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## **OBSERVATION OF EXCESS HEAT DURING ELECTROLYSIS OF 1M LiOD IN A FUEL CELL TYPE CLOSED CELL**

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### **Abstract**

Measurements of electrolytic deuterium loading into Pd and Pd-Rh alloy cathodes and excess heat during electrolysis in 1M LiOD have been conducted simultaneously in closed cells with a fuel cell anode pressurized by deuterium gas. The excess heat up to 4-5W/Pd cc has been reproduced by using Pd rod cathodes from various sources. Excess heat increases with electrolysis current density higher than ca. 0.1-0.2 A/cm<sup>2</sup>, cathode overvoltage and D/Pd higher than 0.80-0.84, but its dependence on D/Pd or D/M appears to be specific to each cathode material in the region of high cathode loading, where the current density or overvoltage appears to be a more important parameter to control the amount of excess heat than the cathode loading.

### **Introduction**

In our previous paper presented at ICCF3 [1,2] we reported our first data to show the excess heat generation as a function of deuterium loading ratio, D/Pd, as well as the electrolysis current density. The data showed existence of the threshold loading ratio and the current density around 0.84 and 100 mA/cm<sup>2</sup>, respectively, and suggested generation of the higher excess heat if we could extend our measurements into the region of D/Pd higher than 0.90. However, we could not realize the experimental condition to have D/Pd higher than 0.88 for the Pd cathode in 1M LiOD even at high current densities close to 1A/cm<sup>2</sup>. The aim of the present investigation is twofold: firstly to reproduce the previous data to show the dependence of the excess heat generation on D/Pd in 1M LiOD, and secondly to investigate the dependence in the region of D/Pd higher than 0.9. In order to obtain the higher D/Pd, however, we had to employ new approaches by modifying the Pd cathode surface with a surfactant, thiourea, and by employing a new cathode material, Pd-Rh alloys.

Surfactants such as thiourea are known to inhibit the Tafel step of the hydrogen evolution reaction at hydrogen electrodes, and Enyo and Maoka [3] showed that hydrogen loading ratio for a given current density at a palladium cathode increases a few percent in 1M H<sub>2</sub>SO<sub>4</sub> in the presence of 10-5M thiourea. We firstly investigated effect of thiourea on the hydrogen and deuterium loading for Pd in 1M LiOD as function of current density and conducted excess heat measurements in the presence of 0.6 mM thiourea. It should be noted that surface modification of the Pd cathode by organic surfactants such as thiourea is possible only in electrolysis cells utilizing fuel cell anodes the potential of which is not high enough to oxidize thiourea electrochemically during electrolysis, while oxygen evolving anodes can easily destroy such organic substances due to its high working potentials. This is probably one of the reasons why

inorganic substances such as aluminum, silicon and boron are employed for the purpose of surface modification of the Pd cathode in electrolysis cells utilizing oxygen evolving anodes [4].

The Pd-Rh alloys are known to have higher D/M(Pd+Rh) under high hydrogen pressures than palladium, where M represents the total number of Pd and Rh atoms in the alloy. D/M = 1.01 was reported for the alloy with 30 atomic % rhodium [5]. The crystal structure of the Pd-Rh alloys is the same as Pd, fcc, and its lattice constant is smaller than Pd and decreases with increasing Rh content. It is expected, therefore, to have much higher deuterium density in the Pd-Rh alloys than Pd because of the higher D/Pd ratio combined with the smaller lattice constants. The Pd-Rh alloys look very attractive as cathodes for excess heat generation for which the higher deuterium density in the cathode lattice is believed to play an important role.

## **Experimental**

The excess heat measurements were carried out in 1M LiOD in closed cells with fuel cell anodes, the details of which were described elsewhere. The deuterium loading ratio, D/M, were measured simultaneously during the measurements to find its role in the excess heat generation. The determination of D/M is conducted by measuring pressure of hydrogen or deuterium gas in the cell, the decrease of which from its initial value is related to D/M by the following equation:

$$D/M = -2V(P_0/T_0 - P/T)/n_M R$$

where V is the internal gas phase volume of the cell,  $n_M$  the total mols of metal atoms in the cathode, R the gas constant, P and T pressure of deuterium gas in the cell and temperature in the gas phase,  $P_0$  and  $T_0$  are their initial values before electrolysis. The D/Pd values have been corrected for the following effects: temperature dependence of the vapor pressure of heavy water, temperature and pressure dependence of solubility of deuterium gas in water as well as PTFE used in the cell. The corrections due to these effects are usually small, i.e., at most a few percent. After ICCF4 we found a small error in the determination of the internal volume, which is typically ca. 200 cc. The correct value has turned out to be ca. 7 cc smaller and this has reduced the D/M value by a few percent according to the above equation.

The reproduction of our previous excess heat measurements have been done firstly in cells with the same structure using the Pd cathodes made from the same batch of Pd rods as before. Secondly Pd rods from different sources were compared in cells with a new structure which is shown schematically in Fig. 1. The inner wall of the cell body containing electrolyte, 1M LiOD, is coated by a ceramic film, while a thick PTFE cap was encased in the cell body in the previous cell design. It was realized later, however, that slow hydrogen/deuterium absorption into a thick PTFE caused serious problems in the accurate determination of D/Pd, and the cells shown in Fig. 1 have been employed in most of the current experiments. The cell was totally submerged in the water bath regulated at 10°C during the measurements. But the loading experiments was conducted without the outer vessel 2 of the cell shown in Fig. 1 to keep the electrolyte temperature at 10°C even at high current densities, at which, however, the electrolyte temperature did go up to ca. 20°C and the cathode loading was reduced by the temperature rise as shown later.

The excess heat measurements were conducted by measuring temperature in the cathodes, Ni and Pd or Pd-Rh alloys, for which Ni served as a reference to make a calibration curve in 1M LiOD. The measurements have been done on Pd and Pd-Rh alloys rods of 4 mm diameter and 20-25 mm long from various sources such as IMRA Materials, Johnson Matthey and Tanaka

Kikinzoku. The Pd and Pd-Rh alloy electrodes were degassed in vacuum at 200°C for three hours before the experiments. Other experimental details have been described elsewhere [1,2].

Hydrogen or deuterium overvoltage at the cathode was determined by measuring the potential difference between the cathode and the RHE or RDE, reversible hydrogen or deuterium electrode in the same solution placed close to the cathode as shown in Fig. 1. The overvoltage has been corrected for the IR drop between the cathode and the reference electrode which has been determined by the galvanostatic pulse method.

## **RESULTS AND DISCUSSION**

### **1. Reproduction of the previous excess heat measurements**

The excess heat data presented at ICCF3 was accompanied by two more data sets taken in different cells but using the Pd cathodes made from the same batch of Pd rods supplied by IMRA Materials during the same period.

The cell structure used for the measurements was the one with a thick pTFE cup encased, the details of which has been described before [1,2]. Figure 2 shows all the excess heat data obtained in the three cells plotted as a function of D/Pd. The data are rather scattered probably due to the experimental errors in the determination of D/Pd in a cell of this type as described before. When plotted as a function of current density, however, the data becomes much less scattered as shown in Fig. 3. The current density between 100mA/cm<sup>2</sup> and 200 mA/cm<sup>2</sup> seems to be the threshold for excess heat generation. We plotted the excess heat data as a function of another experimental parameter, i.e., cathode overvoltage, in Fig. 4, which shows almost linear increase of excess heat with overvoltage but with a different slope for each cell. The data presented in Figs. 2 and 3 show good reproducibility of our previous results as long as we follow the same procedure for the excess heat measurements.

### **2. Excess heat measurements with Pd cathodes from various sources**

#### ***2.1 Blank experiments in 1M LiOH***

The calorimetry was conducted in a new cell shown in Fig. 1 firstly for the light water system, Ni, Pd/1 M LiOH, to test its performance in the blank experiments. Figure 5 shows the relation between the input power and the temperature rise in the cathode observed with Ni and Pd respectively. Difference in the temperature rise between the two cathodes is very small in the input range examined which is up to 1 A/cm<sup>2</sup> in terms of the electrolysis current density. From the difference between Ni and Pd shown in Fig. 5 we calculated “excess heat” on the Pd cathode as a function of input power as well as current density as shown in Figs. 6A and 6B. These data show that the error in the excess heat measurement is ca. +0.5 W and no excess heat is observed on Pd in light water within the experimental error.

#### ***2.2 Excess heat measurements in 1M LiOD with Pd cathodes***

We have conducted excess heat measurements using Pd cathodes from various sources. Figure 7 shows a typical example of the temperature rise in a Pd cathode compared with Ni as a function of input power. The difference between the Ni and Pd cathodes is analyzed as indicative of excess heat generation, which increases at the higher input power. The data obtained for various Pd cathodes are plotted as a function of D/Pd and current density in Figs. 8 and 9,

respectively. The Pd rods supplied by IMRA Materials (I/M) have two kinds of lot numbers, 9112 and 9209, and one of the three excess heat data sets for Pd (I/M 9112) in 1M LiOD is the one which was reported at ICCF3. The Pd (TNK type-C) rod is a cold-worked material manufactured at Tanaka Kikinzoku by drawing under liquid nitrogen temperature and has a high Vicker's hardness value of ca. 140 while the other Pd materials have the value between 90 and 110.

The data shown in Fig. 8 shows evolution of excess heat between  $D/Pd=0.8$  and  $0.84$  but dependence of excess heat on  $D/Pd$  is rather scattered and sharp to know its functional form in this region. It is important therefore to extend the excess heat measurements into the higher  $D/Pd$  region to characterize its significance in excess heat generation. Systematic dependence of the excess heat on current density is seen in Fig. 8 which shows steady increase of excess heat at the higher current densities than  $0.1-0.2 \text{ A/cm}^2$ . The results presented in Figs. 8 and 9 show that the previous data presented at ICCF3 by our group is essentially reproduced by using Pd materials manufactured and processed in different ways at various sources.

It is important to point out that the Pd (TNK) gave the maximum  $D/Pd$  of  $0.78$  in these particular experiments, which is much lower than obtained commonly in loading as well as excess heat measurements. In this experiments no excess heat was observed within the experimental error up to  $0.8 \text{ A/cm}^2$  which is much higher than the critical current density between  $0.1$  and  $0.2 \text{ A/cm}^2$  for Pd. This is a good example showing the importance of achieving the critical loading between  $0.8$  and  $0.84$  for the excess heat generation.

