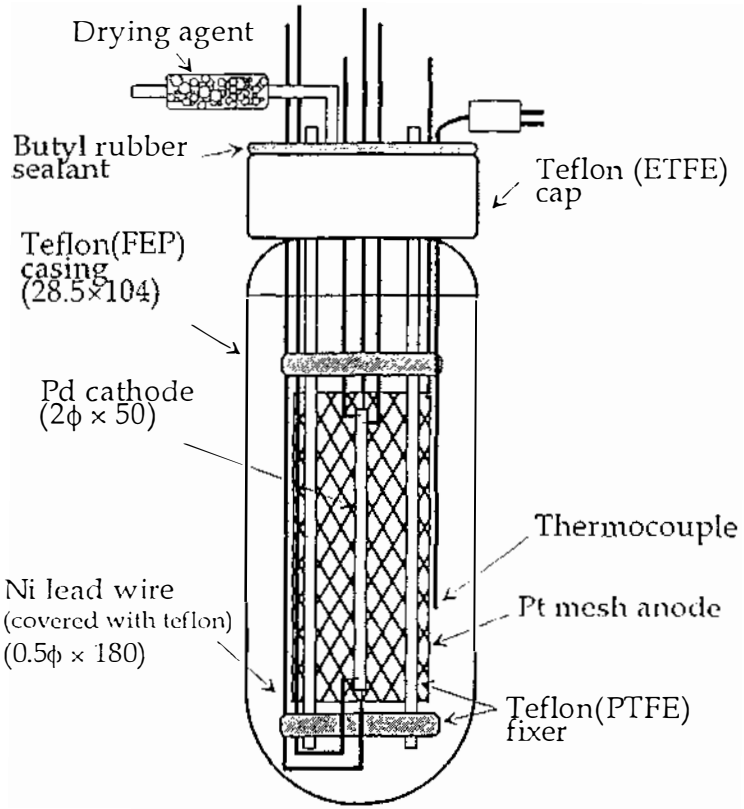

Figure 2. Electrochemical cell for Pd resistance measurements.

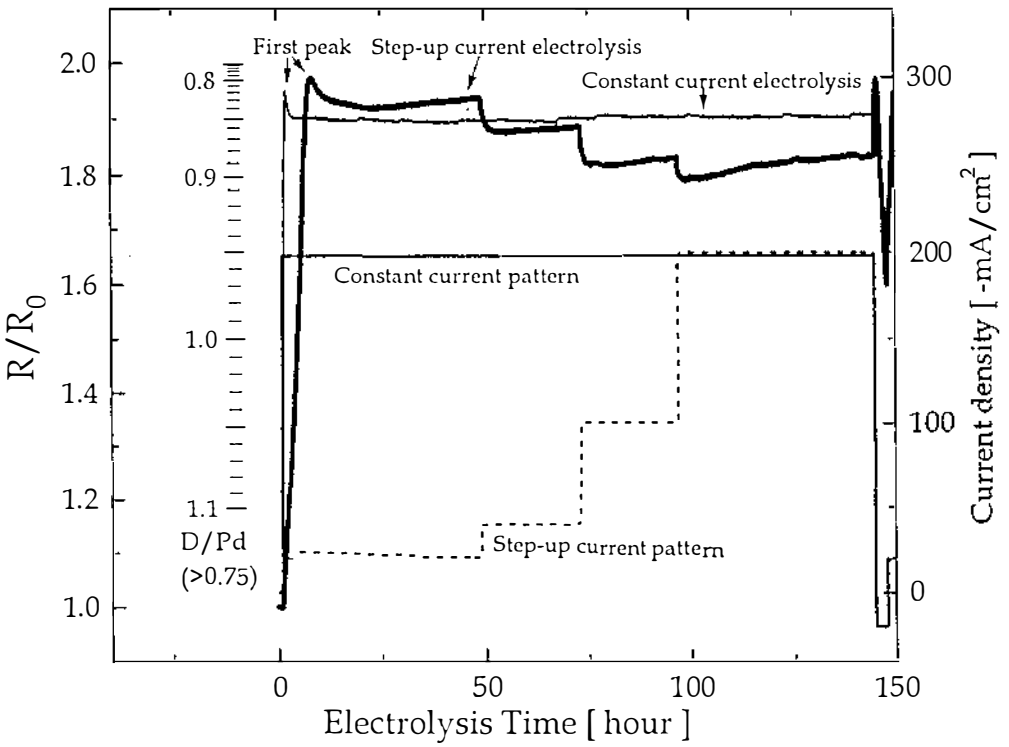

Figure 3. Effect of the current pattern on the loading ratio.

