Kunimatsu, K., et al. *Deuterium Loading Ratio and Excess Heat Generation During Electrolysis of Heavy Water by Palladium Cathode in a Closed Cell Using a Partially Immersed Fuel Cell Anode*. in *Third International Conference on Cold Fusion, "Frontiers of Cold Fusion"*. 1992. Nagoya Japan: Universal Academy Press, Inc., Tokyo, Japan.

Deuterium Loading Ratio and Excess Heat Generation during Electrolysis of Heavy Water by a Palladium Cathode in a Closed Cell Using a Partially Immersed Fuel Cell Anode

K. Kunimatsu, N. Hasegawa, A. Kubota, N. lmai, M. lshikawa, H. Akita and Y. Tsuchida.
IMRA JAPAN CO., LTD.
3-6 Techno Park 2 cho-me, Shimonopporo, Atsubetsu-ku, Sapporo 004
JAPAN

ABSTRACT

We have developed a novel electrolytic cell pressurized by D_2 in which deuterium loading ratio in a palladium cathode can be determined in-situ during the calorimetric measurements of excess heat. A gas diffusion type fuel cell anode is partially immersed in the electrolyte solution to act as a counter electrode, at which electrochemical oxidation of deuterium gas molecules to deuterium ions takes place instead of electrolytic decomposition of water molecules to generate oxygen gas.

Factors controlling the loading ratio such as electrolyte composition, hydrogen overvoltage at the palladium cathode, current density and isotope effect have been examined.

Dependence of the excess heat generation at the palladium cathode on the loading ratio as well as on the current density shows that the critical loading ratio and the current density to generate excess heat are ca. 0.83 and 100mA/cm^2, respectively.

The maximum D/Pd of 0.89 has been achieved in the present study, at which excess heat generation of ca. 35% with respect to the input electrolytic power has been observed.

INTRODUCTION

The difficulty in replicating the Pons/Fleischmann type electrolytic excess heat generation [1],[2] during electrolysis of heavy water has caused strong criticism on their experiments, and the reality of the so-called cold fusion has been questioned. However, to date very few studies have been reported on the fundamental factors controlling the deuterium loading ratio in the palladium cathode which has been believed to be the key factor to control the excess heat generation. The NCFI final report [3] contains some data on the loading ratio under various conditions but they are too preliminary to suggest important factors controlling the loading ratio. Will et al. [4] reported loading ratio higher than 0.85 as key factor for tritium production, while McKubre et al. [5],[6] reported the critical loading ratio around 0.9 to give rise to the excess heat generation. The loading ratio was determined by conducting the electrolysis in a closed cell utilizing a fuel cell anode by Will et al. and by monitoring the electrical resistance by McKubre et al.

Electrolysis in a closed cell utilizing a fuel cell anode offers a direct method to determine the loading ratio by monitoring the deuterium pressure during electrolysis while measurement of the

electrical resistance is an indirect one which relies on the resistivity data as a function of loading ratio observed in gas phase[7].The structure of the electrolysis cell utilizing fuel cell anode proposed by Will[4] is difficult to conduct calorimetry and to carry out long term electrolysis.

The purpose of the present study is firstly to develop a novel new electrolysis cell utilizing a fuel cell anode which allows us simultaneously to carry out calorimetry and to conduct in-situ determination of loading ratio; secondly to examine the factors controlling the loading ratio; and thirdly to investigate the relation between the excess heat generation and the loading ratio.

EXPERIMENTALS

Determination of hydrogen/deuterium loading ratio in a palladium cathode was done first in a closed cell developed in our laboratory which is shown schematically in Fig. 1. The pressure vessel made from SUS316 filled with deuterium gas of 5 - 10 atm has an electrolyte container made from PTFE or glass with four windows at which gas diffusion electrodes are attached with their reaction layers in contact with electrolyte solution. A platinized platinum electrode (PVPt) was placed in the electrolyte and acted as a reference electrode (RHE) to measure hydrogen overvoltage at the palladium cathode.

The cathode and anode reactions in alkaline solutions are given respectively by,

$$\text{Cathode reaction: } 2D_2O + 2e^- \dashrightarrow 2D(\text{ads.}) + 2OD^- \tag{1}$$

$$2D(\text{ads.}) \dashrightarrow \begin{cases} \dashrightarrow D_2 \\ \dashrightarrow 2D(\text{Pd}) \end{cases} \tag{2}$$

$$\text{Anode reaction: } D_2 \dashrightarrow 2D^+ + 2e^- \tag{3}$$

where D(ads.) and D(Pd) denote deuterium atom adsorbed on the cathode surface and absorbed into the cathode respectively.

From (1), (2) and (3) the over-all cell reaction for the electrolysis with a Pd cathode and a fuel cell anode is given by:

$$D_2 \text{ - - - - - > } 2D(\text{Pd}) \tag{4}$$

Therefore,pressure of D_2gas decreases as electrolysis proceeds due to deuterium absorption into the Pd cathode. We have,

$$(P_O\text{-}P)V=(n_O\text{-}n)RT, \tag{5}$$

where P_O and n_O are the pressure and total number of moles of D_2 gas in the pressure vessel at the onset of electrolysis, and P and n are the pressure and the number of moles of D_2 gas at a given time of electrolysis, respectively, while V is the free volume of the vessel which is measured before electrolysis and is taken constant. The loading ratio at a given time is calculated from the pressure decrease by the relation

$$D/Pd = 2V(P_O\text{-}P)/RT/n_{Pd}, \tag{6}$$

where n_{Pd} is the number of gram atoms of Pd in the cathode.