We have replotted the data in Fig. 8 with respect to cathode overvoltage in Fig. 10 in an attempt to find the dependence of excess heat on another important experimentally observable parameter. The dependence of excess heat on the cathode overvoltage presented in Fig. 10 looks almost linear and much more systematic than the dependence on  $D/Pd$  and current density. It should be noted that the cathode overvoltage observed on one of the Pd (I/M 9112) is much higher than the others, and this is the reason why the dependence of the excess heat on overvoltage is extended up to  $-1.5 \text{ V}$  for this Pd cathode. The higher cathode overvoltage on this particular Pd electrode is seen more directly in the plot of overvoltage vs  $\log i(\text{A/cm}^2)$  compared to all the other electrodes as shown in Fig. 11. We do not know, however, why this particular Pd gave much higher cathode overvoltage than others.

### ***2.3 Excess heat measurements on modified Pd cathodes by chemisorbed thiourea, $(\text{NH}_2)_2\text{C}=\text{S}$***

We have shown that surface modification of Pd cathodes by chemisorbed thiourea, although we do not know its surface coverage under hydrogen evolution condition, leads to improved cathode loading by hydrogen as well as by deuterium and gives rise to the maximum  $H/Pd$  and  $D/Pd$  of  $1.0$  and  $0.91$  at  $10^\circ\text{C}$  respectively [6,7]. We conducted excess heat measurements in 1M LiOD containing  $0.6 \text{ mM}$  thiourea in an attempt to see effect of surface modification by chemisorbed molecules.

Figures 12A and 12B show results plotted as a function of  $D/Pd$  and current density respectively, which did not give as much excess heat as observed without thiourea despite the fact that  $D/Pd$  up to  $0.88$  was achieved and the current density was extended up to  $0.5 \text{ A/cm}^2$ . The maximum  $D/Pd$  value lower than obtained before in the loading experiments is due to rise in electrolyte temperature which is inevitable in the excess heat measurements while temperature

was kept below 20°C in the loading experiments to minimize the temperature effect on D/Pd [7]. Comparison between the poor performance presented in Fig. 12 and the results without thiourea shown in Fig. 8 may imply that surface modification or blocking the surface atomic sites by chemisorbed molecules is not good for the excess heat generation. This may lead to further discussion on the nature of the excess heat generating process, i.e., if it is a surface or bulk process, but we would certainly need more information on the nature of the adsorbed species which modify the surface atomic layer of the Pd cathode to go into such a discussion.

## ***2.4 D/M and Excess heat on Pd-Rh alloys in 1M LiOD***

Measurements of D/M and excess heat have been conducted with Pd-Rh(5, 10 atm%) cathodes in 1M LiOD in an attempt to investigate their relation in the higher D/M region than realized for Pd cathodes. The D/M on these alloy cathodes are shown in Fig. 13 as a function of current density [8]. In these measurements temperature of the electrolyte was kept 10°C except at high current densities at which electrolyte temperature went up to ca. 20°C due to the high input power. The D/M on these alloys are 5-15% higher than Pd for a given current density, the maximum values being 0.91 and 0.97 for 5 atm% and 10 atm% Rh-Pd alloy respectively. The tendency to show decrease of D/M at higher current densities commonly observed for Pd and Pd-Rh alloys is due to the electrolyte temperature rise mentioned above.

Dependence of excess heat on D/M on these alloy cathodes were observed in different experiments and the results are shown in Fig. 14. It is rather unexpected to see much smaller excess heat than Pd cathodes and decrease of excess heat with increasing D/Pd on the Pd-Rh alloys. However, when plotted with respect to current density as shown in Fig. 15, we see a systematic increase of excess heat with increasing current density, although the critical current density for the excess heat generation appears to be higher than Pd and lies between 0.2 and 0.4 A/cm<sup>2</sup>. In Fig. 15 we plotted also the D/M observed during the excess heat measurements as a function of current density. The D/M decreases with increasing current density due to the electrolyte temperature rise, which is shown in Fig. 16, and this is the reason why the excess heat looks as if it decreases with increasing D/M. We interpret the data in Fig. 14 in the way that the excess heat is decreasing not because D/M increases but because the current density is a more important factor controlling the excess heat generation in this high D/M region.

We plan to conduct D/M and excess heat measurements for 20 and 30 atm% Rh-Pd alloys in order to extend our investigation up to the full loading, D/M=1.0, which is likely to be achieved on these alloys with higher rhodium content.

## **3. Factors controlling excess heat**

The dependence of excess heat on Pd and Pd-Rh alloys upon D/M, current density and cathode overvoltage reported in the present study strongly suggest that there is a critical cathode loading by deuterium which lies between 0.8 and 0.84 and critical current density between 0.1 and 0.2 Ncm<sup>-2</sup> on Pd cathodes. The role of the critical current density is clearly to load the cathode by deuterium to the critical value and maintain it. Once having reached the critical cathode loading, however, it seems as if the excess heat depends more systematically on current density and cathode overvoltage than D/M as demonstrated clearly by the data on the Pd-Rh alloys. Unfortunately, however, current density and overvoltage are not independent from each other and it is difficult to discuss the role of these two parameters separately on Pd and Pd-Rh alloy cathodes. However, comparison of the cathode overvoltage for a given current density and

dependence of excess heat on current density between Pd and Pd-Rh alloy cathodes as shown in Figs. 17 and 18 respectively indicates that the cathode overvoltage of the Pd-Rh alloys is always higher while the excess heat on the alloys is more or less comparable or smaller than Pd for a given current density. This implies that the higher overvoltage on the Pd-Rh alloy cathodes is not in fact contributing effectively to the excess heat generation.

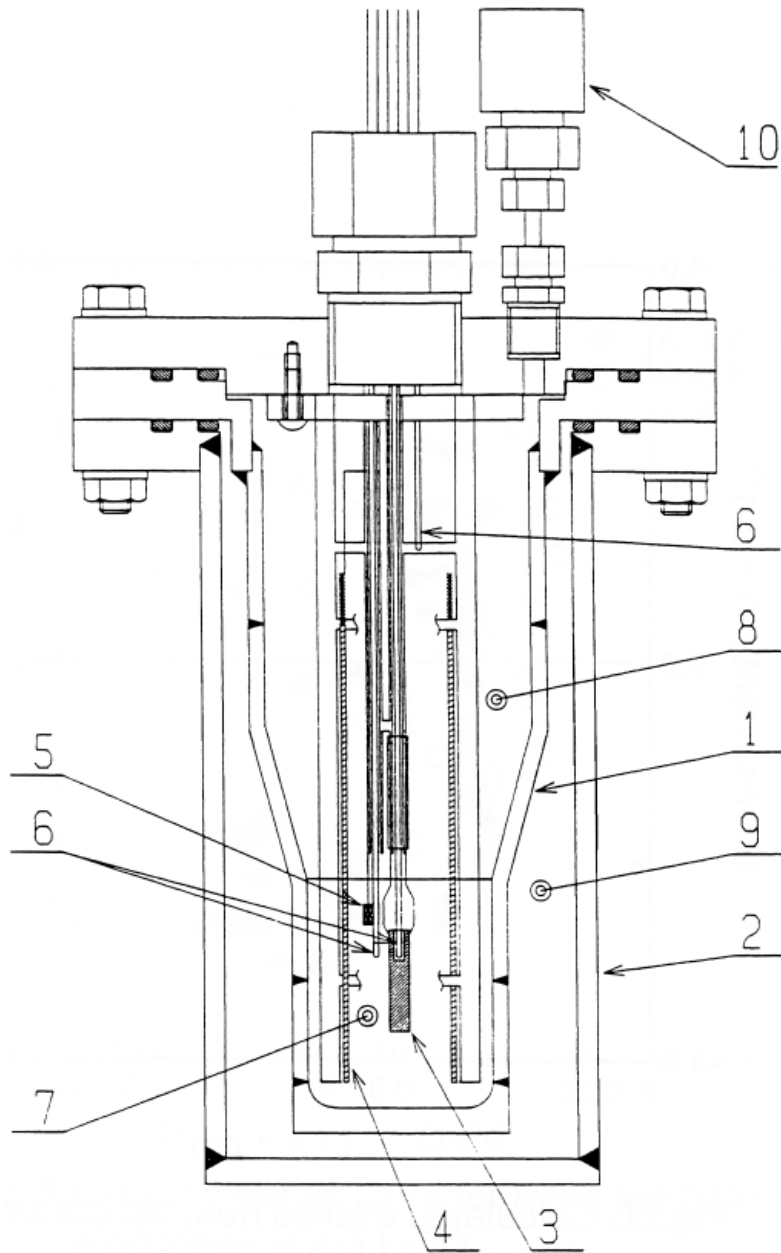
The comparison between Pd and Pd-Rh alloys can be summarized as follows: the excess heat on the Pd-Rh alloy cathodes for a given current density is comparable or smaller while D/M and cathode overvoltage is higher than Pd cathodes. This suggests that current density is the most important parameter controlling excess heat generation among the three experimental parameters above a critical cathode loading. It would be important to conduct excess heat measurements for other cathode materials and for Pd cathodes with modified surface and in other electrolytes, which would make it possible to investigate the significance of D/Pd, current density and cathode overvoltage in the excess heat generation in more comprehensive ways.

There are some more experimental parameters considered significant in excess heat generation, such as length of time to hold the D/Pd higher than the critical value often mentioned by the group at SRI [4]; temperature, as suggested by Fleischmann and Pons in their excess heat measurements at electrolyte boiling [9]; the third element present in the electrolyte and possibly incorporated into or onto the Pd cathode such as B<sup>+</sup> and Li<sup>+</sup>; and micro crystal structure of the Pd cathode lattice which could affect the achievable electrolytic cathode loading by hydrogen and deuterium. However, we have not been able to investigate the effect of these parameters in a systematic way so far, but we hope to conduct such investigations in the near future.

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## Figures



1. Pressure Vessel (SUS316), 2. Vessel (SUS316), 3. Pd Cathode, 4. Fuel Cell Anode

5. RHE (Pt/Pt), 6. Thermocouple, 7. 1 M LiOD, 8. D<sub>2</sub> (5-10Kg/Cm<sup>2</sup>), 9. Air, 10. Pressure Sensor

Fig. 1. Closed Electrolysis Cell with Fuel Cell Anode for D/Pd and Excess Heat Measurement.