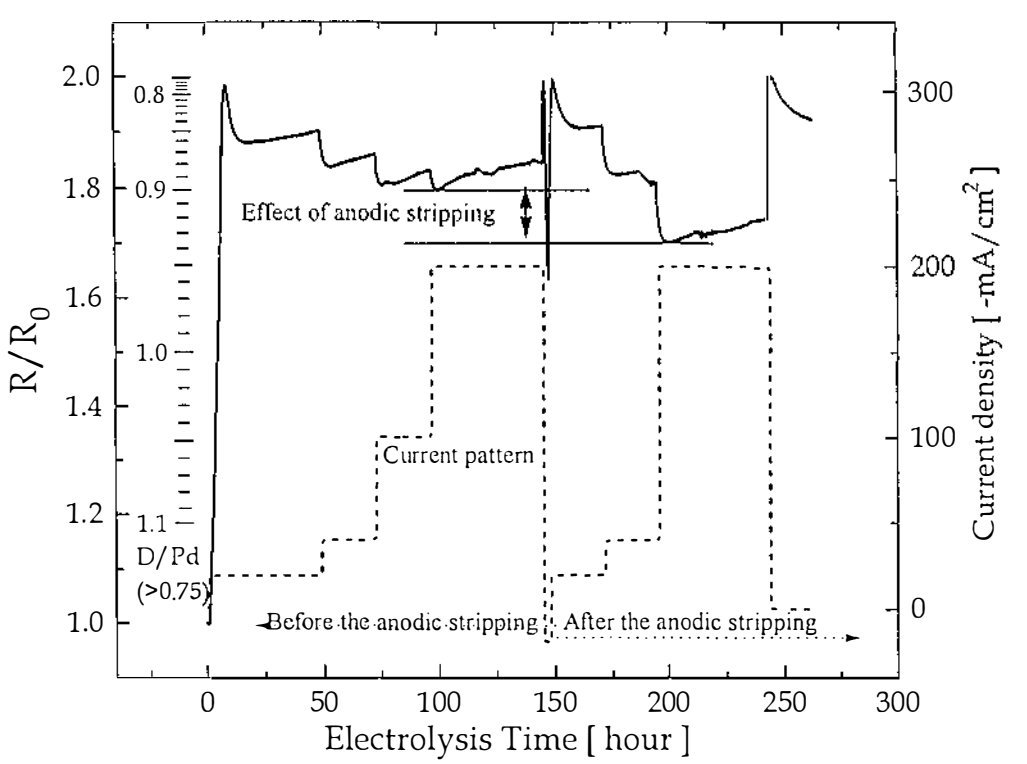

Figure 4. Effect of anodic stripping.