The calculation of D/Pd needs corrections, however, for the change in vapor pressure of D_2O in the gas phase due to the temperature change during electrolysis, change in the solubility

of D_2 gas in the electrolyte solution as well as in PTFE materials in the vessel due to the temperature as well as pressure change in the vessel. These corrections are usually small, 1 - 2%, but the loading ratio reported in the present study have been corrected for them.

There is another advantage of using a fuel cell anode; because no electrolytic decomposition of D_2O takes place, less input power is required for electrolysis and further more, the input power, W_{input}, is given simply by a product of electrolysis current I and cell voltage E_{cell} as,

$$W_{input} = I \times E_{cell} \quad (7)$$

Performance of the cell shown in Fig. 1 was excellent for determination of the loading ratio at low current densities. It turned out, however, that the cell has a serious problem when operated at high current densities. Substantial amount of solvent is lost from the electrolyte container when electrolysis is conducted at high current densities for a long period. The solvent tends to condense at the bottom of the pressure vessel and the electrolysis was no longer possible in that case.

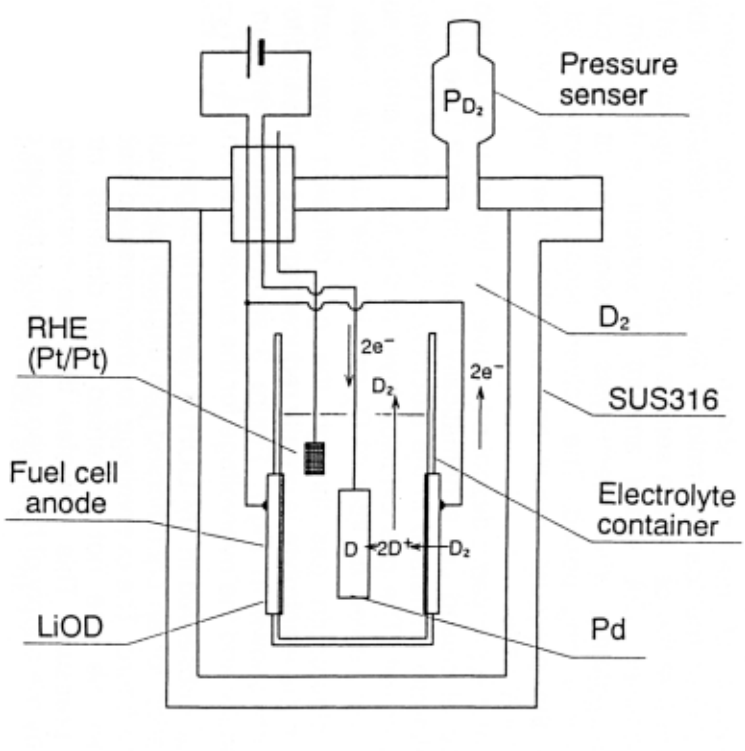

Figure 1. Electrolysis cell using a fuel cell anode.

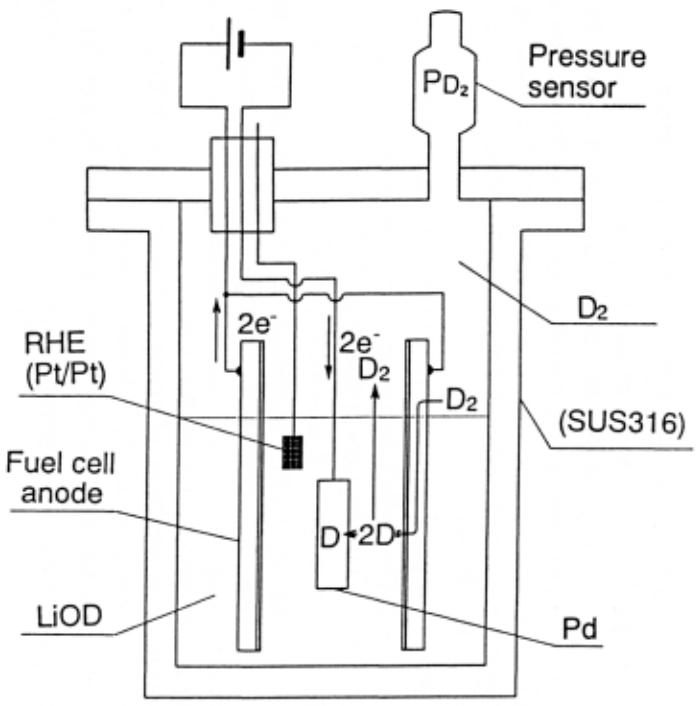

Figure 2. Electrolysis cell using a partially immersed fuel cell anode.

In view of the problems described above, we further have developed a new type of closed cell schematically shown in Fig. 2. The fuel cell anode is directly immersed in the electrolyte leaving some portion of it in the gas phase. The gas diffusion layer of the fuel cell anode above the electrolyte served as inlet of D_2 gas into the fuel cell anode. The supply of deuterium gas through the gas diffusion layer partially immersed in the electrolyte is greatly reduced, however, compared to the configuration shown in Fig. 1. Figure 3 shows relation between the current density and the overvoltage for the anode reaction, i.e., $H_2 \text{--->} 2H^+ + 2e^-$, observed in 1M LiOH at various hydrogen pressures. The similar relation for an unimmersed gas diffusion electrode is compared in the same figure. The overvoltage for the immersed electrode is much higher than the one not immersed and depends strongly on the hydrogen pressure. This indicates that the overvoltage is primarily governed by the supply of hydrogen gas through the gas diffusion layer.