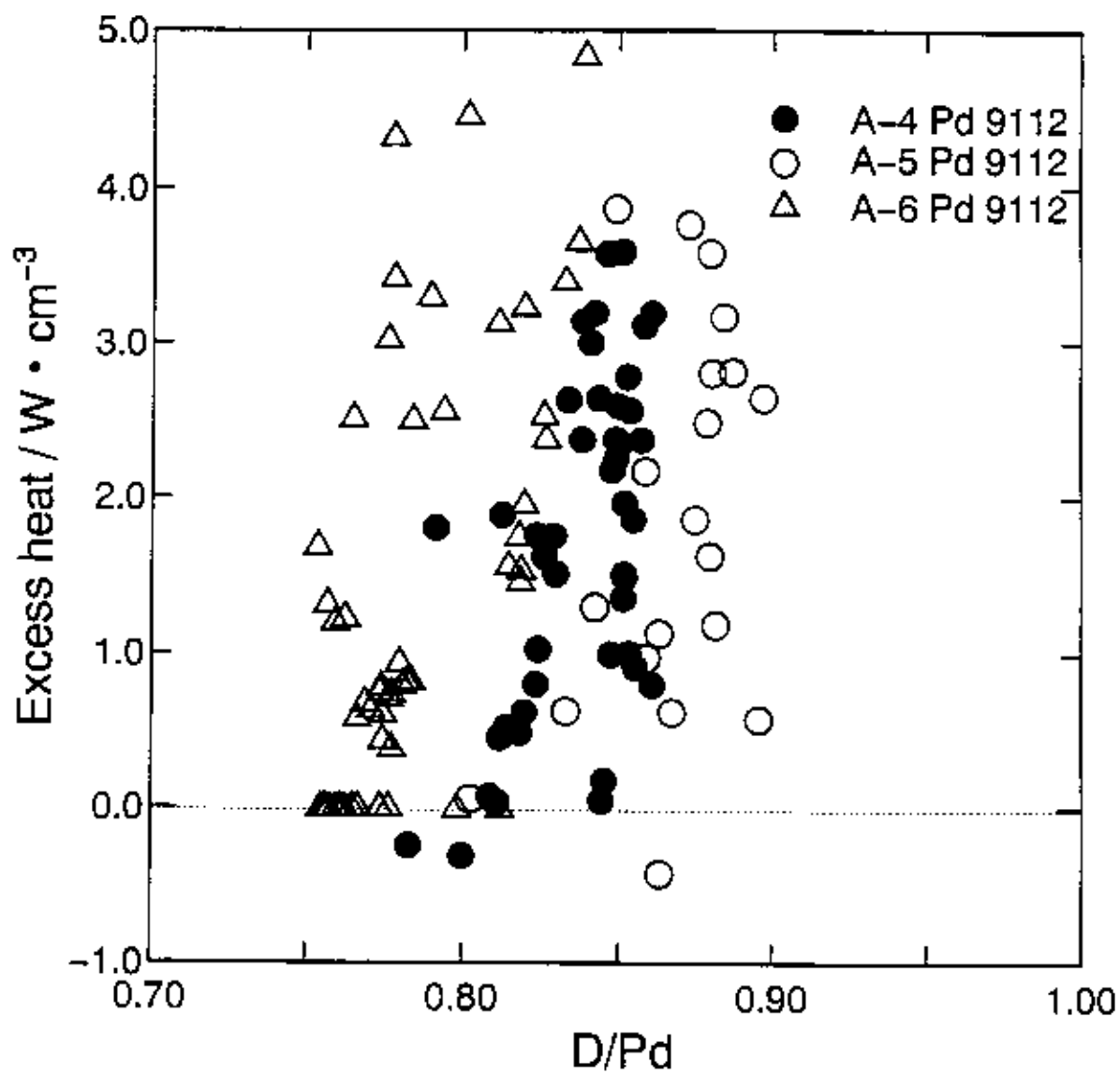


Fig. 2 Excess heat vs  $D/Pd$  for three Pd (I/M 9112) rod electrodes in 1M LiOD.



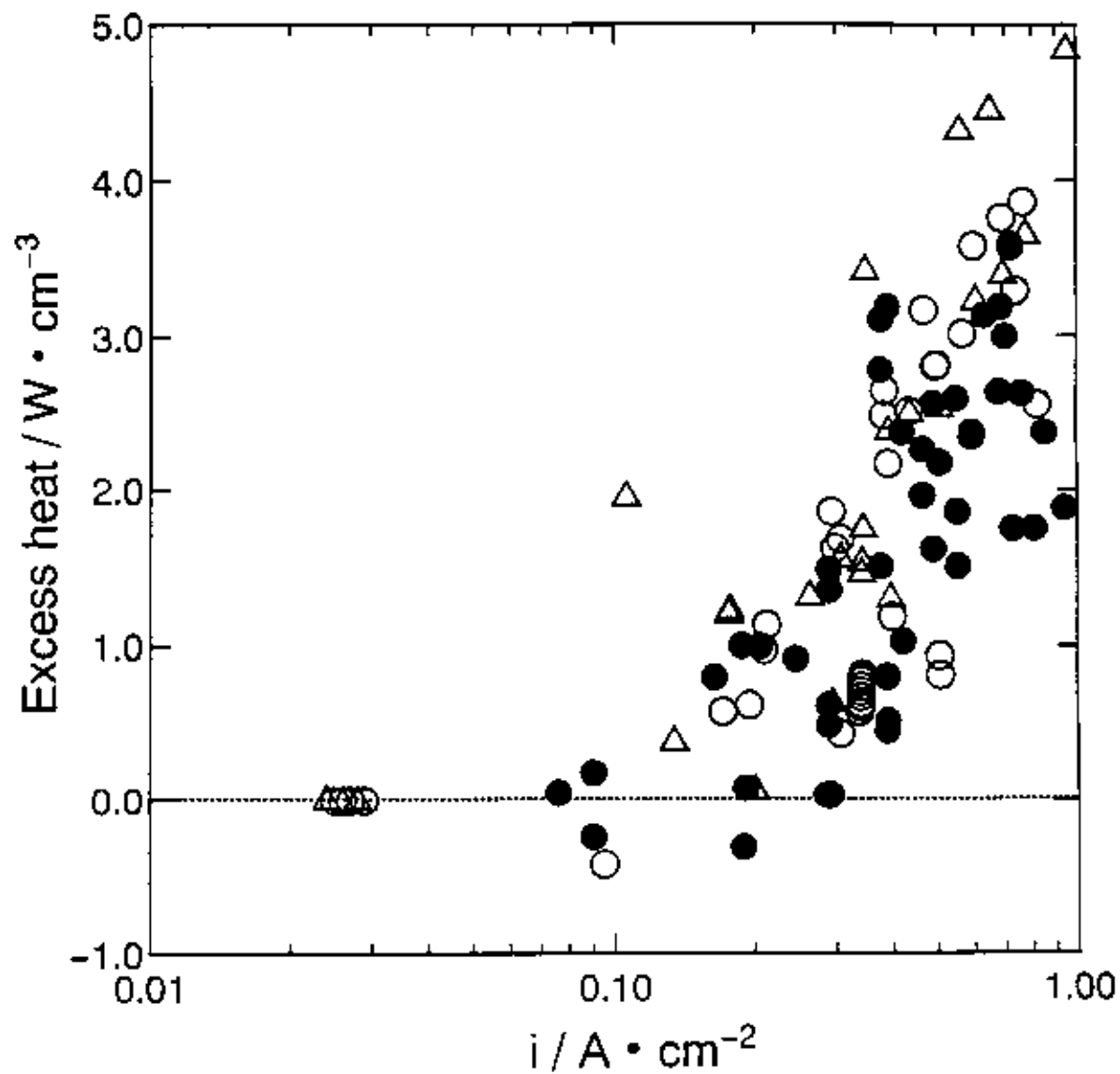


Fig. 3 Excess heat vs current density for three Pd (I/M 9112) rod electrodes in 1 M LiOD.

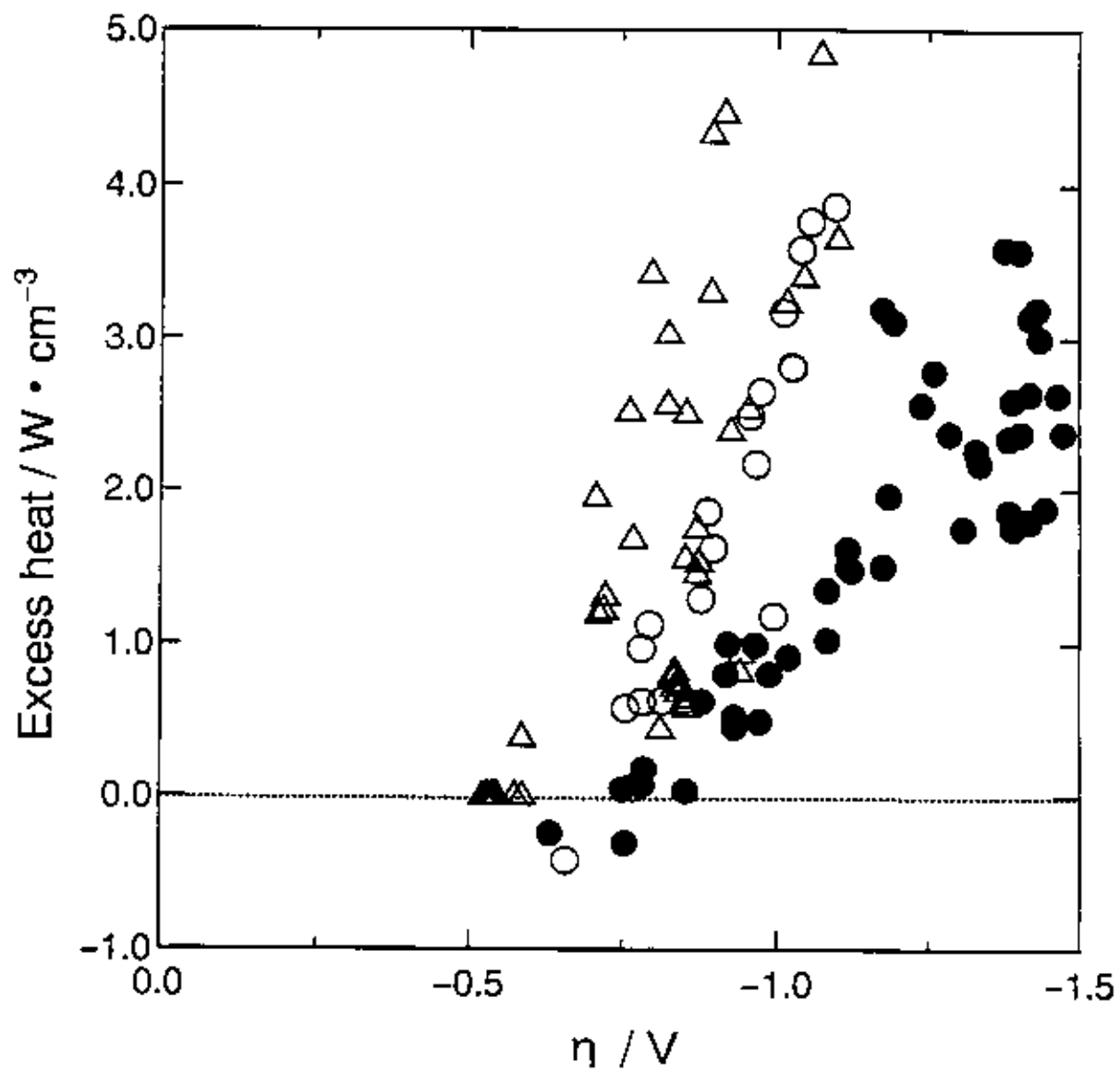


Fig. 4 Excess heat vs cathode overvoltage for three Pd (I/M 9112) rod electrodes in 1 M LiOD.

