

**Sustentation of Higher Deuterium Loading Ratio
in Palladium**

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Abstract

Higher deuterium loading and its sustentation are considered to be a key issue for generating excess heat on "cold fusion". In our previous works, several conditions to achieve a high deuterium loading ratio of palladium were found. It is, however, often observed that the deuterium loading ratio starts decreasing after reaching a maximum value under a same electrolytic condition, and the maximum loading ratio could not be sustained for a necessary period of time to come up to observe any excess heat.

To maintain such achieved high loading ratio, we have devised and confirmed a new technique based on a finding that a cell voltage during the electrolysis is one of the most important key factors to control such deloading.

As the result of our new method, when the cell voltage is kept constant, accordingly electrolytic currents increase at a certain rate, the maximum deuterium loading can be maintained for more than 200 hours. It is found that the decrease in cell voltages is mostly due to the decrease in the deuterium overpotential, by measuring the deuterium overpotential on a palladium cathode.

1. Introduction

M. McKubre and coworkers of SRI [1] reported necessary conditions for the reproducibility of excess heat with their empirical formula. In our previous works [2], two kinds of palladium surface treatments were found to be effective to increase the deuterium loading ratio. One is by etching a palladium rod with aqua regia, and the other is by annealing it under a vacuum. After either/both of these conditionings, a loading ratio as high as $D/Pd = 0.95$ was achieved by our "step-up current" electrolysis method.

It is, however, often observed that the loaded deuterium start deloading after

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reaching a maximum loading ratio if the same current density is kept. Figure 1 shows a typical example. Therefore, the higher loading ratio could not be sustained for a necessary period of time to come up to observe any excess heat generation.

The present paper reports on studies on new techniques that make it possible to maintain the achieved high loading ratio and on the primary factors of which lead to such deloading.

2. Experimental

2.1 Method to Suppress Deloading

Figure 2 shows changes of a cell voltage (the voltage between the anode and the cathode), and the electric resistance ratio of the palladium rod cathode during the electrolysis. As already mentioned, the cell voltage is observed to decrease, after reaching a maximum cell voltage with each current density which is kept constant. And the deuterium loading ratio is observed to decrease in accordance with the cell voltage. It is considered that the cell voltage during the electrolysis is one of the key factors to control the deloading, and two kinds of new technique to hold the cell voltage constant have been devised. The schematic figures to explain our new methods are shown in Fig.3.

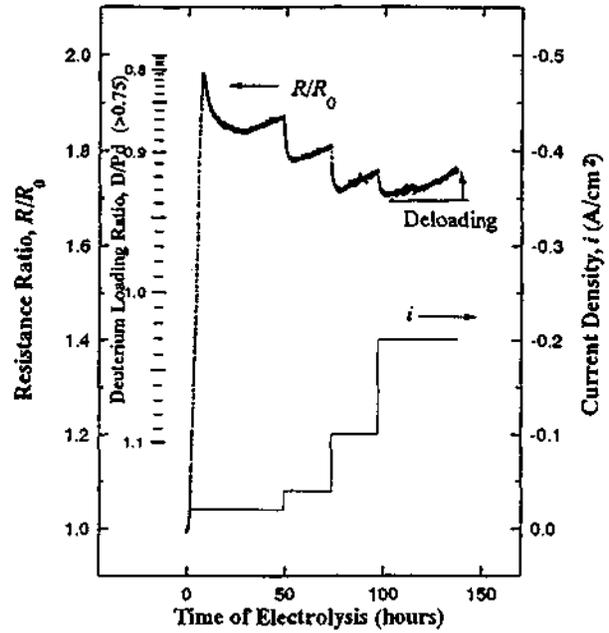


Fig. 1. Changes of the resistance ratio of a palladium cathode and the step-up current density during the electrolysis of 1M-LiOD at 298 K.