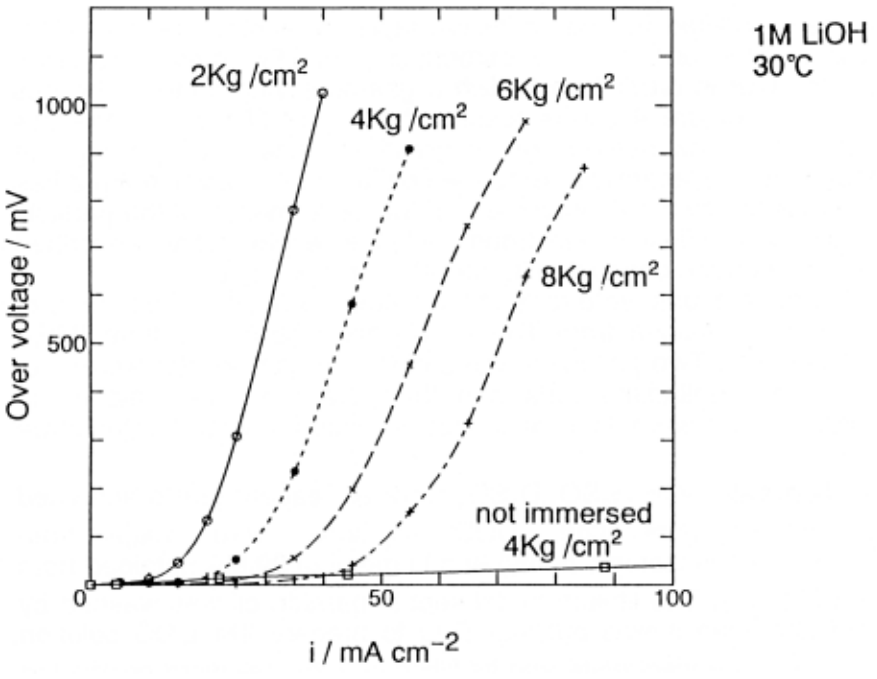

Figure 3. Polarization curves of the immersed electrode.

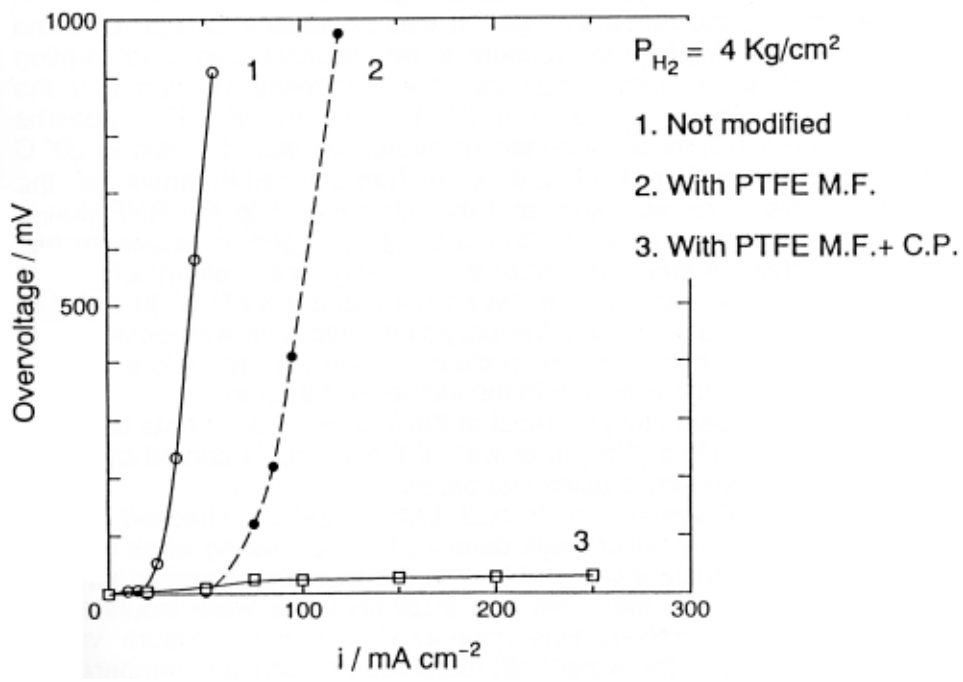

Figure 4. Polarization curves of the modified electrodes.

We then modified the gas diffusion layer by adding firstly a PTFE membrane filter and then a carbon paper/PTFE membrane filter composite layer in order to establish a gas supply route to the gas diffusion layer. Figure 4 shows results of such modification of the gas diffusion layer. The overvoltage is greatly reduced by applying the composite layer. Electrolysis using the configuration shown in Fig. 2 has become feasible by the improvement of the performance of the

partially immersed gas diffusion electrode. All the experiments described hereafter have been conducted in the cell shown in Fig. 2.

