Observation of Excess Heat during Electrolysis of 1M LiOD in a Fuel Cell Type Closed Cell

Norifumi HASEGAWA, Keiji KUNIMATSU, *Tamio OHI, *Toshihisa TERASAWA.
IMRA JAPAN CO., LTD. *AISIN MATERIAL R&D CO., LTD.
2-3-6 Techno Park Shimonopporo, Atsubetsu-Ku, Sapporo 004, Japan
*5-50 Hachiken-Cho, Kariya, Aichi 448, Japan

ABSTRACT

Measurement of the excess heat generation during electrolysis of 1M LiOD has been conducted in a closed cell pressurerized by deuterium gas in which a fuel cell type gas diffusion electrode was employed as an anode, and a platinized platinum electrode served as the RHE for determination of hydrogen overvoltage at the palladium cathode. This has allowed us simultaneous determination of both excess heat generation and deuterium loading ratio, D/Pd, in the course of long term electrolysis which lasted for nearly two months.

Dependence of excess heat generation on D/Pd has been observed up to D/Pd = 0.88 with the maximum output/input ratio of 1.35. The minimum D/Pd to produce the excess heat has been found around 0.83-0.84.

Dependence of D/Pd on the overvoltage and the dependence of the excess heat generation on the D/Pd suggest that the dependence of the excess heat generation on the current density reported originally by Fleischmann and Pons and later by Storms can be interpreted in terms of the dependence of the loading ratio on the electrolysis current density. In other words, higher current density is necessary to maintain the high loading ratio.

1. Introduction

Since Fleischmann and Pons et al,[1] reported their observation of large amounts of excess heat during the electrolysis of heavy water with a Pd cathode, laboratories around the world have attempted to reproduce their results. It has been shown recently that the phenomenon of excess heat generation is closely related to achievement of deuterium loading ratio D/Pd greater than 0.9[2]. The purpose of the present investigation is to find the quantitative relation between excess heat generation and the deuterium loading ratio in the palladium cathode.

2. Experimental

2-1. Measurement of deuterium loading ratio

Electrolysis was conducted in a hermetically sealed cell containing 1M LiOD and pressurized by deuterium gas in which a fuel cell anode partially immersed in the electrolyte served as an anode as shown in Figs. 1 and 2. The gas diffusion layer of the fuel cell anode was modified by an additional composite layer made from PTFE membrane filter and a carbon paper to facilitate the deuterium gas supply through the layer when the anode is partially immersed in the electrolyte. The electrode reactions at anodes and cathodes are given by,

Anode $D_2 \rightarrow 2D^+ + 2e^-$.

Cathode $2D^+ + 2e^- \rightarrow D_2$ or $D_{(Pd)}$.

The over all reaction is given by $D_2 \rightarrow 2D_{(Pd)}$.

The deuterium loading ratio is determined from the D_2 pressure decrease after initiation of electrolysis and can be monitored in-situ throughout the electrolysis. The electrolysis was conducted by using Pd and Ni cathode (4mm $\phi \times$ 18.5mm) at the initial pressure of 7Kgf/cm^2 by changing the current density between 50 and 1000mA/cm^2. The Pt/Pt electrode was placed dose to the cathode and this served as the RHE(Reversible Hydrogen Electrode) for the measurement of the hydrogen overvoltage at the cathode. The overvoltage reported in the present study has been corrected for the ohmic overvoltage which was measured by galvanostatic pulse experiment. After installation of the cell in the high pressure vessel, air in the vessel was evacuated and the cell was filled with D_2. Before electrolysis, the potential of the Pd electrode was kept 1000mV against the anode to avoid deuterium absorption into the Pd cathode.