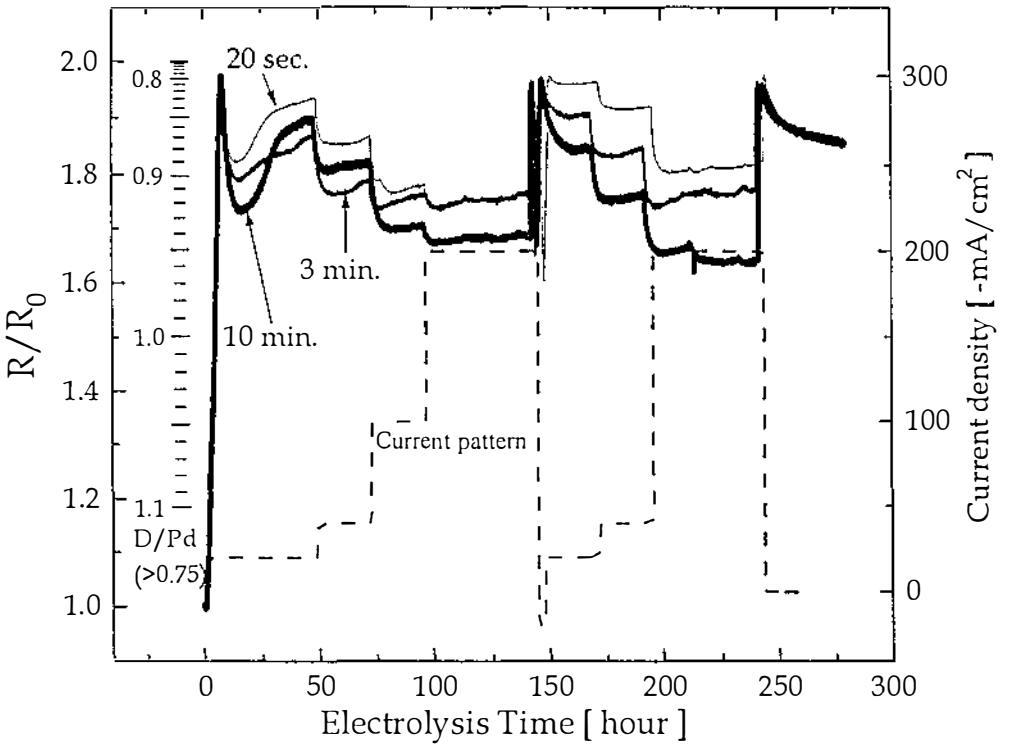

Figure 5. Effect of etching time by aqua regia for a different period of treatment.

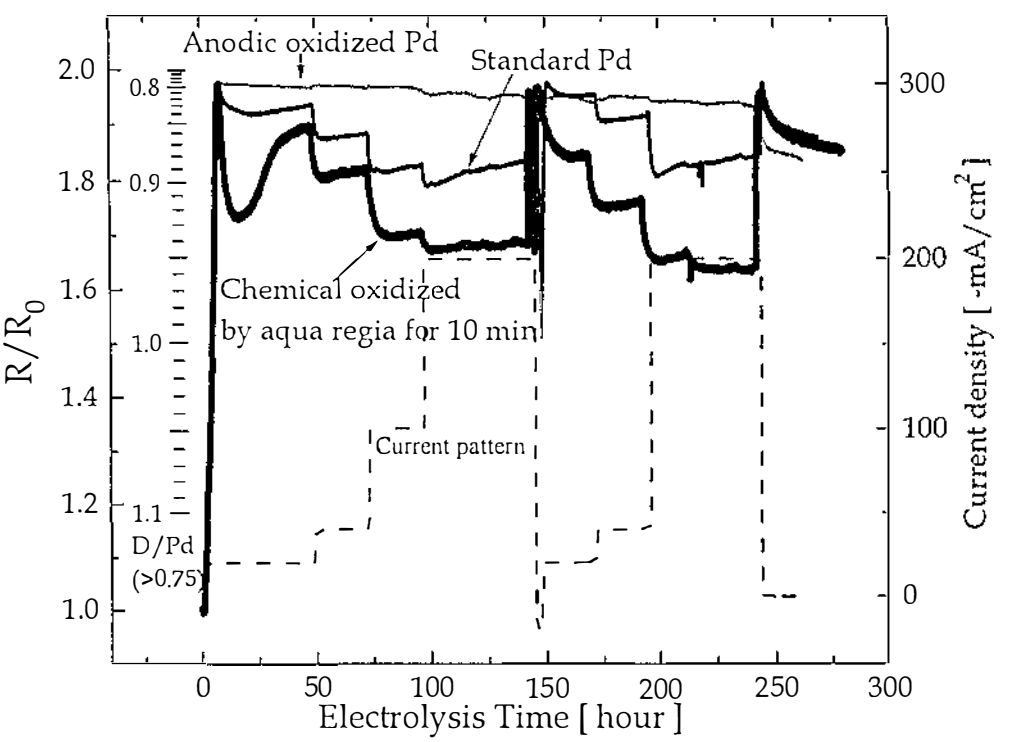

Figure 6. Effect of electrochemical oxidation.