Palladium cathodes were rods of 2mm, 4mm or 5mm diameter, of 99.99% purity obtained from Tanaka Kikinzoku and also from IMRA Materials co., Ltd. Two palladium wires of 0.5mm in diameter were spot welded to the palladium rods and then the rods were etched in conc.HNO_3. They were then degassed in vacuum at 200°C for three hours.

The chemicals LiOH, H_2SO_4 and D_2SO_4 were all reagent grade and were used without further purification. LiOD solutions were made from D_2O (lsotech, 99.9% isotopic purity) and Li metal of 99.9% obtained from Johnson Matthey. The lithium metal kept in paraffin oil was washed by propanol and then it was put into D_2O to prepare 1M LiOD solution. Preparation of the electrolyte and its filling into the cell were conducted in a glove box purged continuously with dry air. After filling, the cell was purged with hydrogen or deuterium gas for half an hour and then pressurized by the respective gas. It was necessary to wait for some time, typically a day, for the pressure to stabilize, due to absorption of hydrogen or deuterium gas into the electrolyte solution and the electrolyte container made from PTFE. One ml of PTFE absorbs approximately 0.7 ml of hydrogen or deuterium gas at 1 atm at 20°C with diffusion constant of $2.6 \times 10^{-7} cm^2 sec^{-1}$ [8]. Potential of the palladium electrode was kept at 1.0V with respect to the RHE during the waiting period to prevent absorption of hydrogen or deuterium gas into the palladium electrode. After the purging, cyclic voltammogram of the Pd electrode was taken between 0.4V and 1.5V/RHE in order to clean the Pd surface. Finally the palladium electrode was polarized at 1.5V/RHE for 15 min. in order to clean its surface just before starting electrolysis when the pressure in the vessel is stabilized.

A pressure vessel used for most of the loading experiments is shown schematically in Fig. 5. The inner wall of the vessel is coated by a thin ceramic layer resistant to acids and bases.

The pressure vessel which had been carefully checked for its pressure leakage by helium leak detector has several Ag wires of 1mm diameter for electrical leads and k-type thermocouples sealed through a sealing ground. All the wires and thermocouples were insulated by PTFE tubing. Electrolysis was conducted with the pressure vessel totally submerged in the water bath regulated at a constant temperature typically 10°C. The content of light water in the electrolyte when using D_2O was checked by NMR after a two months electrolysis period but no change in the light water content was detected.

The cell shown in Fig. 5 has a low thermal cell constant, ca. 1°C/W, when submerged in the water bath, therefore the temperature of the electrolyte remained almost constant during the loading experiments.

Electrolysis was conducted at constant currents supplied by a DC power supply for each cell. The power supplies were controlled by a computer, by which data acquisition was also conducted throughout the electrolysis period.

Calorimetry was conducted in another type of cell with higher thermal cell constants, 5 - 8°C/W. The experimental detail is given elsewhere [9].

Most of the loading experiments were conducted in a constant temperature room regulated at 20 ±0.1°C.

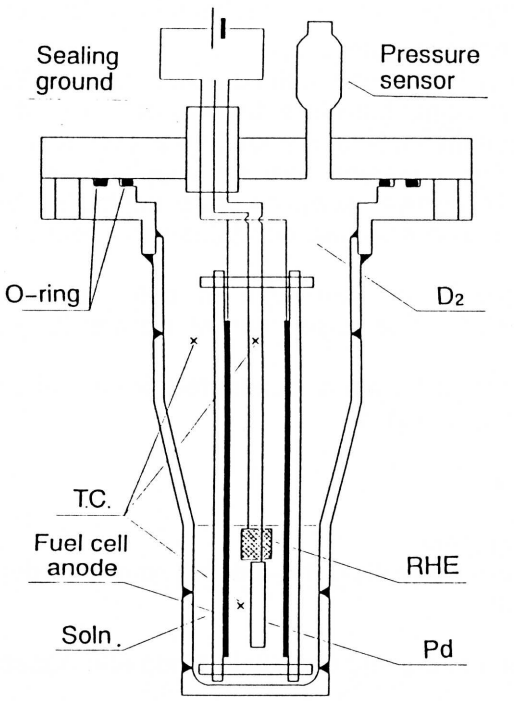

Figure 5. Electrolysis cell for loading experiments.

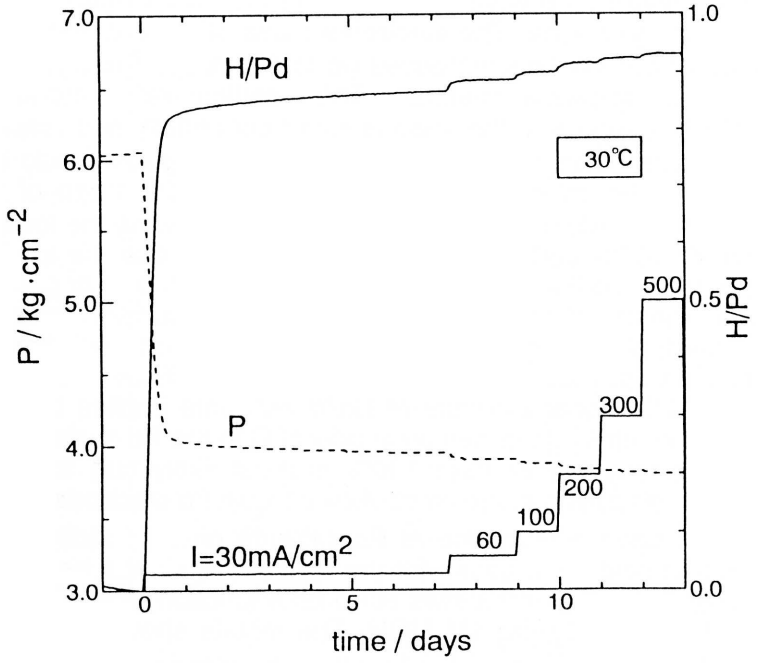

Figure 6. Change of H/Pd with current density in 1M LiOH.

