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Experimental Study of Electrochemical Deuterium Loading of Pd Cathodes in the LiOD/D_2O System

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Abstract

The electrochemical loading behaviour of Pd cathodes in the LiOD/D_2O system has been studied experimentally. The preparation conditions of Pd cathodes significantly affect the D/Pd loading ratios. In addition, the D/Pd ratio is affected by the current density profile, current increasing pattern and anodic treatments. The major treatments were (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. It was concluded that higher annealing temperatures (~1000 °C) result in a higher D/Pd ratio. 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 ratios. The electrolysis current pattern and anodic treatment cycles likewise affected the D/Pd ratio. The effects are also discussed in detail below.

Keywords: Palladium; Deuterium; Loading ratio; Resistance measurement

1. Introduction

Many results have been reported regarding the D/Pd ratio reached during electrolysis, but the maximum D/Pd ratio is dependent upon on the manufacturing history of the electrodes and the conditions of electrolysis.

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

2. Equipment and D/Pd measurement

Fig. 1 shows the schematic figure of the electrolysis cell and system which were used for this study. The D/Pd ratio values were estimated from the resistance of the Pd measured by 4-point probe measurements with an AC signal (1 mA, 1 kHz) during electrolysis, and the D/Pd

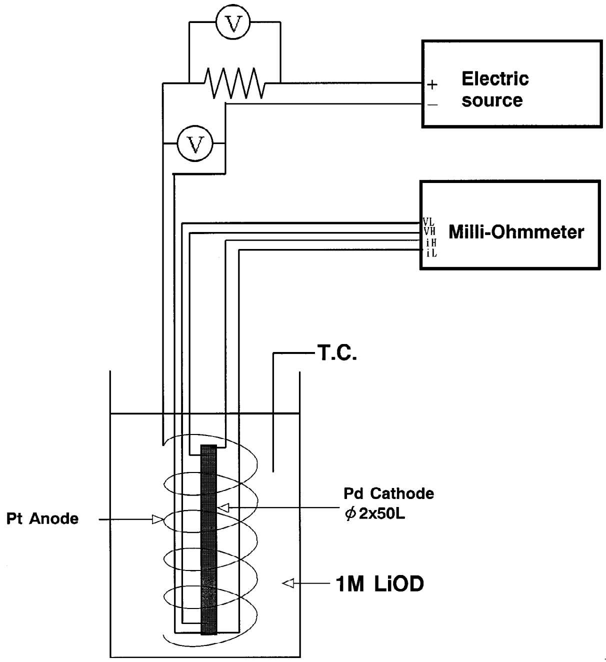

Fig. 1. Electrolysis cell for Pd resistance measurements.

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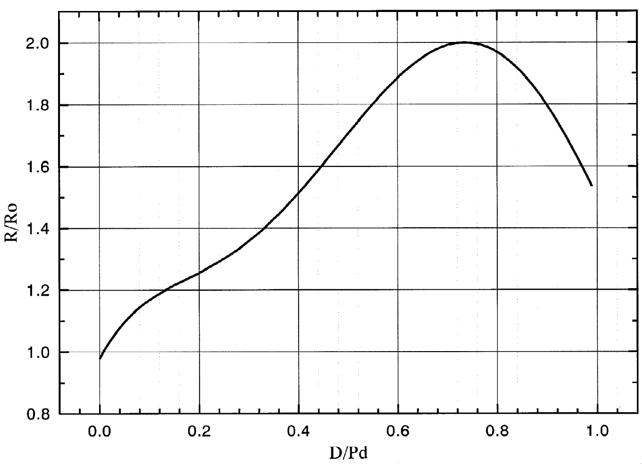

Fig. 2. Correlation between D/Pd and R/R_0 [1].

ratio was calculated as a function of R/R_0 as shown in Fig. 2 [1]. Five Pt wires (2 current leads, 2 potential leads and one electrolysis lead) were spot welded on a Pd electrode 2 mm in diameter and 50 mm in length. All electrodes were made of Pd with a purity of more than 99.99%. This electrode was positioned at the centre of a spiral Pt anode in an open electrolysis cell filled with 1M LiOD. The current of electrolysis was changed as a step function. At the end of the electrolysis cycle, anodic treatments were performed.

3. Results and discussion

3.1. Heat treatment of electrodes

Fig. 3 shows the resulting R/R_0 and D/Pd ratio for electrodes with different heat treatments. There was 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 h (dehydrogenation treatment), 850 °C for 3 h, 1000 °C for 3 h after manufacturing were used in this study. Samples annealed at 1000°C attained a D/Pd ratio of 0.95, which was higher than similar samples with no treatment (about 0.85). Thus, the results show that electrodes heat treated at higher temperatures yield a higher D/Pd ratio.