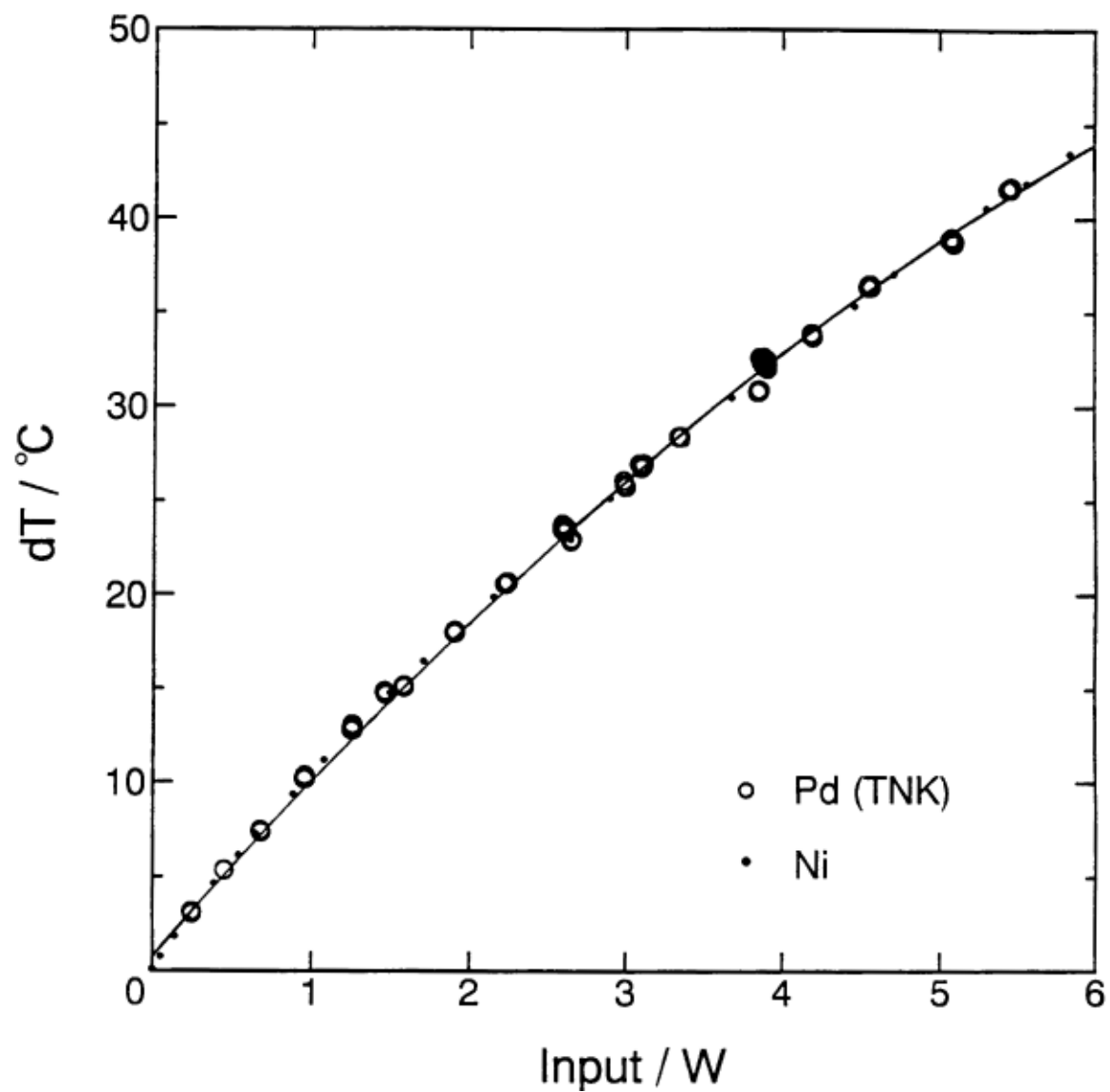


Fig. 5. Change of electrode temperature with input power for Pd and Ni cathodes in 1 M LiOH.

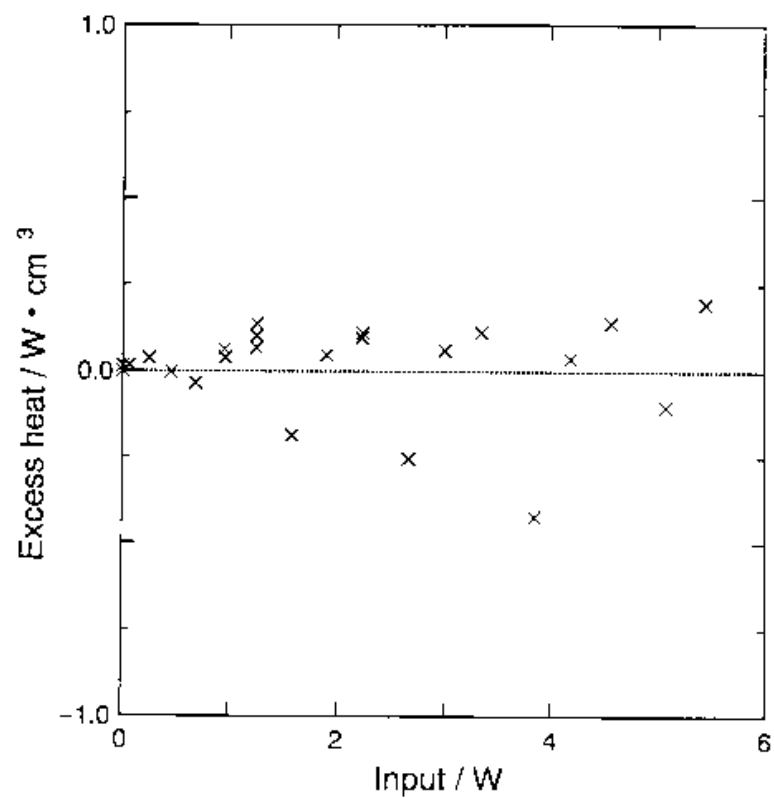


Fig. 6A. Calculated excess heat vs input for Pd in 1M LiOH.

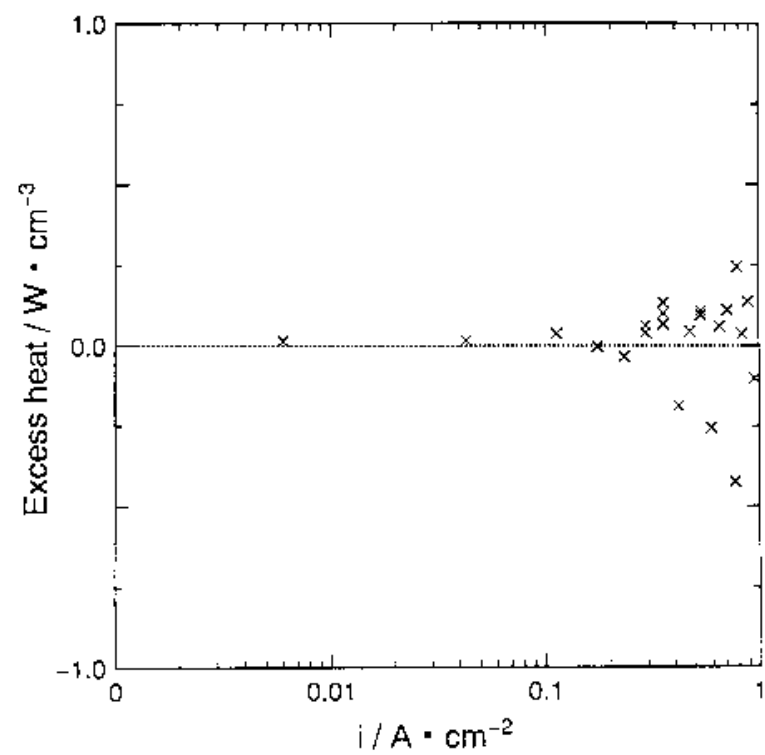


Fig. 6B. Calculated excess heat vs. current density for Pd in 1M LiOH.