RESULTS AND DISCUSSION

I. Factors controlling loading ratio

We investigated firstly factors controlling the loading ratio in order to find optimum loading conditions.

1. Dependence on overvoltage and current density in acids and bases.

A typical example of a loading experiment in 1M LiOH is shown in Fig. 6, in which the change of pressure and loading ratio are displayed as a function of electrolysis time. The electrolysis was started at 30mA/cm^2 and then current density was increased up to 500mA/cm^2 nearly every 24 hours in a stepwise manner. The loading ratio increases systematically in response to the change in current density and reaches 0.930 at 500mA/cm^2. The example shows clearly that loading ratio can be controlled by current density. Figure 7 shows initial stage of the loading at 30mA/cm^2 which is compared to the line showing the loading ratio change for 100% current efficiency. We can see that the loading proceeds almost at 100% current efficiency up to H/Pd=0.5. In general the current efficiency of loading increases at lower current densities. Figure 8 shows that loading at 3mA/cm^2 proceeds linearly with time at current efficiency slightly higher than 100% throughout the entire loading period. The linear increase of D/Pd with time implies that the loading process is totally governed by supply of D to the Pd surface, and the current efficiency higher than 100% is most likely due to direct absorption of D_2 dissolved in the electrolyte into the Pd electrode.

The effect of hydrogen overvoltage at Pd cathode on the loading ratio was compared in acids and bases for the light water as well as for the heavy water system. Figure 9 shows H/Pd as a function of overvoltage observed in 2.8M H_2SO_4, and 1M LiOH. The results show clearly that the loading ratio increases systematically with overvoltage increase and that the data in both media almost coincide. It should be particularly noted that the highest H/Pd achieved in acidic solutions is much lower than in alkaline solution. This is simply because the hydrogen overvoltage in acids is usually much lower than in bases for a given current density. Therefore the difference between acid and base becomes clear when H/Pd is plotted as a function of current density as shown in Fig. 10.

The loading ratio in acid and base was compared also for deuterium in 1M LiOD and 2.8M D_2SO_4 at 10°C and the result is shown in Fig. 11. The loading ratio in the common overvoltage region below -500mV coincides in the two media but the difference between the two media becomes evident when D/Pd is plotted as a function of current density as shown in Fig. 12.

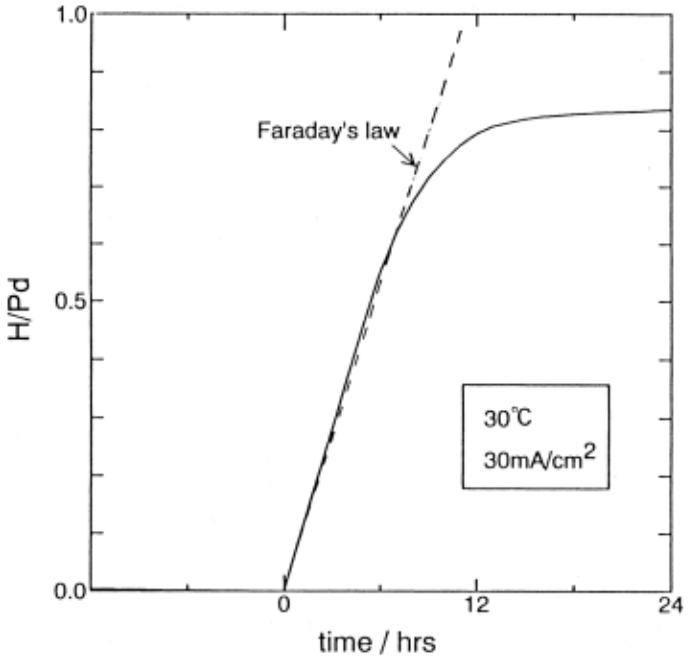

Figure 7. Change of H/Pd with time in 1M LiOH.

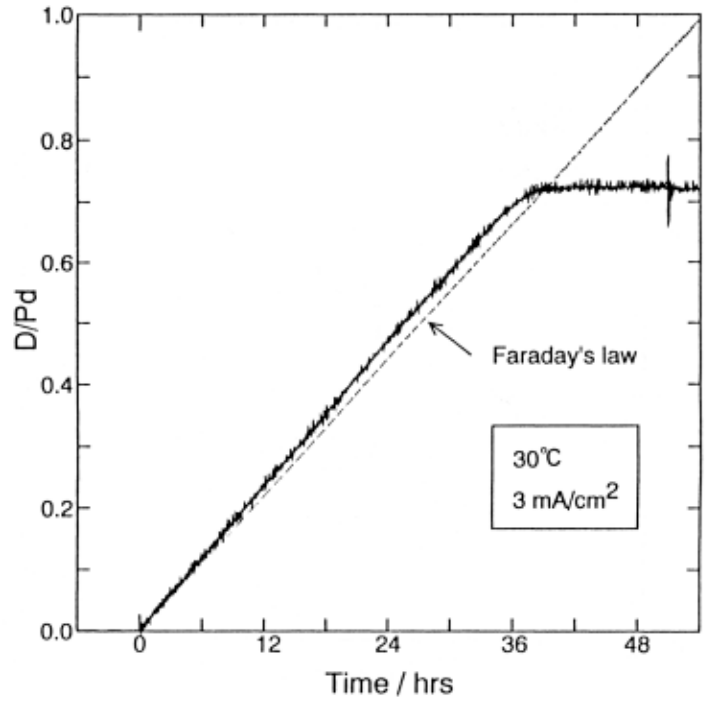

Figure 8. Change of D/Pd with time in 1M LiOH.