3.2. Current density of electrolysis

In our study, the current density was changed stepwise. Fig. 4 shows the resulting D/Pd ratio obtained from four electrolysis current density patterns during two cycles. This result shows that a current pattern which starts from a lower current density (20 mA cm^{-2}) gives a higher D/Pd ratio (D/Pd=0.90) than a current pattern with a higher starting current density (200 mA cm^{-2}), which gives a lower D/Pd ratio (D/Pd=0.83).

3.3. Repetition of current cycles

Electrolysis was performed with stepwise current density patterns and repetition of cycles. Fig. 5 shows how the D/Pd ratio changed as the cycle was repeated.

This result shows that the maximum D/Pd ratio reached in the first cycle (D/Pd=0.86) was lower than those reached in the second (D/Pd=0.91) and the third cycle (D/Pd=0.96).

3.4. Surface treatment of electrodes

We also studied the effect of surface treatments of Pd electrodes. There are surface treatments to remove surface defects and to clean the surface. Fig. 6 illustrates the manufacturing process of Pd electrodes which we used in this study. Fig. 7 shows the D/Pd ratio for electrodes with different subsequent surface treatments; i.e. polishing with diamond grit and etching with aqua regia. Electrodes etched for 1 min with aqua regia showed higher D/Pd

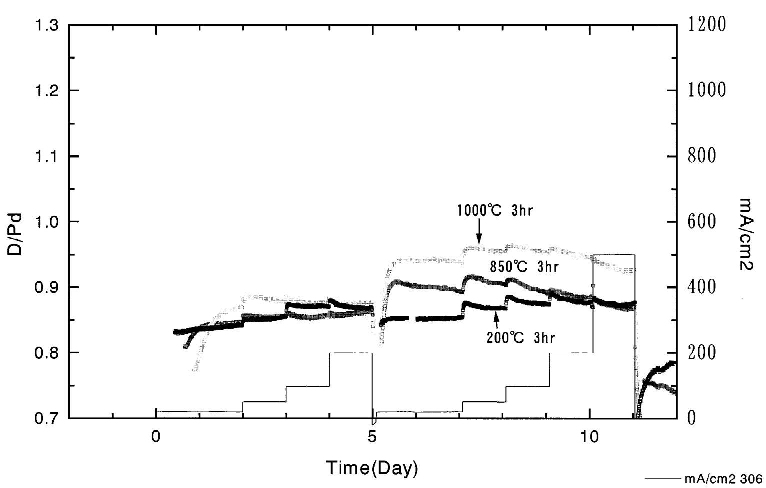

Fig. 3. Effect of heat treatment on D/Pd.

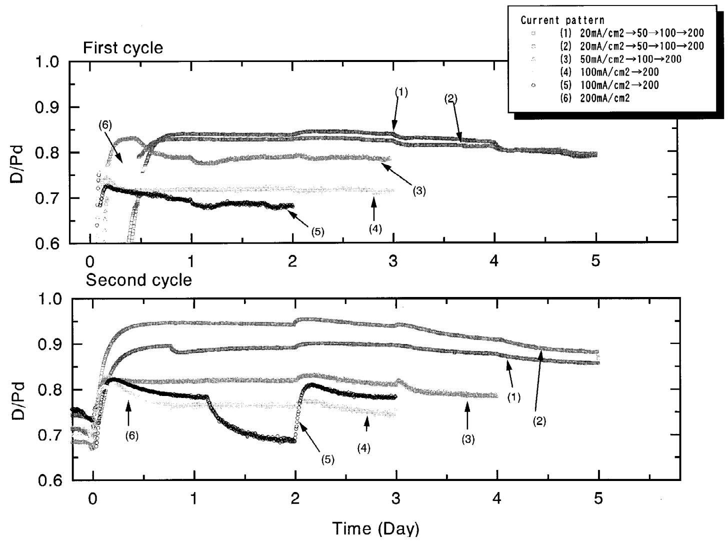

Fig. 4. Effect of initial current density on D/Pd.