Pd cathode: 2 mm dia. and 50 mm length
Etched in HCl/HNO₃ (4:1)

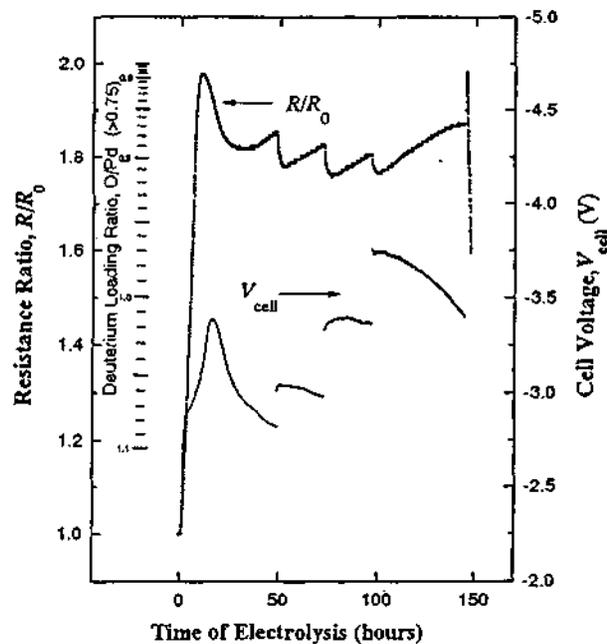


Fig. 2. Changes of a cell voltage during the electrolysis of 1M-LiOD.

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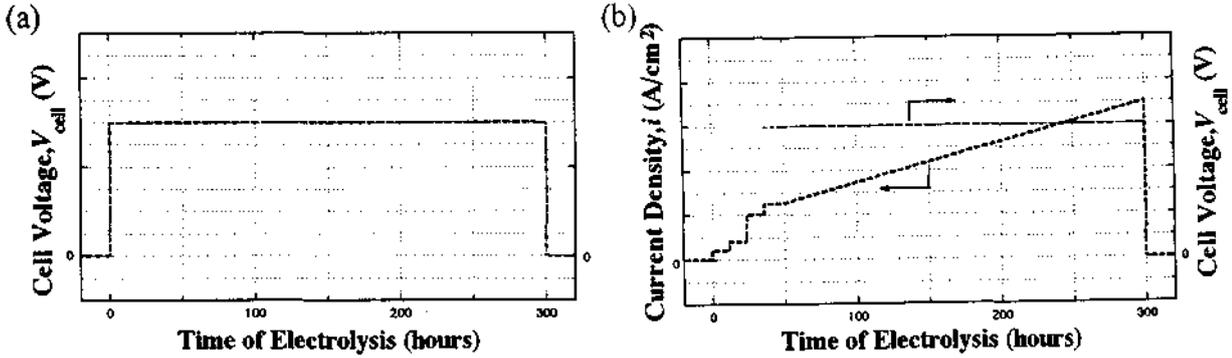


Fig. 3. Schematic figures to explain our new methods:

(a) Full constant cell voltage electrolysis and (b) Step-up and ramp current electrolysis

Method 1: Full constant cell voltage electrolysis

The predesigned cell voltage is applied at the start of the electrolysis and is kept constant.

Method 2: Step-up and ramp current electrolysis

After the maximum loading ratio is attained by the “step-up” current electrolysis, the cell voltage is kept constant, and accordingly the electrolytic currents increase at a certain rate under the constant cell voltage.

2.2 Experimental Confirmation

Deuterium loading into a palladium rod was performed by electrolysis in an open cell. Figures 4 and 5 show the electrolytic cell and the detailed configuration of electrodes used in the loading experiments detail, respectively.

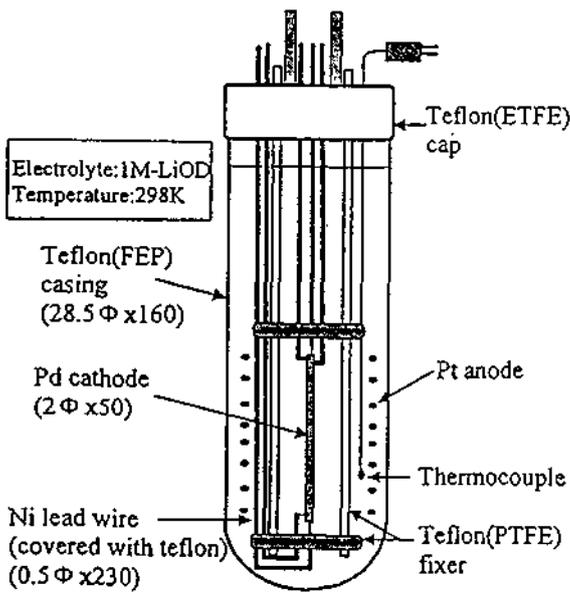


Fig. 4. Electrolytic cell for the palladium resistance measurement.