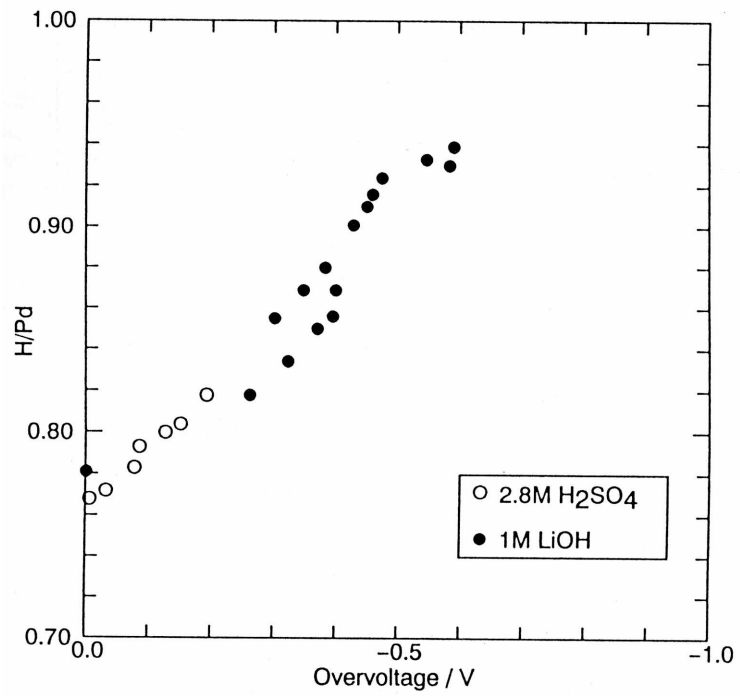

Figure 9. Dependence of H/Pd on overvoltage in acid and base.

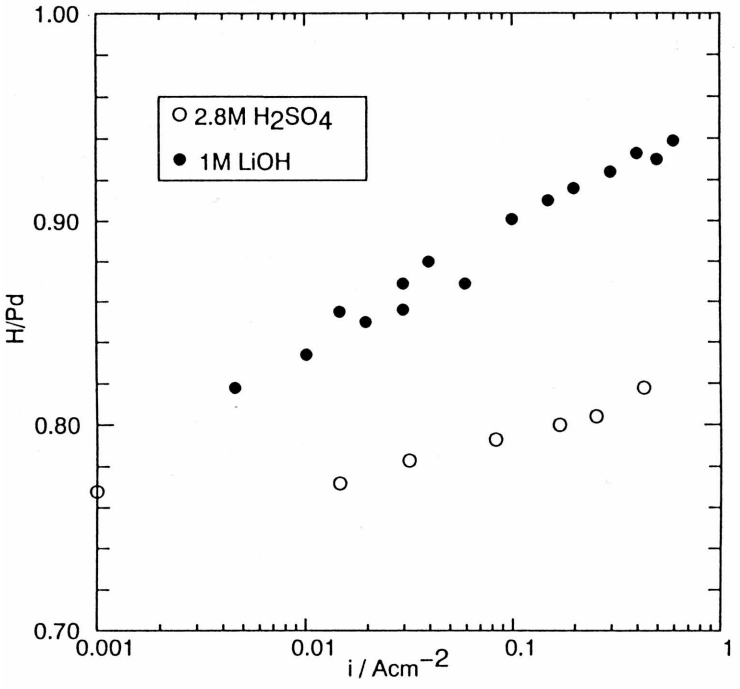

Figure 10. Dependence of H/Pd on current density.

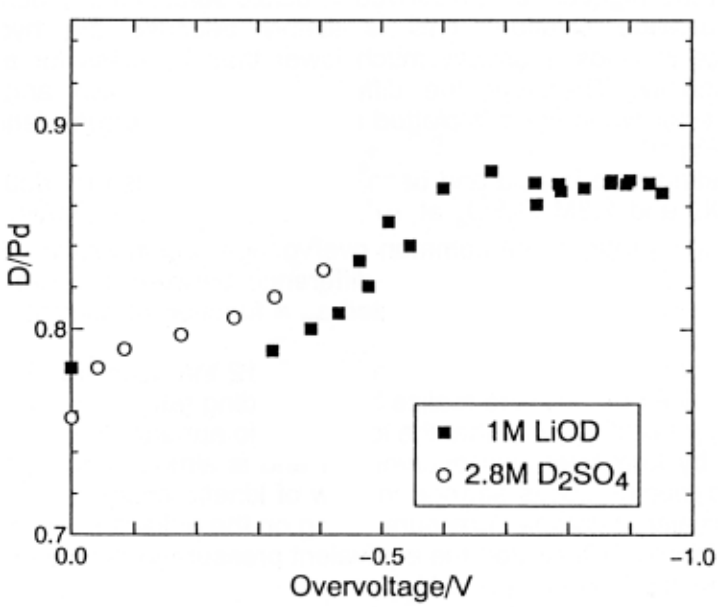

Figure 11. Dependence of D/Pd on overvoltage in 1M LiOD and 2.8M D_2SO_4 at 10ºC.