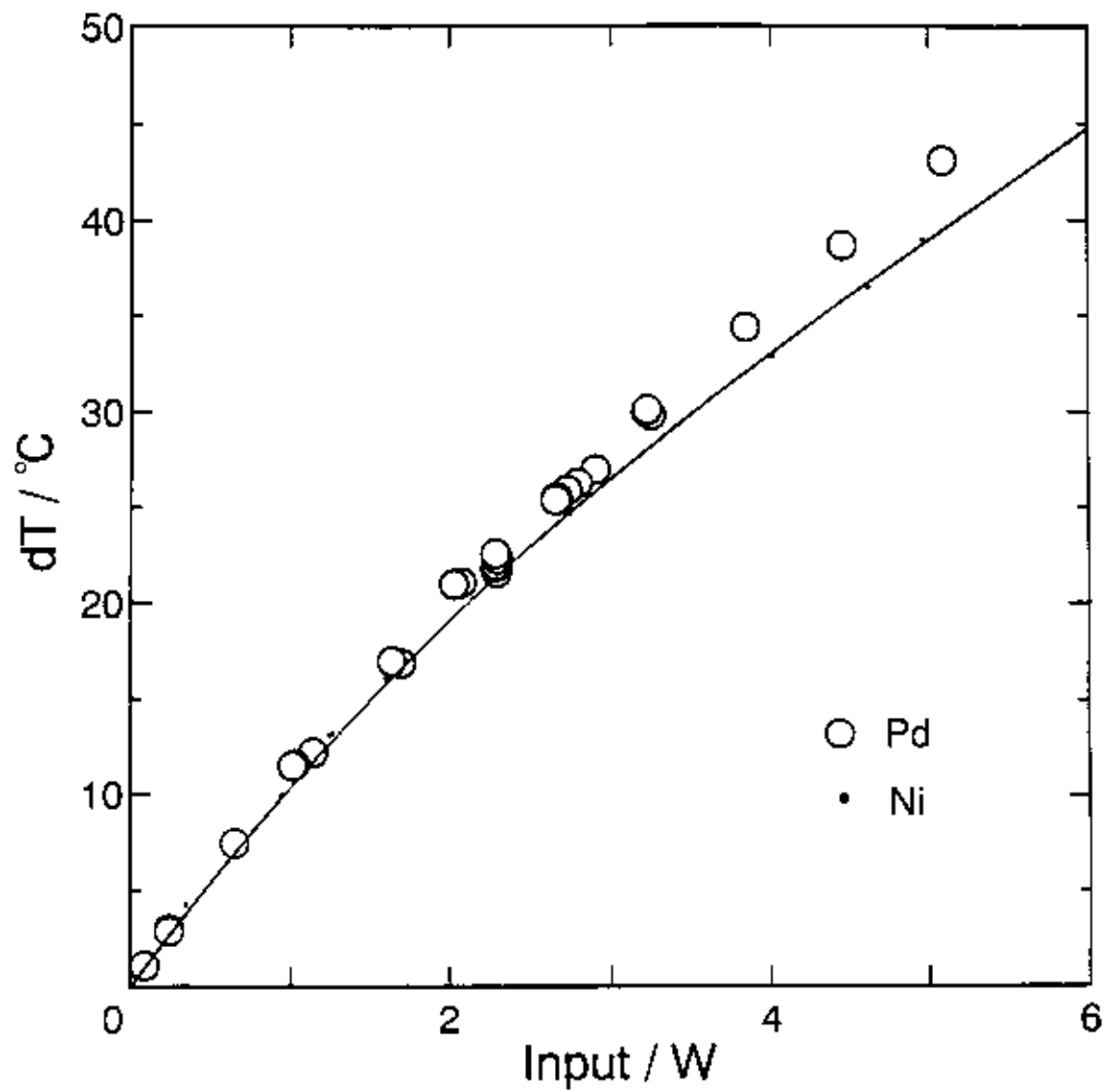


Fig. 7. Cathode temperature change vs input power for Pd (I/M 9209) in 1M LiOD.

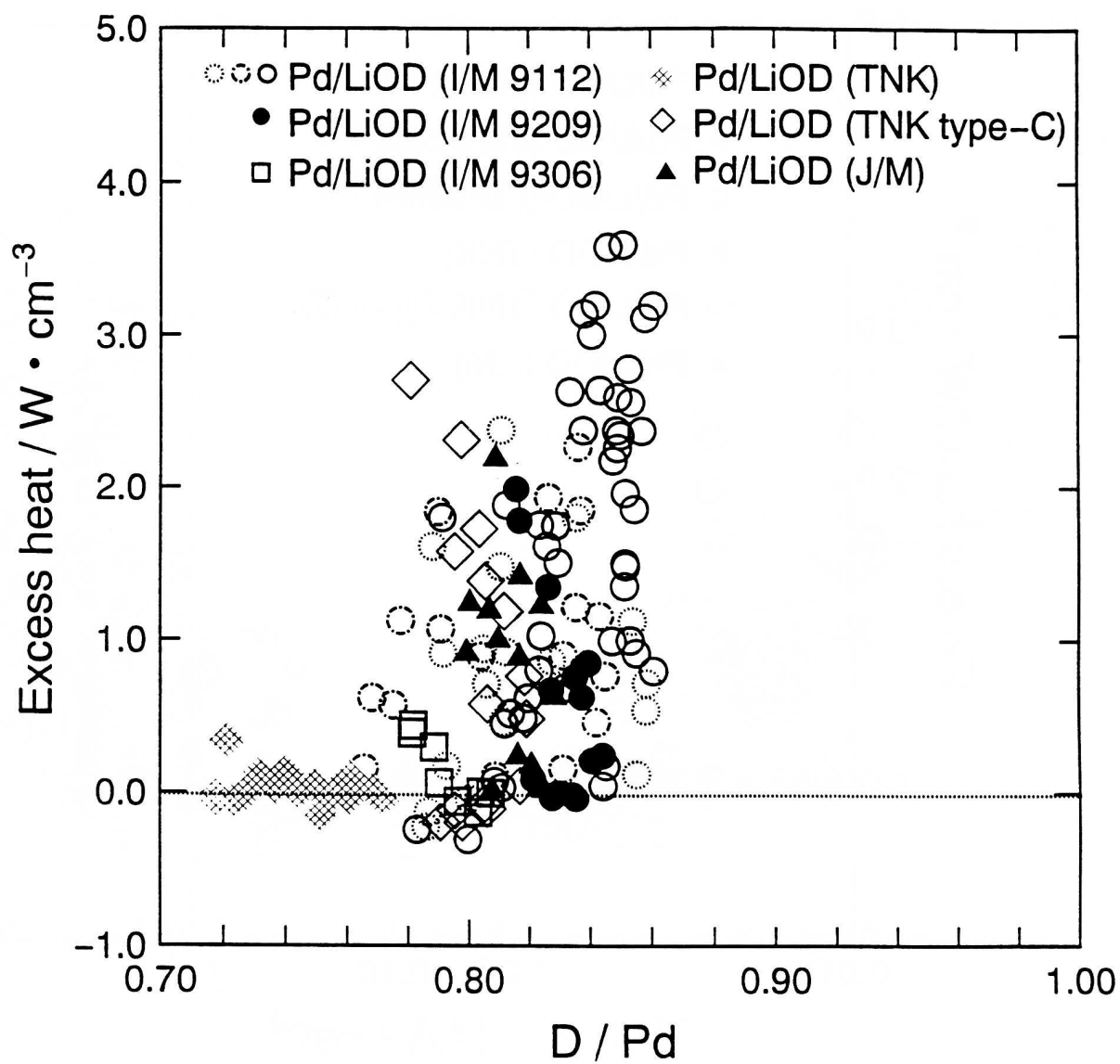


Fig. 8. Excess heat vs cathode loading for Pd cathodes in 1M LiOD.

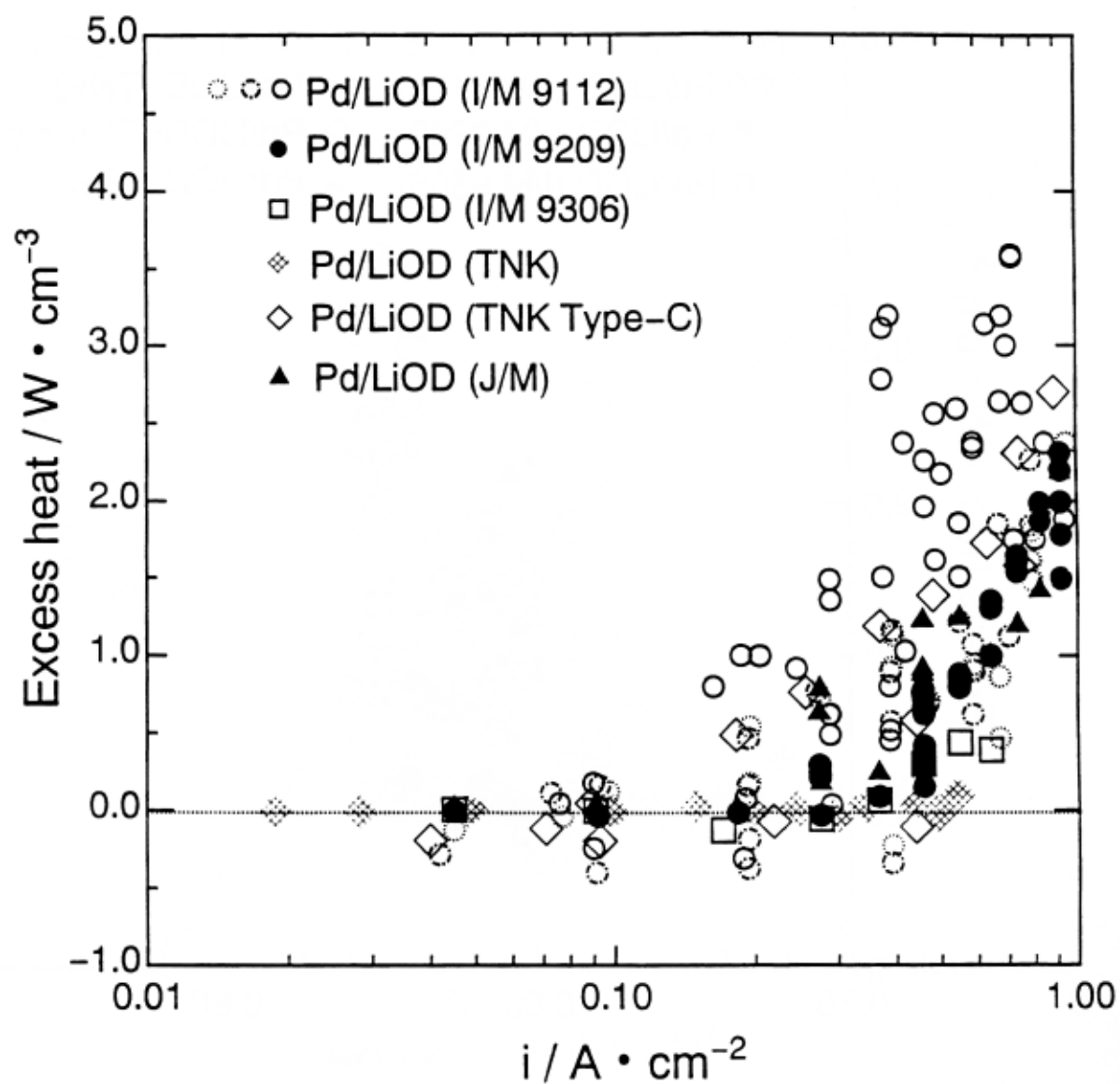


Fig. 9. Excess heat vs current density for various Pd cathodes in 1M LiOD.