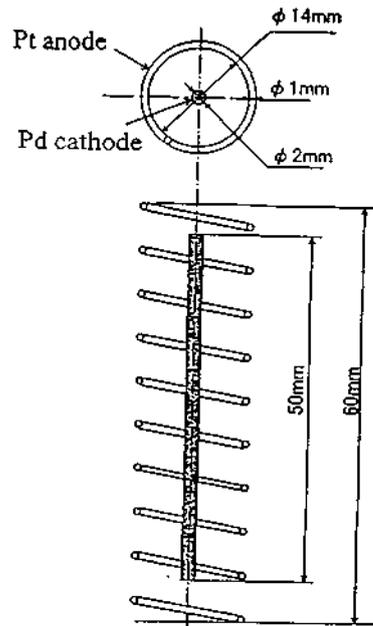


Fig. 5. Detailed configuration of the electrodes.

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Raw material	Purity of palladium: 99.95% up
Casting	Melted under vacuum to form a rod of 16mm in dia.
↓	
Homogenizing	Annealed under vacuum at 750°C for 1 hour
↓	
Swaging	Cold-worked to 10mm in dia.
↓	
Annealing	Annealed under vacuum at 750 °C for 1 hour
↓	
Swaging	Cold-worked to 2mm in dia.
↓	
Cutting	Size: 2mm in dia. and 50mm in length
↓	
Annealing	Annealed under vacuum at 850°C for 4 hour
↓	
Polishing	Polished with diamond slurry for 30 min.
↓	
Etching	Etched in HCl/HNO ₃ (4:1) for 10 min. at 20°C
↓	
Degassing	Degassed in furnace for 24 hours at 200°C

Fig. 6. Working processes of palladium cathodes.

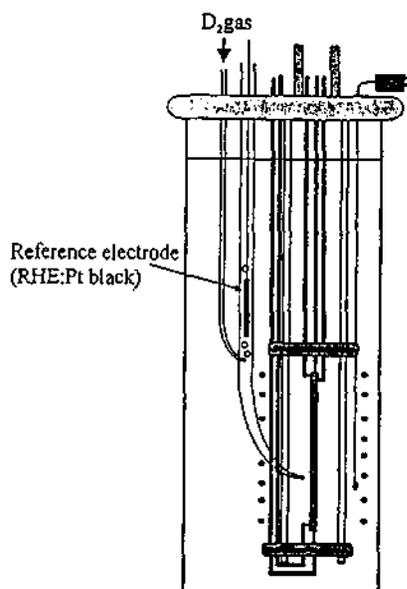


Fig. 7. Schematic electrolytic cell for measuring the electrode potential on the palladium.

Working processes of palladium cathodes are shown in Fig. 6. The experiments were carried out with palladium rods etched with aqua regia for 10 min. at 293K under a cathodic condition, because the rods could reach higher loading ratios above 0.90. The rods were 2 mm in diameter and 50 mm in length. The deuterium loading ratios were determined by the resistance method, whose details were given in reference [2].

The full constant cell voltage electrolysis was accomplished by employing a potentiostat/galvanostat (Hokuto Denko Co., Ltd., HA-301). For the step-up and ramp current electrolysis a function generator (Hokuto Denko Co., Ltd., HB-105) was employed. The ramp rate was determined in reference to the constant cell voltage during the electrolysis.

2.3 Measuring Ohmic Drop and Deuterium Overpotential

The ohmic drop between the anode and the cathode was measured by the current interruption method. To measure the electrode potential, RD(H)E was installed as a reference electrode in the cell without any structural change as shown in Fig. 7. A platinum black electrode with bubbling D₂ gas in a Luggin capillary as an RDE located near by the palladium cathode. The deuterium overpotential on the palladium cathode was approximately determined by subtracting the ohmic drop from the electrode potential.