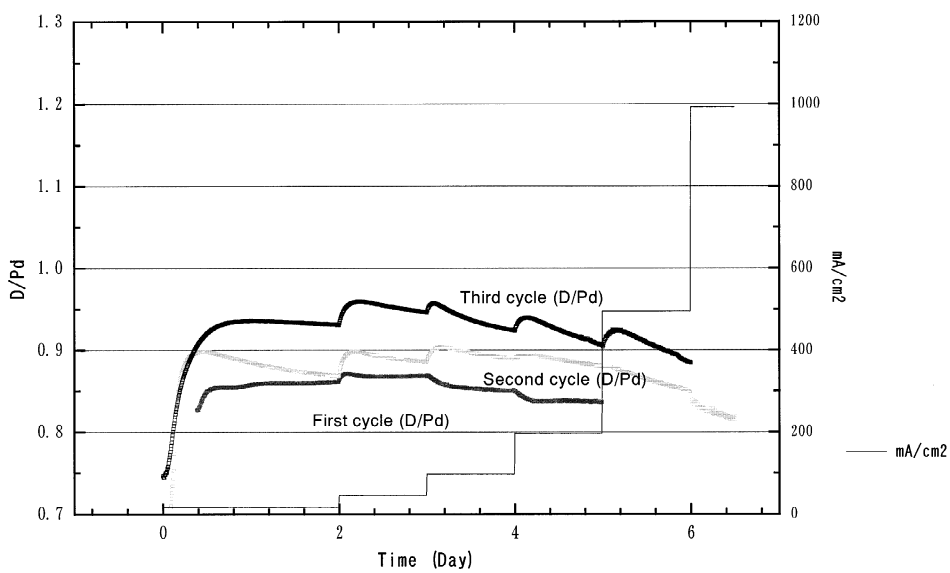

Fig. 5. Effect of current cycle repetition on D/Pd treatment: 850 °C 10 hr etched 10 min.

Modification of Grain size

Process	Form
Raw material	Purity of Pd:99.99%up
Casting melted in vacuum	30 □ mm
Machining	30 □ mm → 27 □ mm
Forging 900 ℃ × 1h in air	27 □ mm → 23 □ mm
Working	23 □ mm → 15 ϕ mm
Homogenizing	Annealed in N2 at 850 ℃ for 30 min
Working	15 ϕ mm → 4.5 ϕ mm
Machining	4.5 ϕ mm → 4.0 ϕ mm
Polishing	
Cutting	Size 50mm length
Modification of grain size	Annealed in Ar at 850 ℃ for 30 min

Fig. 6. Manufacturing procedure of Pd electrode.

ratios (D/Pd=0.96) than electrodes polished with diamond grit (D/Pd=0.92).

4. Conclusions

1. Electrodes heat treated at higher temperatures yield a higher D/Pd ratio.
2. The D/Pd ratio can reach a higher value if the initial current density is low.
3. With the repetition of electric cycles, the maximum D/Pd ratio was larger than the D/Pd ratio reached in the previous cycle. This is presumably because of the

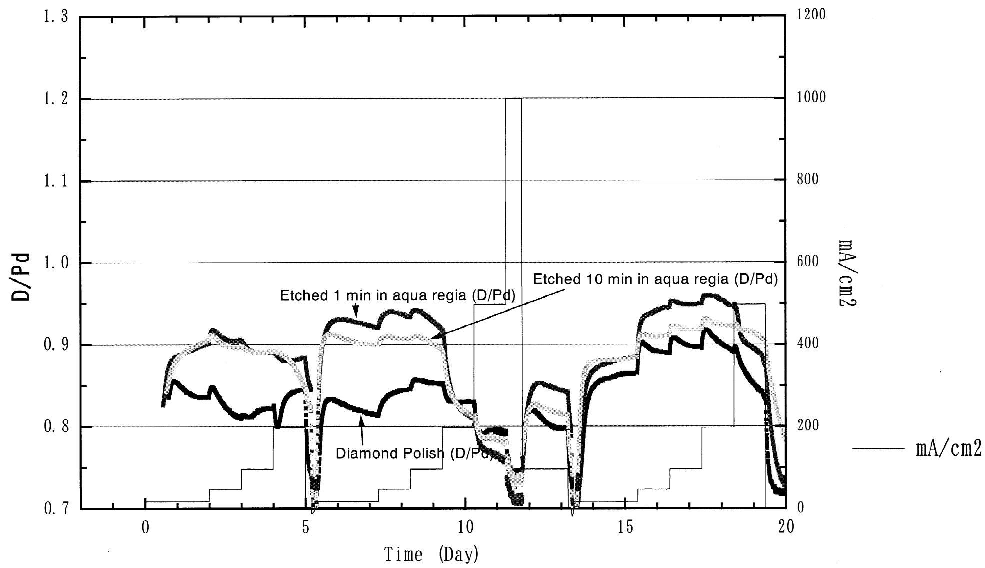

Fig. 7. Effect of surface treatment on D/Pd 4N Pd small grain.

reverse potential applied on the electrode after each cycle of electrolysis. By this reverse potential, deuterium absorbed on the surface layer was desorbed. Thus the deuterium content was decreased in the surface layer. As a result in the next cycle more deuterium was absorbed. However, there is still a limiting value of the D/Pd ratio value for reasons which are not entirely clear.

4. In this study etching was more effective than mechanical polishing. Etching appears to have removed more impurities from the surface than polishing. Short etching times were better than etching for longer times.
5. In future studies we intend to study the effect of grain size and impurities in palladium electrodes on the D/Pd ratio.

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