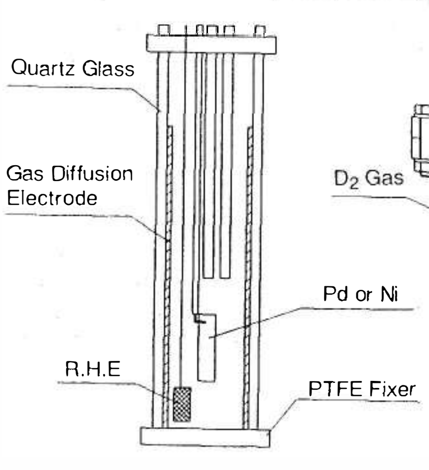

Fig-1 Electrolysis geometry

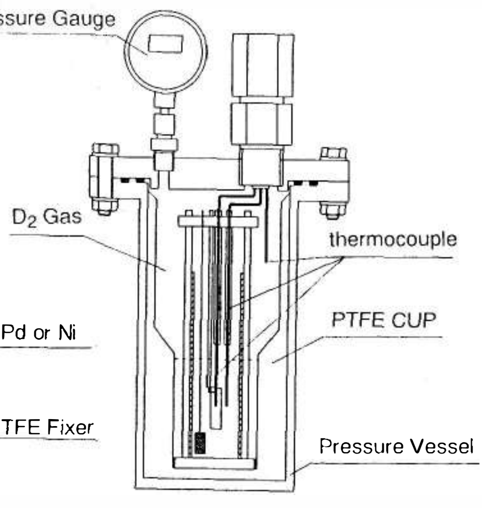

Fig-2 Structure of the pressure vessel

2-2. Detection of excess heat

Detection of excess heat at cathode was conducted by measuring the temperature rise in the cathode by a thermocouple inserted in it through a hole (1.5mm $\times$ 7mm) made at it's top. The temperature rise was first observed as a function of input power for the Ni cathode. The relation between the temperature rise and the input power thus observed served as a calibration curve. The Ni cathode was then replaced by a palladium cathode and the relation between the temperature rise and input power was measured. The estimation of the excess heat was conducted by comparing the temperature rise for a given input power between the Ni and Pd cathodes. The cell was totally submerged in a water bath in which temperature was regulated at 10°C or 30°C ±0.1°C.

4. Result and Discussion

Figure-3 compares the relation between the temperature rise in the cathode and input power observed by Ni cathode, given by the straight line, and by Pd cathode. The calibration curve obtained by Ni cathode makes a good straight line while the data points observed by Pd cathode lie on the calibration line up to the input power of ca 1W, above which, however, they lie above the calibration line.

A similar experiment was conducted in 1M LiOH to see if the deviation of the palladium data from the calibration line demonstrated in Fig.3 is characteristic of the palladium/deuterium system.

Figure-4 shows the result obtained for the palladium/hydrogen system, in which there is a close agreement between the palladium data and the calibration line obtained by using a Ni cathode. We conclude from Figs.3 and 4 that the temperature change observed in the palladium cathode in 1M LiOD is caused by joule heating due to the input power as well as by additional excess heat generation in the palladium cathode. The excess heat generation calculated from Fig.3 are related to the deuterium loading ratio in ways as shown in Figs.5 and 6.

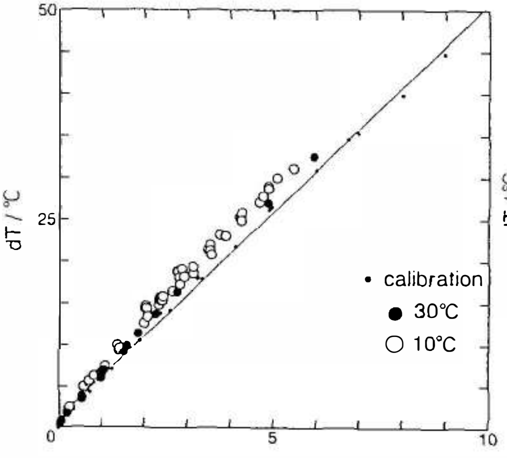

Fig.3 Comparison of the relation between temperature rise in cathode and input power observed with Ni and Pd electrodes in 1M LiOD.

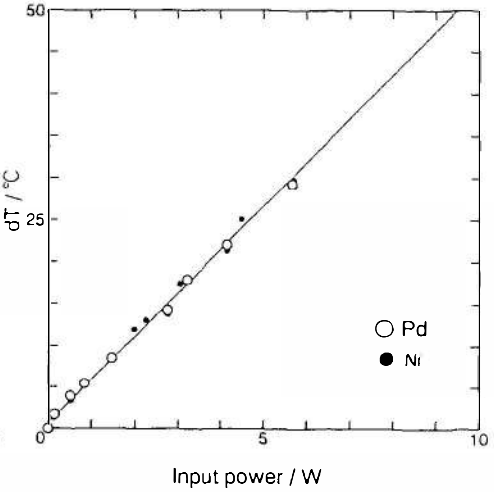

Fig.4 Comparison of the relation between temperature rise in cathode and input power observed with Ni and Pd electrodes in 1M LiOH at 10°C.