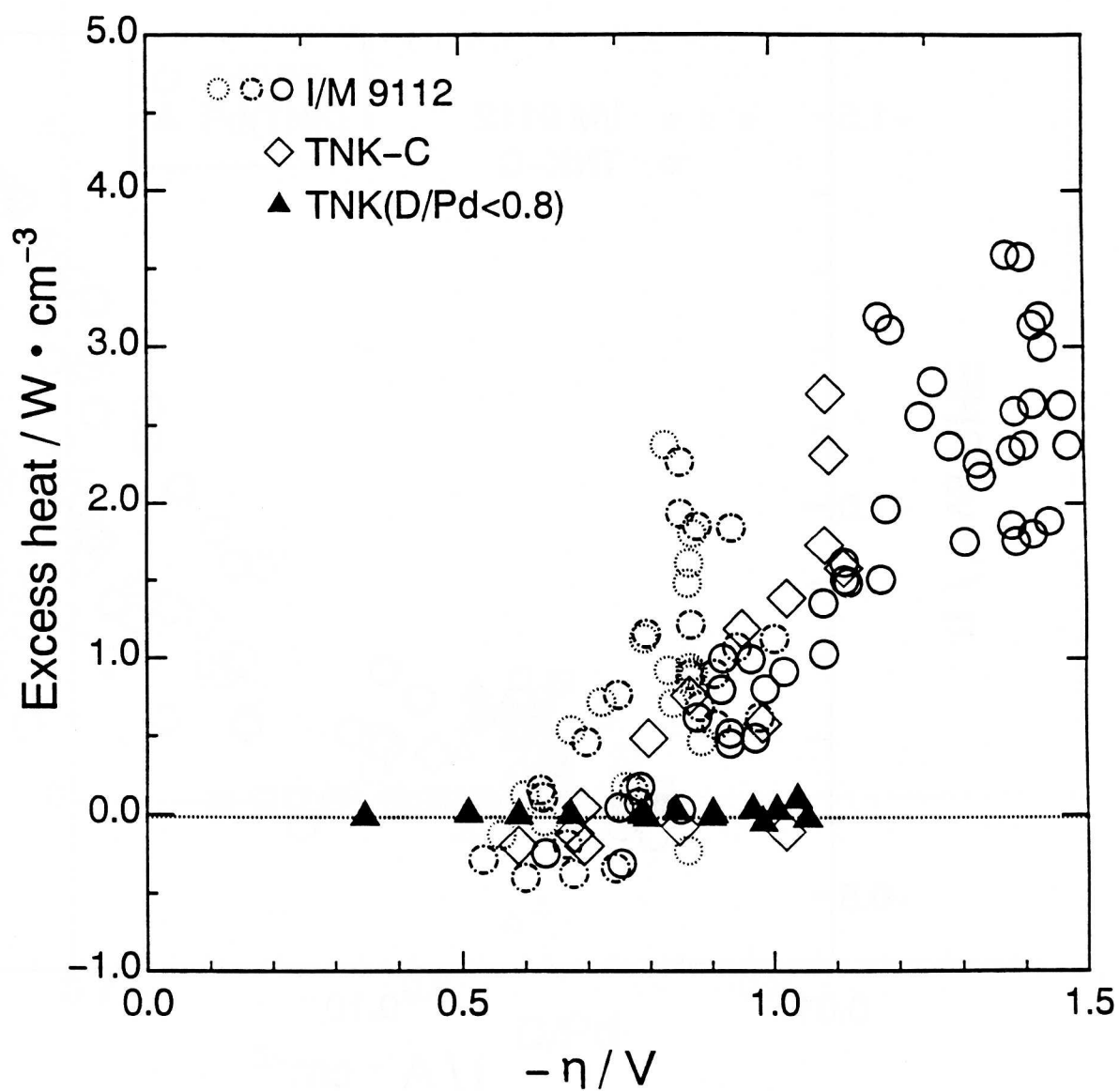


Fig. 10. Excess heat vs overvoltage for various Pd cathodes in 1M LiOD.



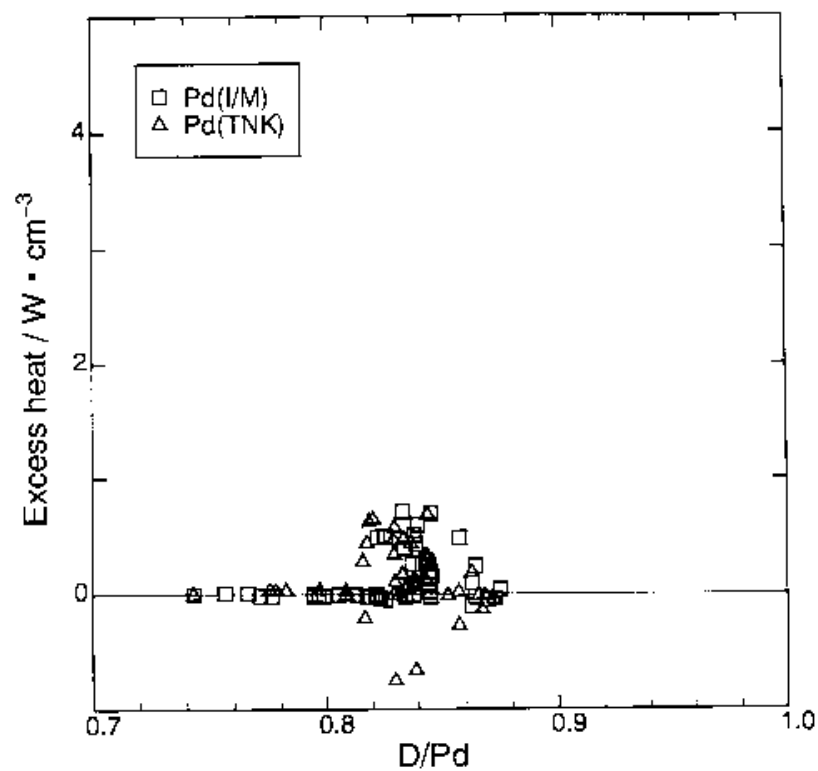


Fig. 12A. Excess heat vs.  $D/Pd$  for diam. 4Pd in 1M LiOD+0.6 mM thiourea.

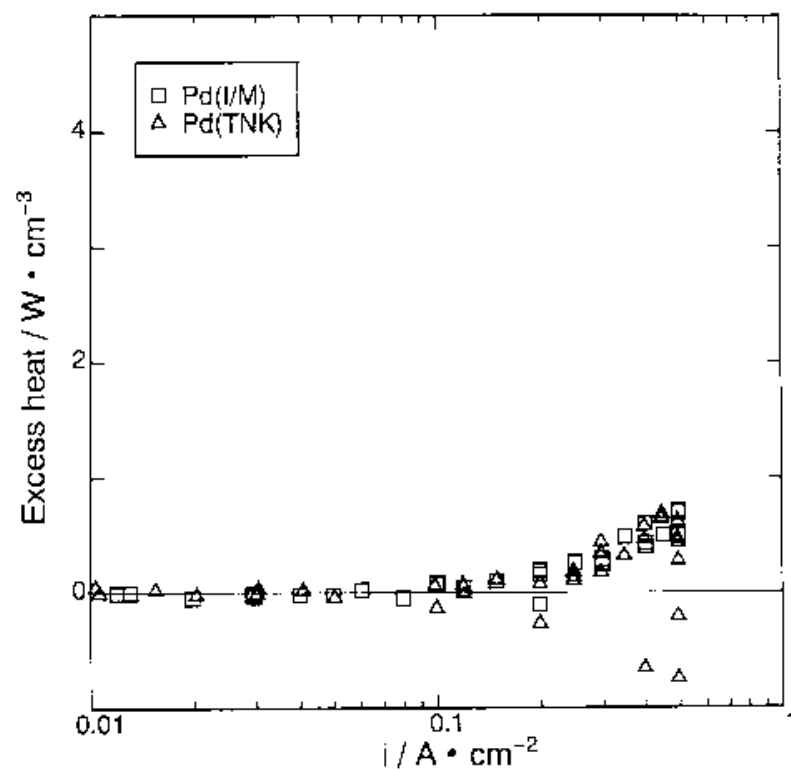


Fig. 12B. Excess heat vs. current density for diam. 4Pd in 1M LiOD+0.6 mM thiourea.

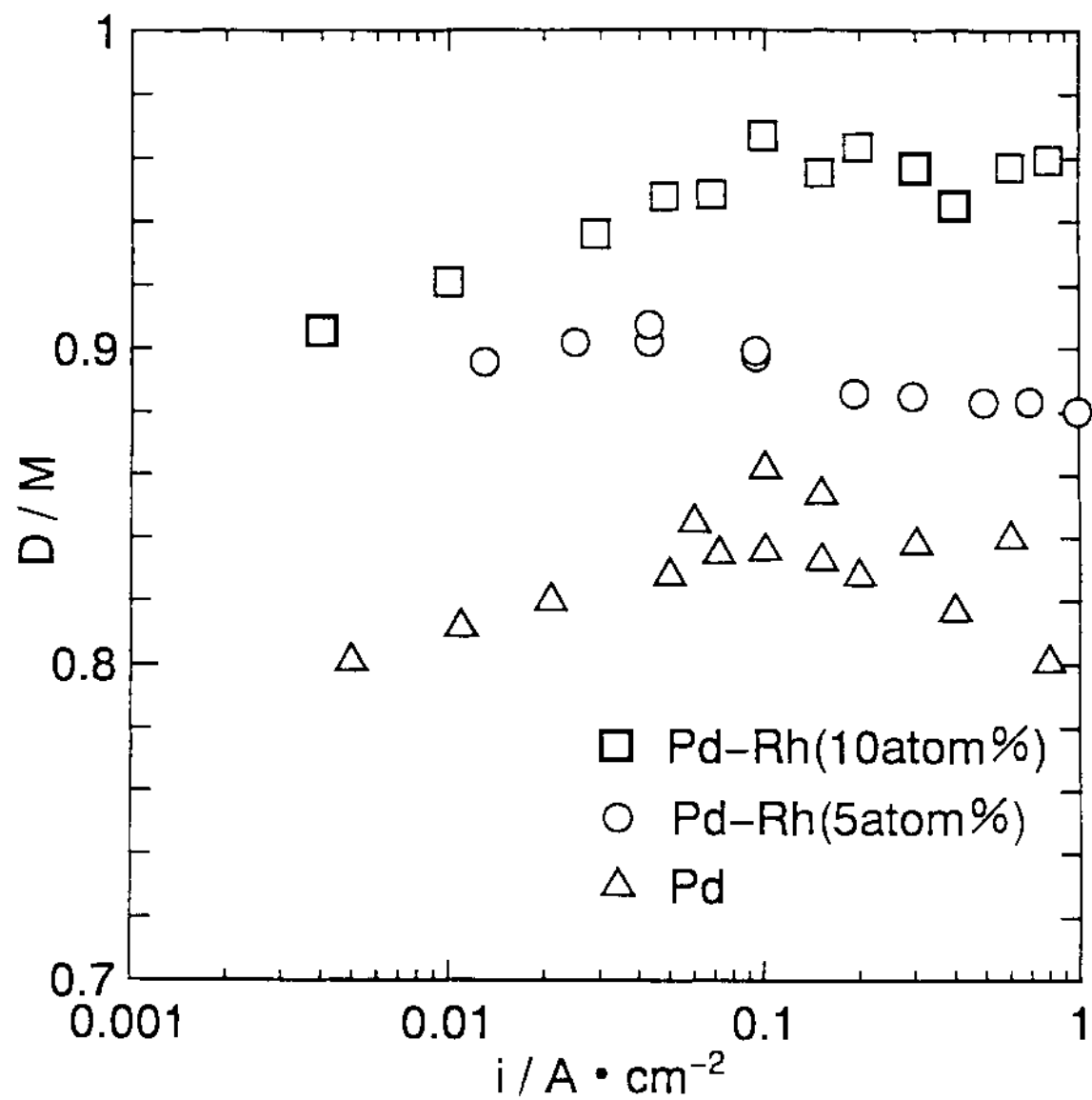


Fig. 13. Dependence of  $D/M$  on current density for Pd and Pd-Rh alloy cathodes in 1 M LiOD at 10°C.