3. Results and Discussion

3.1 Full Constant Cell Voltage Electrolysis

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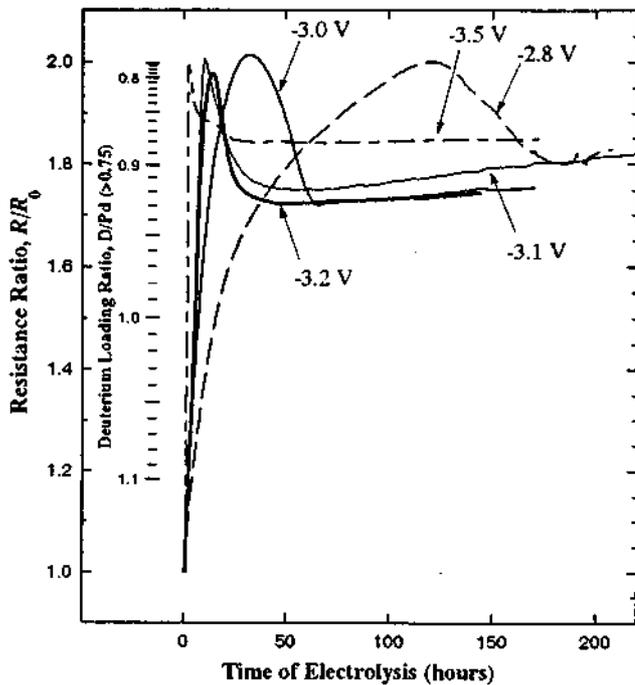


Fig. 8. Changes of the resistance ratios (R/R_0) with various fixed cell voltages.

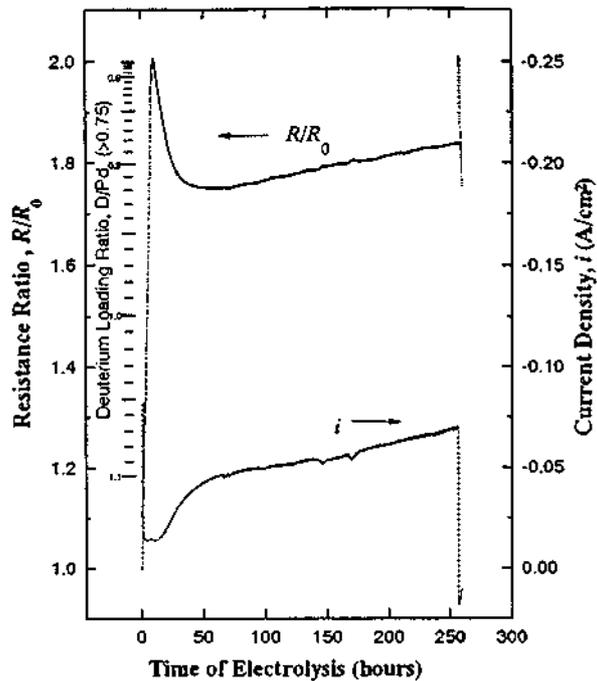


Fig. 9. Changes of the resistance ratio of a palladium cathode with the full constant cell voltage (3.1 V).

Changes of the resistance ratios (R/R_0) with various fixed cell voltage are shown in Fig. 8. From these results, the deuterium loading rate was observed to increase, as the cell voltage increased. With the cell voltage above 3.5 V, the maximum loading ratios over 0.90 could not be obtained. With the cell voltage less than 2.8 V, the time to reach the maximum loading ratios was too long and the value of the maximum loading ratios was lower than those obtained with the cell voltage between 3.0 V and 3.2 V. Therefore, the optimal constant cell voltage is estimated to locate between 3.0 V and 3.2 V in our cell.

One of the results with our full constant cell voltage electrolysis is shown Fig. 9. The constant cell voltage is chosen at 3.1 V. The maximum loading ratio exceeding 0.92 is attained, but the loaded deuterium is observed to decrease gradually. The decrease rate, however, was smaller than some of those constant current electrolyses followed by a step-up current electrolysis. Therefore *full constant cell voltage electrolysis* is effective in a loading enhancement, but not perfect with regard to the deloading.

Observation of the electrolytic current revealed, current spikes were generated at the start of electrolysis. Then, until the resistance ratio went up to $(R/R_0) = 2.0$, the small electrolytic current flew. Subsequently, the electrolytic current rapidly increased with the decrease of the resistance ratio. And then the electrolytic current increased gradually with the decrease of the loading ratio after the loading ratio reached the maximum value.

3.2 Step-up and Ramp Current Electrolysis

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Figure 10 shows the variation in time of the resistance ratio of a palladium cathode rod with a step-up and ramp current electrolysis, as compared with that with a step-up and constant current electrolysis. The ramp rate was chosen as $0.625 \text{ A}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1}$.