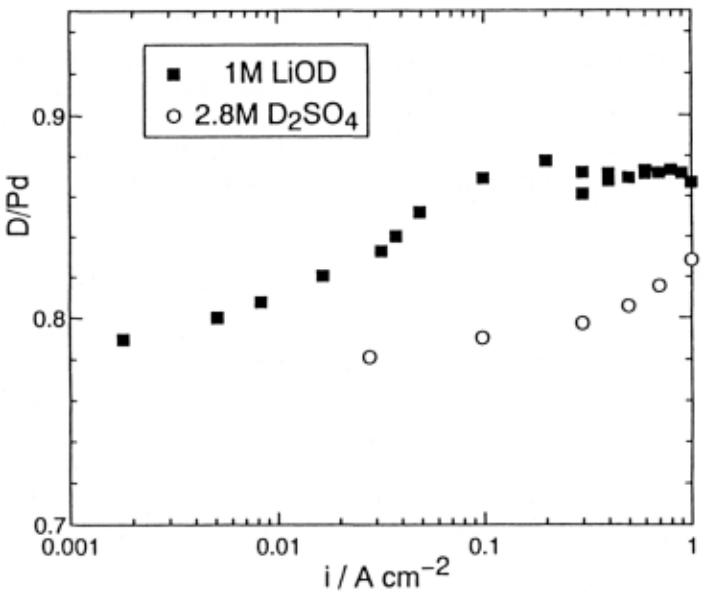

Figure 12. Dependence of D/Pd on current density in 1M LiOD and 2.8M D_2SO_4 at 10ºC.

We can conclude from the data in Figs. 9 - 12 that alkaline media is a better choice than acids to realize higher loading ratio. On the other hand, the fact that the loading ratio appears to be controlled by total hydrogen overvoltage and is almost independent of electrolytic medium looks strange in view of kinetic analysis of the so-called equivalent hydrogen pressure acting on the palladium electrode. Enyo and Maoka [10] related the equivalent pressure to the overvoltage of the Tafel step [2H(ads.) --->H_2];

$$P^*=P_{H2}\exp(-2F\eta_2/RT) \quad (8)$$

where P* and P_{H2} are the equivalent pressure and the actual pressure of hydrogen in the electrolysis cell, respectively, and η_2 is the overvoltage of the Tafel step. The equation becomes the so-called Nernst equation if η_2 is replaced by the total overvoltage.

Analysis of the data in Figs. 9 and 11 based on the equation (8) leads to a conclusion that the overvoltage of the Tafel step is common in the acid and base for a given total overvoltage. The validity of the conclusion and hence of equation (8) could be tested by measurements of the component overvoltage of the Tafel step or that of the Volmer step in various media.

2. Isotope effect

The isotope effect on the loading ratio has been investigated elsewhere [11] for both acidic and alkaline media. The lower loading ratio for deuterium can be interpreted in terms of the higher plateau pressure in p-c-T curve of Pd/D_2 system in gas phase than Pd/H_2 system. This makes it rather difficult to conduct excess heat measurements at D/Pd close to 1. Our excess heat measurement was conducted up to D/Pd=0.89 as shown in the following section.

II. Excess heat measurement

The details of excess heat measurement has been described elsewhere [9].

The relation between the excess heat and D/Pd in 1M LiOD is plotted in Fig. 13, which suggests that the critical loading ratio to give rise to the excess heat is ca.0.83. Unfortunately the highest loading ratio achieved in the present study is 0.89 and we cannot predict the dependence of excess heat on D/Pd at higher loading ratios.

The critical D/Pd which is ca. 0.83 found in the present study is well compared to the results reported by McKubre et al. [6].

We derived relation between the excess heat and current density from the data described in the proceeding part and the result is shown in Fig. 14. The figure suggests that excess heat is almost proportional to current density and that the critical current density to give rise to excess heat is close to $100mA/cm^2$. The data is in agreement with those reported by Pons and Fleischmann in 1990[2]. The role of high current density needed to produce excess heat is obvious from Fig. 12 which shows the current density dependence of D/Pd. Below $100mA/cm^2$, D/Pd decreases sharply and current density higher than $100mA/cm^2$ is necessary to maintain high loading ratio.

