

EFFECT OF BORON FOR THE HEAT PRODUCTION AT THE HEAVY WATER ELECTROLYSIS USING PALLADIUM CATHODE

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Abstract

The heat balance during the electrolysis of 1M LiOD heavy water solution using Pd cathode has been measured using the flow calorimeter with the constant power supply and the thermochemically closed cell. The special attention was paid on the concentration of B in the palladium cathode. The B concentration was controlled from 127 to 1000ppm.

Using Pd that contained 127ppm and 1000ppm B, the excess heat was not observed. While, using Pd that contained 267ppm and 500ppm B, the small excess heat was observed at 3 runs out of 5 runs. The excess heat appeared continuously from the beginning of the electrolysis. These concentration of B might be effective for the excess heat generation.

1. Introduction

The excess enthalpy during the heavy water electrolysis using Pd cathode mainly in LiOD solution has been reported by the many groups¹⁻⁴⁾. However, the excess enthalpy is not well reproduced in most of the groups. In order to get a good reproducibility, the materials science of Pd cathode should be promoted more. The history of Pd processing and the composition of Pd metal are the interesting factors. In this study the attention was paid on the B impurity in Pd cathode.

Another point for the cold fusion study is how to measure the excess heat precisely. There is no fixed method for heat production during the electrolysis. In our group the heat balances during the heavy water electrolysis using Pd cathodes have been measured by the flow calorimeter using the constant power electrolysis in the thermochemically closed cell. In this system the input electrical energy completely converted to the thermal energy at the output. We can compare the input and the output energy very easily.

In this paper the effect of B concentration in Pd cathode on the excess heat generation during the heavy water electrolysis has been studied using our flow calorimeter system.

2. Experimental

The heat balance measurements have been carried out in an acrylic electrolysis cell with the recombination catalyst on top where the recombination reaction proceeds completely up to 4A. The recombination catalyst is fine Pd powder on Al₂O₃. Figure 1 shows the schematic

drawing of the electrolysis cell. The flow calorimetry was applied with copper tubing surrounded the cell where cooling water flows with picking up the generated heat by the electrolysis and the recombination reaction. The increase of cooling water temperature was measured by the CA thermocouples and the heat output was calculated. We adopted the constant power generator for the electrolysis (generally 5W) and controlled the cooling water temperature $296 \pm 0.05\text{K}$ at the entrance. The electrolysis was conducted up to 1500-2000 h at each run, if possible.

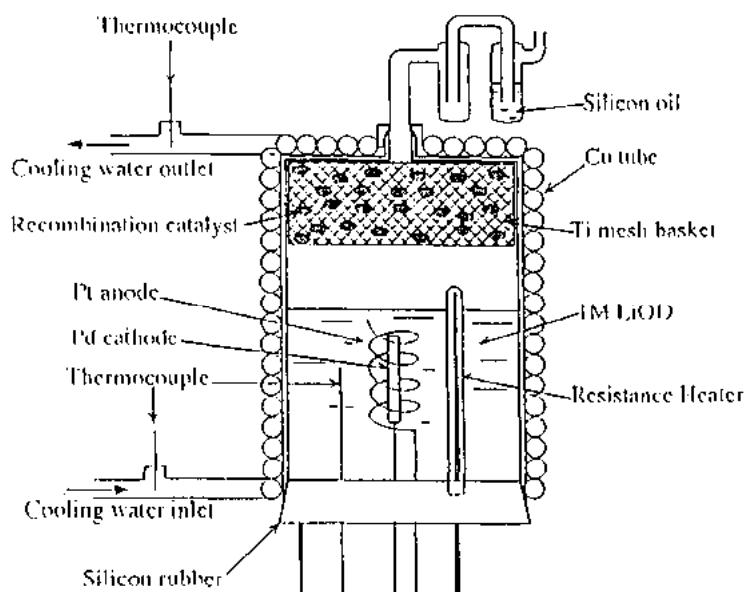


Fig. 1 Electrolysis cell.

The cathodes were Pd rods (4mm ϕ x20mm) or Pd plates (1x2x20mm) which contained the controlled concentration of B. These materials are obtained from Tanaka Kikinzoku Kogyo (TNK) and IMRA Material (IM). The B concentration was changed from 127 to 1000 wt. ppm. The anode was Pt wire (1mm ϕ) which surrounded the Pd cathode. The electrolyte was 1M LiOD heavy water solution which was made by solid LiOD.D₂O (99 at. % D).

3. Results_and Discussion

Table I. Heat balance of heavy water electrolysis with B-controlled Pd cathode

Run	Palladium	Sample	Win (W)	C.D. (mA/cm ²)	Heat balance max(%)	Av.(%)
23	B 267ppm	TNK	5	750-300	107	103
25	B 127ppm	TNK	5	850-440	99	97
29	B 500ppm	IM	5	750-360	105	101
31	B 267ppm	TNK	5	900-540	103	100
33	B 500ppm	IM	5	740-660	104	103
34	B 500ppm	IM	5,10	1180-500	103	100
37	B 1000ppm	TNK	5	1040-945	101	100

Table 1 shows the summary of the results of the heat measurements at the electrolysis in heavy water. During these days the light water electrolyses were carried out 2 times using Pt cathode(Run 32 and 36) in order to check the performance of the calorimeter. In light water system the excess heat could not be observed. Although the heat output was fluctuated a little bit around 100%, the average output heat was balanced with input power. We detected in average 100% of input power at the output.