At the conventional step-up and constant current electrolysis, after the maximum loading ratio, $D/Pd = 0.92$ was obtained at the maximum cell voltage during the 0.125 A/cm^2 constant current electrolysis, deuterium loading ratios were observed to decrease in association with a decreasing cell voltage with the constant current still maintained.

On the other hand, at the step-up and ramp current electrolysis, the cell voltage was kept constant at about 3.6 V by slowly increasing the current, and, as expected, the maximum loading ratio as high as 0.93 could be maintained for more than 200 hours. This satisfactory result can be obtained only by the step-up and ramp-up current electrolysis.

Concerning the difference between these two methods, the sustentation of higher loading ratios were considered to be affected by electrolytic procedures before attaining to the maximum loading.

3.3 Cause of Cell Voltage Decrease

A possible mechanism to cause the cell voltage decrease under a constant current electrolysis was considered. In general, the cell voltage, V_{cell} , can be expressed by Eq. (1).

$$V_{\text{cell}} = V_d + \eta_D + \eta_O + IR, \quad (1)$$

where V_d , η_D , η_O and IR are theoretical decomposition voltage, deuterium overpotential, oxygen overpotential, and ohmic drop, respectively. The decomposition voltage, V_d , is an invariant under a constant condition, and it is specifically 1.26 V at 293 K under 0.1 MPa.

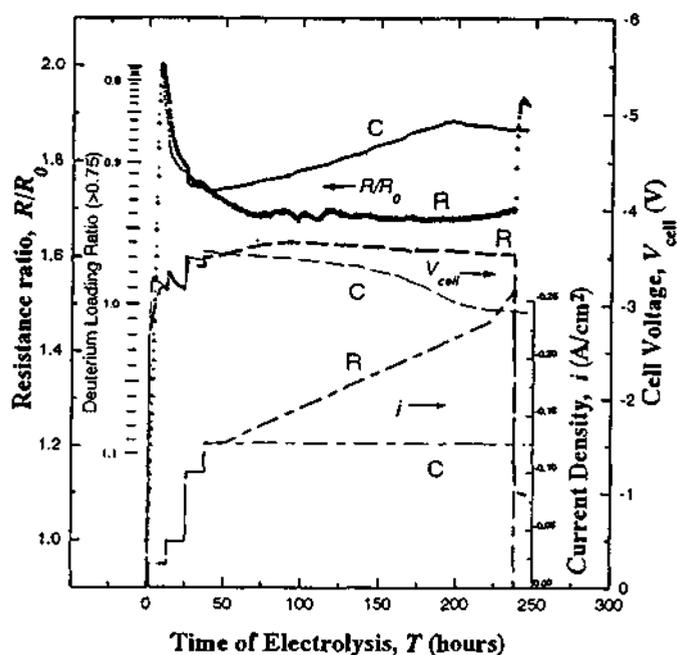


Fig. 10. Variation in time of the resistance ratio of a palladium cathode rod with a step-up and ramp current electrolysis (R), as compared with that with a step-up and constant current electrolysis (C).

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Our deuterium loading was carried out in an open cell, where the electrolysis always concentrates the electrolyte. Consequently, the ohmic drop between the anode and the cathode lowers due to a decrease in the electrolyte resistance, and the deuterium and oxygen overpotentials will change also as the concentration changes.

It is conceivable that the deuterium and oxygen overpotentials should change as well, since the electrode surface will be modified with the electrolysis.

The changes of ohmic drop and overpotentials are considered as follows:

a) Ohmic Drop

Changes of the ohmic resistance between the anode and the cathode in our electrolytic cell against the total electric charge is shown in Fig. 11. The cell ohmic resistance is observed to decrease linearly with the total electric charge. The decrease of the ohmic drop was estimated to be approximately 0.1 V for the electrolysis with 0.125 A/cm² (electrolytic current 0.4 A) for 200 hours (the total electric charge $Q = 2.9 \times 10^5$ C). Therefore, the cell voltage decrease in excess of 0.6 V cannot be accounted for only by the ohmic drop.

b) Deuterium and Oxygen Overpotential

Changes of the deuterium overpotential with electrolysis time at the constant current density 0.125 A/cm² followed by step-up current electrolysis are shown in Fig. 12. The deuterium overpotential is observed rapidly to decrease with the electrolysis, despite with the constant current. Furthermore, relationship between