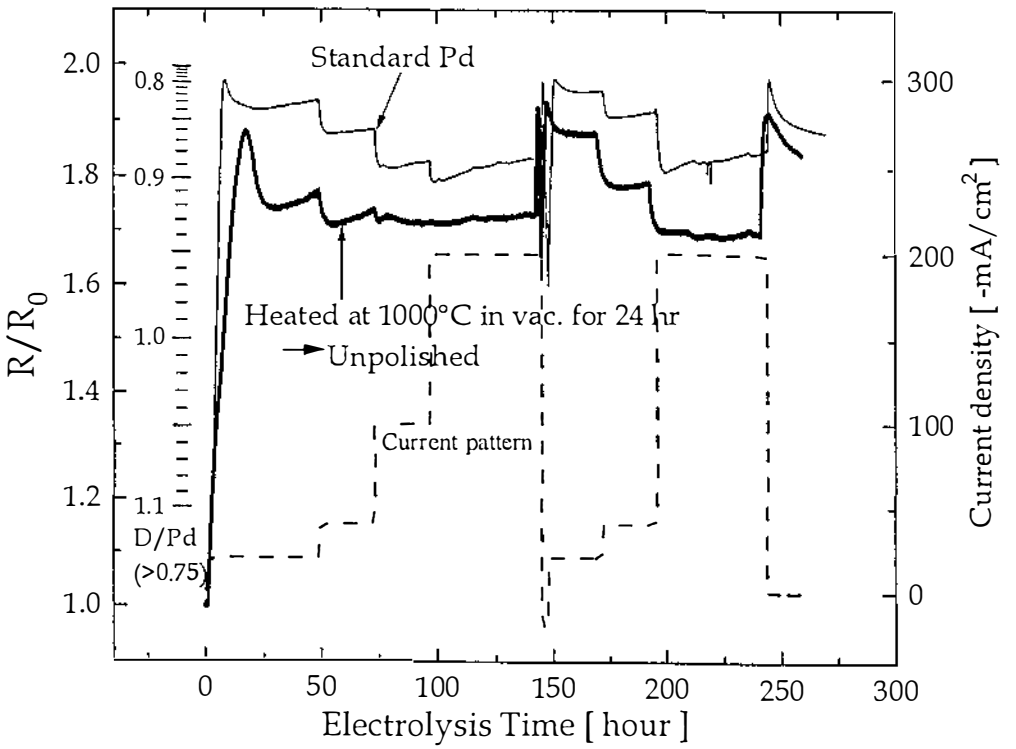

Figure 7. Effect of heat treatment in the vacuum.

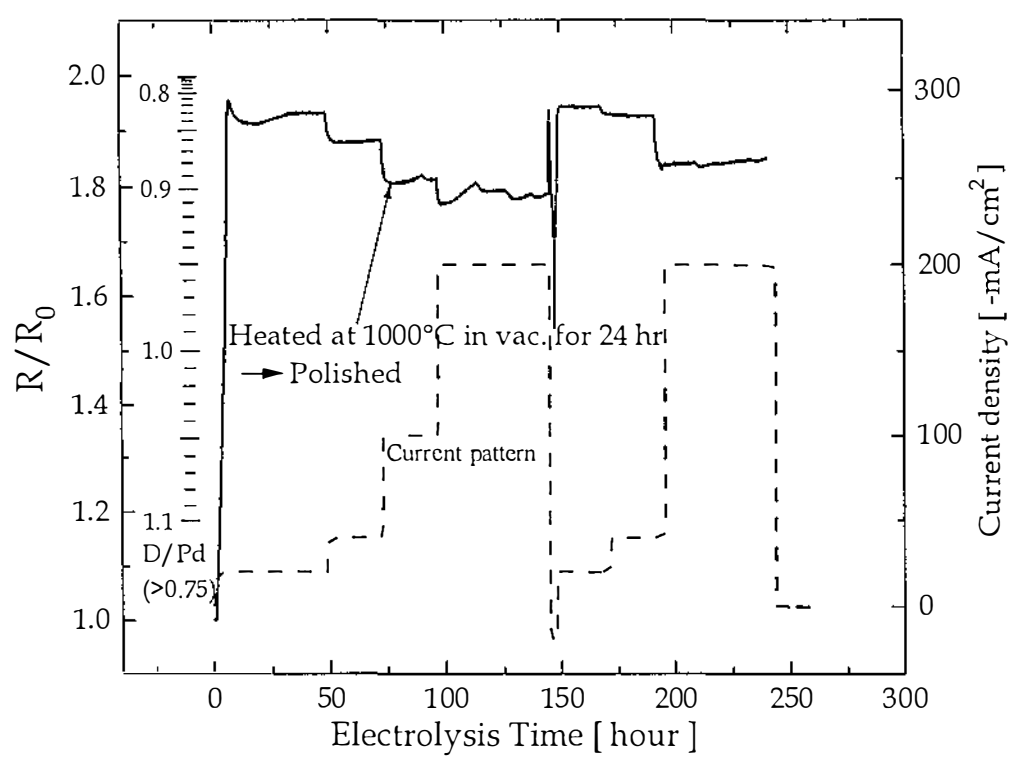

Figure 8. Effect of polishing after heat treatment in the vacuum

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