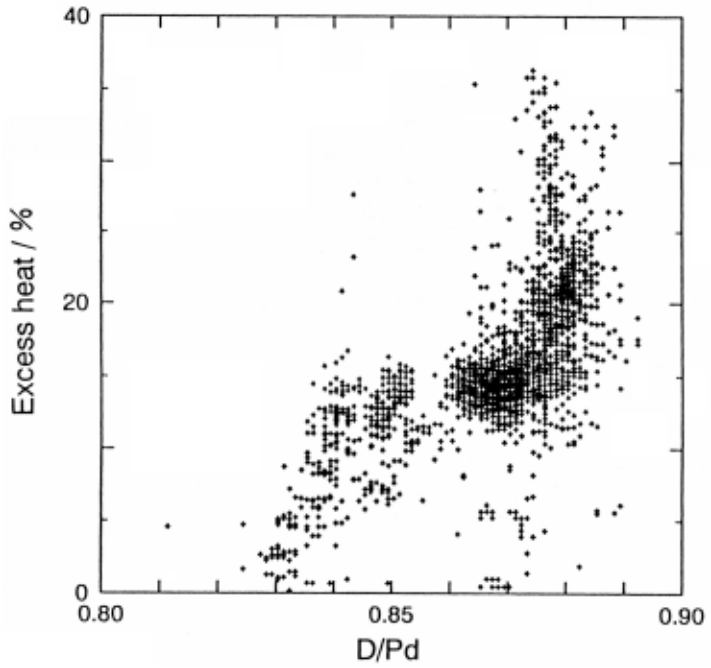

Figure 13. Dependence of excess heat generation on D/Pd.

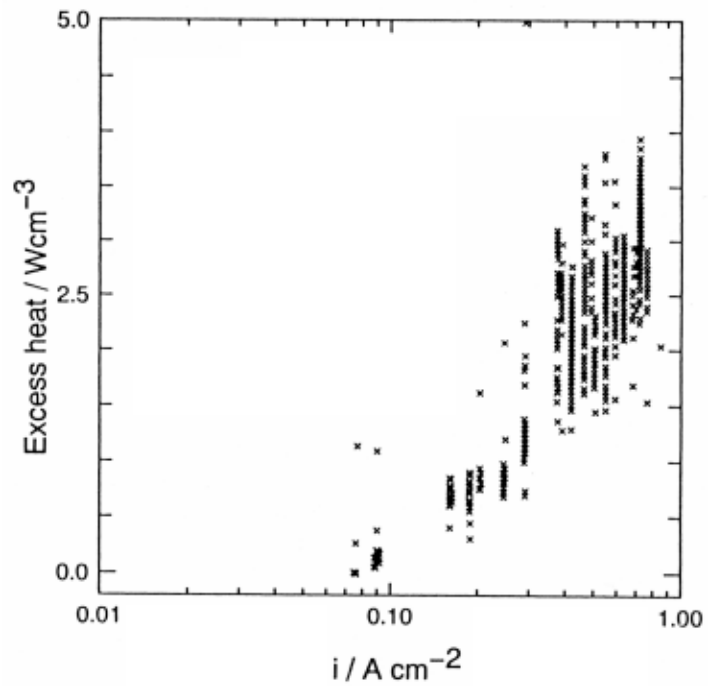

Figure 14. Dependence of specific excess heat on current density.

III. Conclusion

A new method of electrolysis in a closed cell pressurized by D_2 gas has been developed utilizing a partially immersed fuel cell anode modified by a composite layer of PTFE and carbon paper. The cell allows us to conduct simultaneous measurement of excess heat and D/Pd during electrolysis. We can summarize the following conclusions:

(1) The loading ratio is primarily controlled by hydrogen overvoltage at the Pd cathode.

(2) D/Pd is lower than H/Pd by 5-10% for a given overvoltage.

(3) Excess heat generation increases at higher D/Pd between 0.83 and 0.89.

(4) Excess heat is proportional to the current density above 100mA/cm^2, the role of the current density being to maintain high D/Pd.

Confirmation of these conclusions by repeated investigations and improvement of D/Pd will be necessary in future experiments. They are currently in progress in our lab and will be reported in due course.

Acknowledgement

Financial supports for the present study by Aisin AW Co., Ltd. and by Technova Inc. is greatly acknowledged. Supply of Pd from IMRA Materials Co., Ltd. and discussions with Prof. N. Furuya are also greatly acknowledged.

REFERENCES

1. M. Fleischmann, S. Pons and M. Hawkins: J. Electroanal. Chem. , 261 (1989) 301. Erratum, 263 (1989) 187.
2. M. Fleischmann, S. Pons, M. W. Anderson, L. J. Li and M. Hawkins: J. Electroanal. Chem., 287 (1990) 293.
3. A. M. Riley, J. D. Seader, D. W. Pershing, D. C. Linton and S. Shimizu: NCFI Final Report Vol. II (1991) 123.
4. F. G. Will, K. Cedzynska and C. Linton : NCFI Final Report Vol. I (1990) 131.
5. M. C. H. McKubre, R. Rocha-Filho, S. I. Smedley, F. L. Tanzella, S. Crouch-Baker, T. O. Passel, J. Santucci: The Science of Cold Fusion, Proceedings of ICCF2 (1991) 419.
6. M. C. H. McKubre: Review of Fatal Accident at SRI January 2 (1992).
7. J. C. Barton, F. A. Lewis and I. Woodward: Trans. Faraday Soc., 59 (1963) 1201.
8. A. Ya. Kupryazhkin, I. A. Korolev, P. V. Bolobuev and P. E. Suetin: Sov. Phys. Tech. Phys., 22 (1977) 1406.
9. N. Hasegawa, K. Kunimatsu, T. Ohi and T. Terasawa: Proceedings of ICCF3 (1992).
10. T. Maoka and M. Enyo: Electrochim. Acta, 26 (1981) 607.
11. A. Kubota, H. Akita, Y. Tsuchida, T. Saito, Akiko Kubota, N. Hasegawa, N. lmai, N. Hayakawa and K. Kunimatsu: Proceedings of ICCF3 (1992).