Figure-5 hows the variation of D/Pd and excess heat generation during the two months period of electrolysis. The excess heat generation started several days after the initiation of electrolysis and continued for over fifty days during which the electrolysis current density was varied between 50 and 1000 mA/cm^2 and the bath temperature was changed between 10°C and 30°C.

The relation between loading ratio and the excess heat generation derived from Fig. 5 is shown in Fig. 6. The clear dependence of the excess heat generation on D/Pd is evident in Fig. 6. We can notice also that the critical D/Pd to give rise to the excess heat generation is around 0.83. The critical D/Pd value found in the present study is lower by

0.05 than that reported by SRI[2]. The origin of the different values of the critical D/Pd for the excess heat generation is not clear at the moment.

It could be related to the different methods employed for the determination of D/Pd, i.e, electrical resistivity measurement at SRI and pressure measurement during electrolysis using a fuel cell anode.

Figure-7 shows the dependence of the loading ratio on the overvoltage at the palladium cathode. At 30 ℃ (bath temperature) we can see a steady increase of the loading ratio with overvoltage, while change of the loading ratio is much smaller at 10 °C (bath temperature) in the current density range studied. It is evident from the dependence at 10 ℃ that higher current density is necessary to achieve D/Pd closer to unity. The relation between the excess heat generation and the current density reported originally by Fleischmann and Pons [3] and later by Storms [4] for the excess heat normalized for the unit surface area could be understood in terms of the overvoltage (current density) dependence of the loading ratio as shown in Fig. 7.

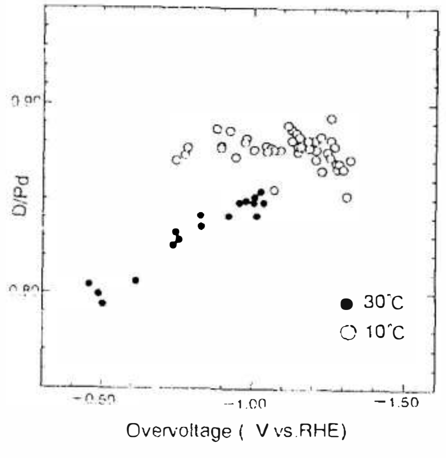

Fig.7 Dependence of deuterium loading ratio on overvoltage at 10°C and 30°C in 1M LiOD.

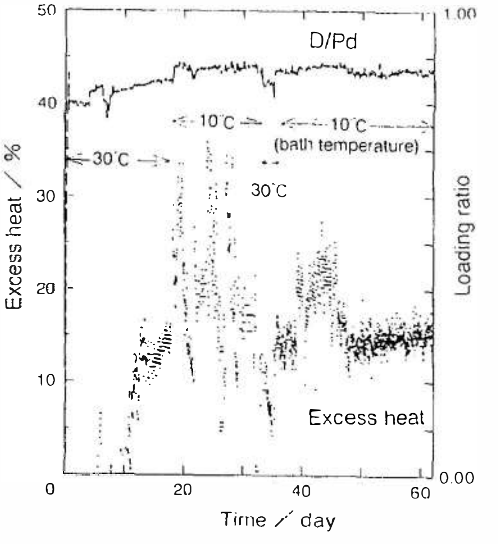

Fig.5 Change of loading ratio and excess heat generation in Pd during electrolysis in 1M LiOD.

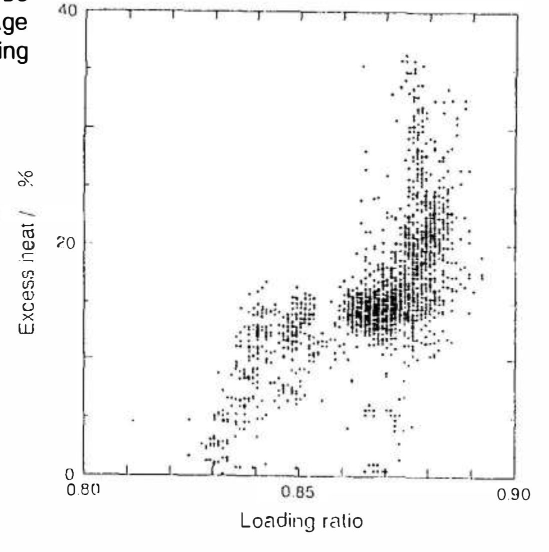

Fig.6 Dependence of excess heat generation on D/Pd in 1M LiOD.

5 Reference

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