At these runs(Table 1) the large excess heat that exceeded 10% of input power observed neither in continuous form nor in burst. The Pd cathodes those contained low(127ppm) and high(1000ppm) concentration of B did not produce the excess heat. However, the small excess heats in average were observed at the electrolyses using the Pd cathodes that contained 267ppm and 500ppm B at 3 runs(Run 23, 29 and 33) out of 5 runs. Most excess heat appeared continuously during the electrolysis, not in burst.

Figure 2 shows the heat balance of Run 23, where the 267ppm B containing Pd cathode was used. Most of the data points are above 100%. The excess heat appeared continuously throughout this run. The highest excess heat is 7% and the average excess heat is 3.5%. The total excess heat was calculated to be 0.6MJ. This value can not be explained by any chemical reactions that might occur in this system. Figure 3 shows the trends of the electrolysis current and the cell voltage at Run 23. Since we used the constant power electrolysis, the current and the cell voltage changed simultaneously. Generally, the cell voltage increased as the electrolysis reaction proceeded.

Figure 4 shows the heat balance of Run 29, where 500ppm B containing Pd cathode was used. The trend of the heat balance is same as that of Run 23, although the absolute value is relatively small compared to Run 23. After this run the surface of the Pd cathode was analyzed by EPMA, Auger Electron Spectroscopy and X-ray Fluorescence. Pt was found up to 1000Å from the surface in relatively high concentration compared to the surface of Pd that could not produce excess heat.

At Run 34 the input power was changed periodically(12h

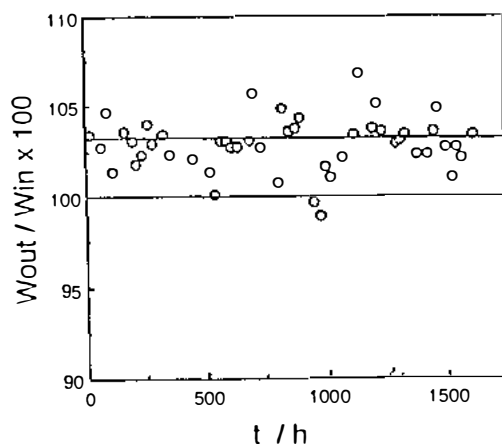


Fig.2 Heat balance at Run 23(267ppm B)

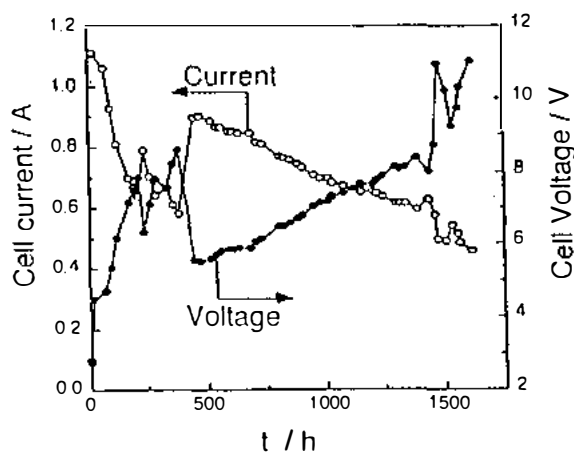


Fig.3 Cell current and cell voltage at Run-23

interval) from 5W to 10W or vice versa in order to see the effect of the change of electrolysis condition. No excess heat was observed during this run. Such a long time interval might not be effective for the excess heat production.

The largest excess heat in this study was obtained at the 267ppm B containing Pd and the 500ppm B containing Pd was next. No excess heat was observed at 167 and 1000ppm B. There is no correlation between B content and the excess heat.

Although our experiments are very limited and needs more data to confirm the effect of B, a suitable concentration (200~500ppm) of B in Pd might exist to produce the excess heat.

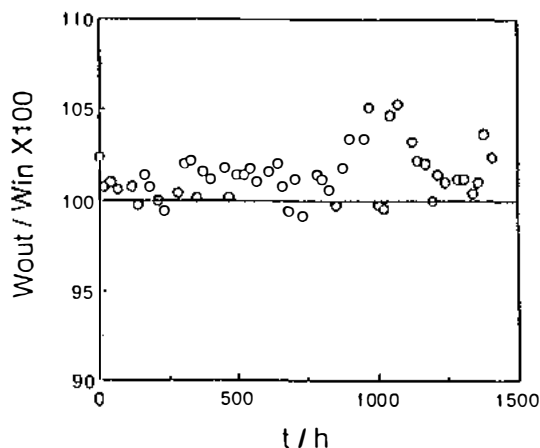


Fig.4 Heat balance at Run-29(500ppm B)

4. Conclusion

The heat balance was measured by the flow calorimetry during the heavy water electrolysis using the Pd cathode that contained the controlled concentration of B. Large excess heat that exceeded 10% of input power was not observed. The small excess heat looks appeared continuously during the electrolysis using the Pd cathode that contained 200~500ppm B. However, the excess value is so small that more precise measurement is necessary in order to confirm this results as well as the repeated studies.

The new heat measurement system is developing in our group. Using this system more precise heat measurement will be possible and the effect of B for the excess heat production will be confirmed.

Acknowledgement

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