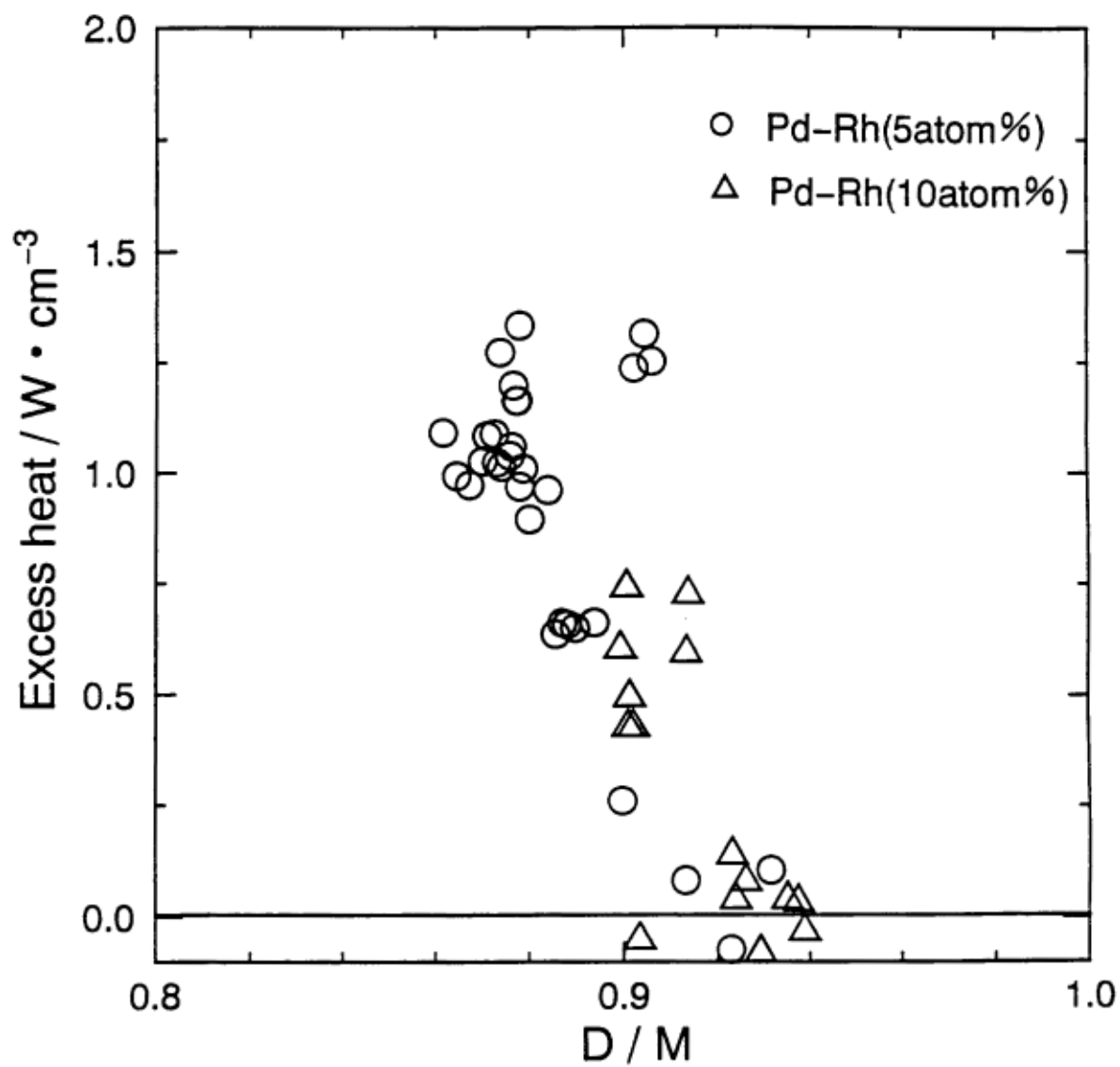


Fig. 14. Excess heat vs.  $D/M$  on Pd-Rh(5 atom%) and Pd-Rh (10 atom%) cathodes in 1 M LiOD.

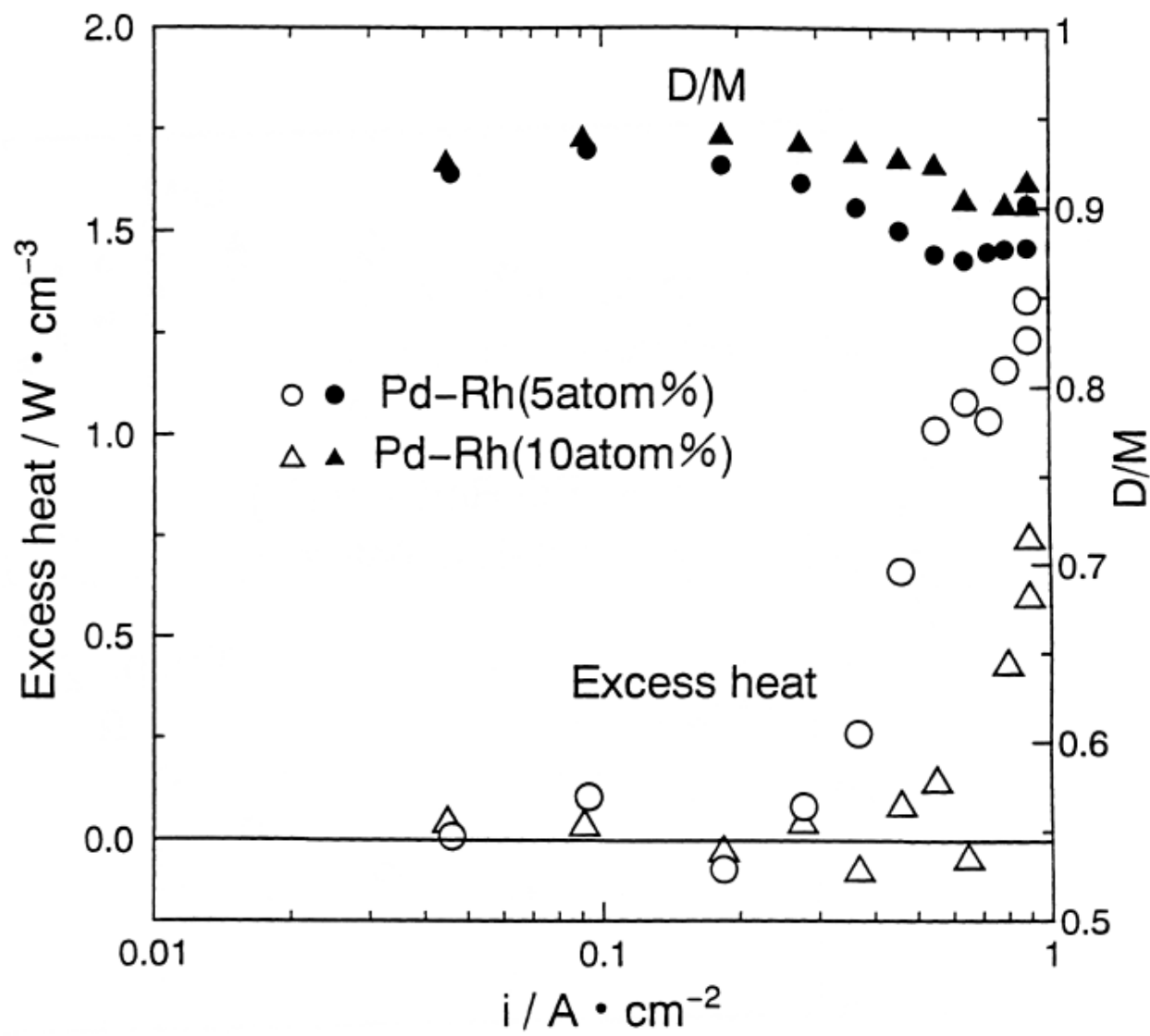


Fig. 15. Excess heat and D/M vs current density on Pd-Rh (5 atom%) in 1M LiOD.