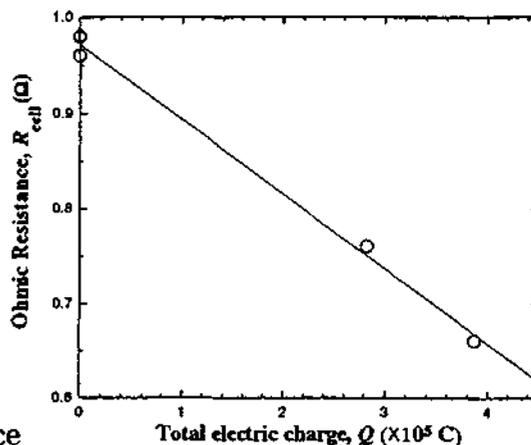


Fig. 11. Changes of the ohmic resistance between the anode and the cathode in our electrolytic cell against the total electric charge.

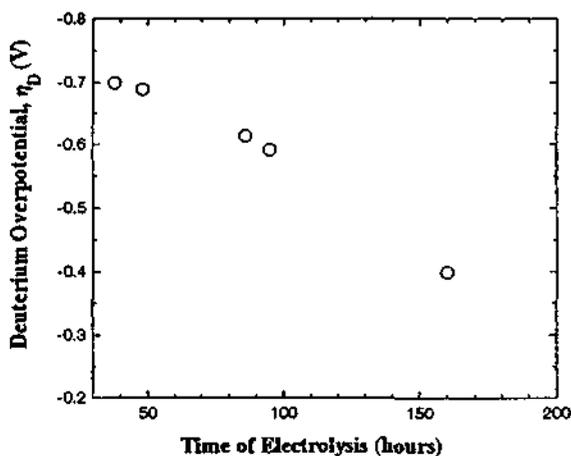


Fig. 12. Change of the deuterium overpotential on the palladium cathode with electrolysis time at the constant current density 0.125 A/cm².

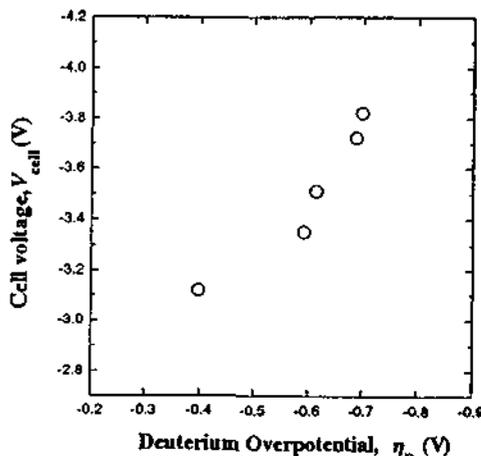


Fig. 13. Relationship between the cell voltage and the deuterium overpotential during electrolysis at the constant current density 0.125 A/cm².

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the cell voltage and the deuterium overpotential is shown in Fig. 13, which indicates an approximately linear relation between the cell voltage and the deuterium overpotential. The rate of decrease in the deuterium overpotential, $\Delta\eta_D$, can be estimated to be approximately 0.3 V for the corresponding cell voltage decrease of 0.7 V.

In Eq. (1), the decrease of the oxygen overpotential, $\Delta\eta_O$, will be considered almost equal to the one of the deuterium overpotential, $\Delta\eta_D$.

Concerning the deuterium overpotential, K. Ota et al. claim that it is higher with a higher concentration of LiOD electrolyte, which leads to the conclusion that the decrease of the deuterium overpotential cannot be ascribed to the concentration change of LiOD. Consequently, it is clear that the decrease of the cell voltage is mostly due to the decrease in the deuterium and oxygen overpotentials.

Judging from these, it is concluded that those changes in deuterium loading ratios are attributed mainly to the changes in the deuterium overpotential, and that it is necessary to control the deuterium overpotential to suppress the deloading.

4. Conclusions

- (1) The maximum deuterium loading ratio of the palladium cathode can be maintained for more than a week by using the palladium cathode etched by aqua regia and by electrolytic loading with the increasing electrolytic currents.
- (2) During a long term electrolysis, the deuterium overpotential on a palladium cathode is observed to decrease, which will cause the deloading.
- (3) It is confirmed that when the deuterium overpotential is controlled not to decrease by our method of increased current electrolysis, the deloading can be suppressed.
- (4) Higher deuterium loading ratios can be maintained by our method for a substantially long period of time.

References

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