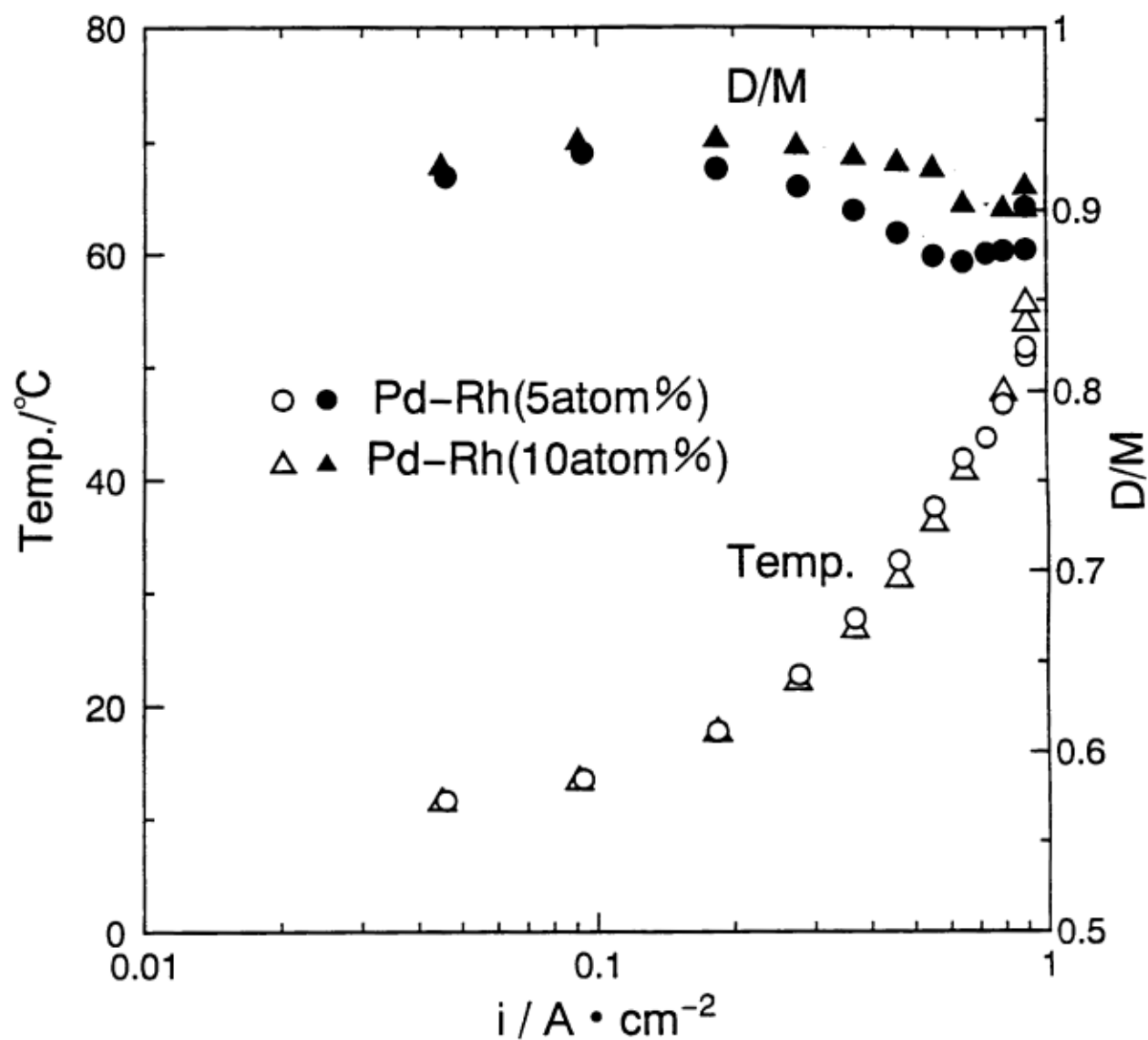


Fig. 16. D/M and electrolyte temperature vs current density during excess heat measurement on Pd-Rh (5 atom%) and Pd-Rh (10 atom%) in 1M LiOD.

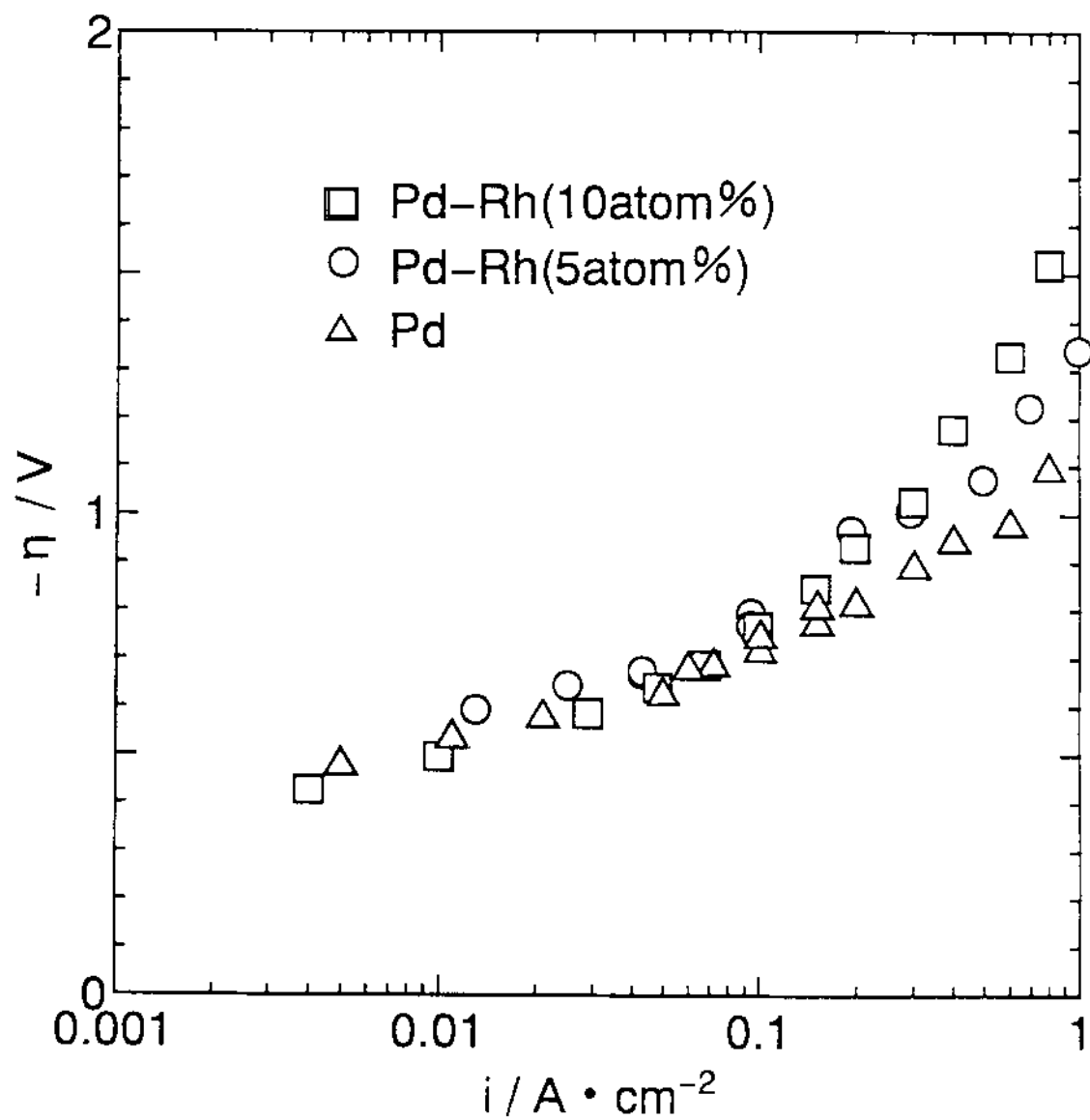


Fig. 17. Cathode overvoltage vs current density for Pd and Pd-Rh alloy cathodes in 1 M LiOD at 10°C.

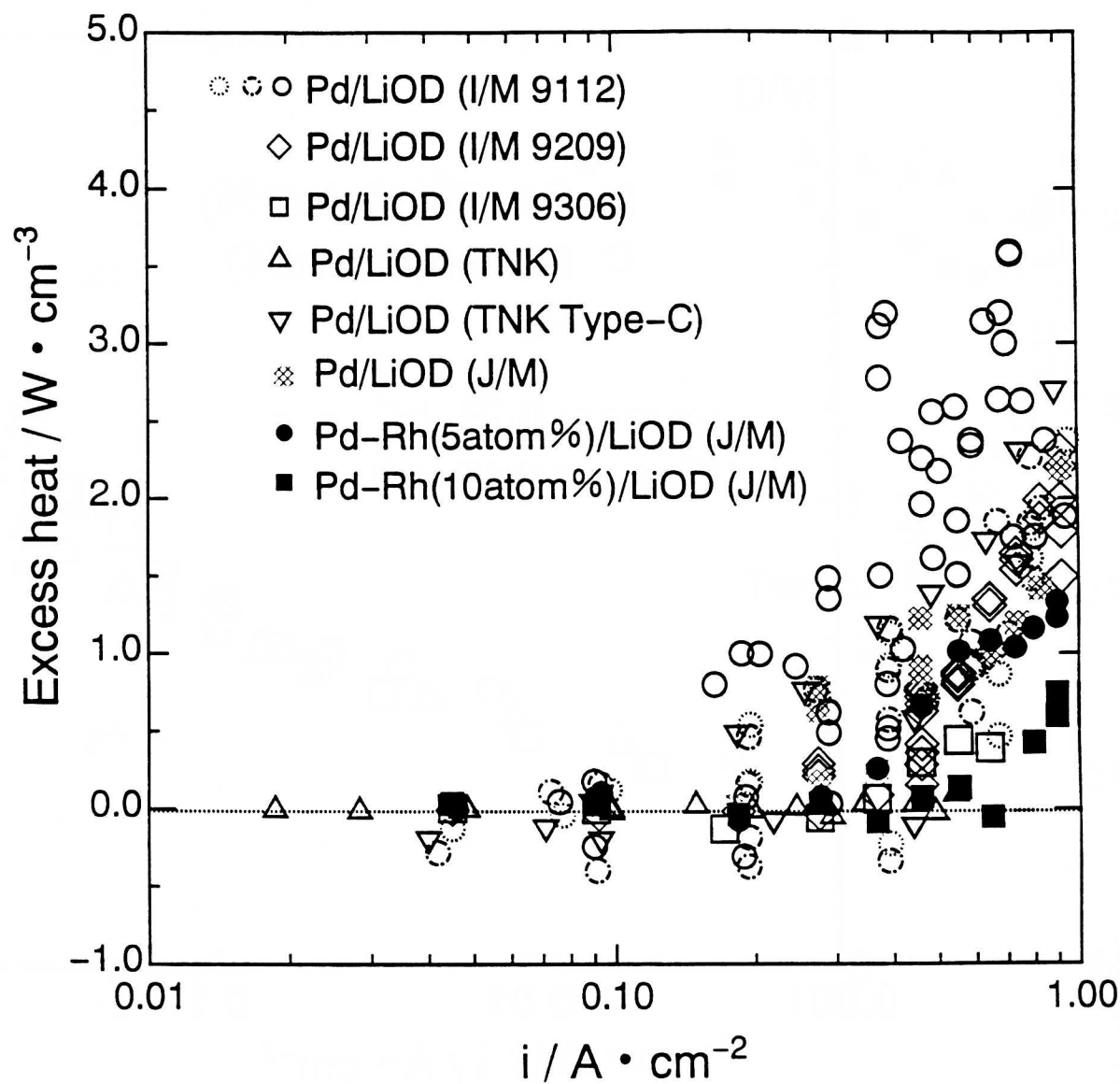


Fig. 18. Excess heat vs current density for various Pd and Pd-Rh alloy cathodes in 1M LiOD.