Heat Production and Trial to Detect Nuclear Products from Palladium-Deuterium Electrolysis Cells

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Abstract

A burst-like excess heat release, equivalent to 110% of the input electric power, was clearly observed for the first time in our newly built open type electrolysis cell using Pd/0.1MLiOD/Pt. After being precharged, the cell was driven to boiling three times the last of which continued for about 16 hours to almost dryness. The burst occurred just during the calm period about 6 hours after the first boiling. The temperature of the cell, about 100 ml in volume, increased by 7.5 K in 13 minutes. A palladium cathode, $2\text{mm}\phi \times 7.05\text{mm}$, was a heat source, although the mechanism of the heat generation is still uncertain. During the whole period of this run, however, the phenomenon took place only once. Neither increase of neutron emission nor that of tritium concentration has been detected. Mass analysis showed that any traces of D_2 as well as ^{4}He have not remained in the Pd sample used. Detection of γ ray emission as well as ^{3}He and ^{4}He in off gas during or just after release of excess power should be yet to be pursued further.

1. Introduction

The most important issue about the cold fusion research is to reproduce the claimed large amount of excess heat experimentally. The question of whether it is nuclear origin or not, can be clarified only by repetition of the heat phenomena. Among many experimental results, we have thus been particularly interested in observing with our own eyes a "burst" of excess enthalpy as originally reported by Fleischman, Pons and Hawkins [1]. Until very recently, however, no clear-cut heat bursts have been observed in our open type cell experiments. On the other hand, aiming to explain the lack of neutron (n) or tritium (T) consistent with the heat excess, new nuclear reaction mechanism in solid has been conjectured. Coincidental determination of the presence or absence of nuclear products like ^{3}He, ^{4}He and γ as well as n and T became essential. In order to accomplish a complete experiment, several improvements have been made so far: 1)A new cell was designed and prepared; 2)A new method of sample preparation was invented; 3)Mass spectroscopy of ^{3}He and ^{4}He was made possible; 4)High energy *in situ* γ ray spectroscopy system was prepared.

2. Electrochemical Cells

A new cell as illustrated in Fig.1 was designed and prepared whose heat insulation was reinforced by silver mirror, super insulation muffler and thick TFE inner flange. Palladium cathode (99.80% pure, Johnson Matthey) is screwed together with

1mmϕ Pt wire that is enclosed with FEP shrinkable tubing and 1.5/4mmϕ Pyrex glass tubing. Pt wire for anode (1mm in diameter and 3m in length) is symmetrically wound around 6 Pyrex glass supports with rather coarse pitch for upper 7 turns but with dense pitch for lower 29 turns. As the reference electrode a palladium wire of 1mm in diameter is immersed outside the anode spiral. Special care has been taken so that cathode may be centered by virtue of TFE bead and thick perforated flange.

No metal surface, Pt in particular, is exposed to gas phase with the aid of teflon coverage, which avoids spontaneous recombination between D_2 and O_2. A cartridge resistance heater of 10W is used for heat calibration. Temperature was measured with a chromel-alumel thermocouple also covered with teflon. Electrolytic current, voltage and temperature of the cell were continuously monitored. Two identical cells were prepared and installed in positions of 5 (VI05) and 6 (VI06) in a constant temperature bath kept at 20.0$\pm$0.01°C (see Fig.3 in the reference [2]). Evolved gas was passed through a 250ml buffer bottle and escaped to the air through 100ml D_2O and Si oil bubblers in series.

Two Pd cathodes were prepared. One for VI05 was 2mmϕ×7.05mm, mass and surface area of which are 0.227g and 0.435cm^2, respectively. It was cut from a 2ϕ×100 rod, shaped round with diamond files, polished with W wool and degreased. The other for VI06 was 3.2mmϕ×5.25mm, mass and surface area of which are 0.388g and 0.60cm^2, respectively. This sample had been remelt *in vacuo* using an Al_2O_3 crucible and stored in D_2O. The surface was filed, shaped and degreased. Both were annealed *in vacuo* up to about 800°C and charged with D_2 gas in the furnace just before installed in the cell. The electrolyte used was 0.1M LiOD solution, prepared by the addition of lithium metal to D_2O (99.9at.%, Aldrich Chemical Company). A different batch of electrolyte was used: an old one for VI05; and a new one for VI06, which means that the former contains more Si dissolved from glass container whose teflon lining peeled off after long storage of the solution. Electrolysis has been done in constant current mode. After precharging period of 28 and 8 days, the current density was increased from 35 to 920mA/cm^2 and 22 to 663mA/cm^2 for VI05 and VI06 cells, respectively. Heavy water of about 12ml was added twice a week to make up for losses due to electrolysis.

3. Measurement of Nuclear Products and Mass Spectroscopy

Neutron measurements were performed by positioning two different types of counter, BF_3 and ^{3}He, next to the electrolysis cells and another BF_3 counter about 3m apart for BG monitoring [2]. A fourth one, ^{3}He type, was also set below the furnace to check the abnormal emission during D_2 gas charging in Pd. Tritium concentrations, before, during and after electrolysis, were measured with a liquid scintillation counter by an external standard method. A γ ray survey meter using a 1"ϕ×1"NaI(Tl) scintillator and an MCA system using a 3"ϕ×3"NaI(Tl) scintillator were prepared. In the updated system γ ray signals up to 32 MeV can be accumulated every two hours and processed for anomalies in energy spectra. These scintillator detectors can be placed on top of the bath, but unfortunately could not be ready for the measurements when the boiling and the heat burst phenomena of the cells were observed.

Samples of Pd after electrolysis were degassed up to 770°C in a closed vacuum furnace. The extruded gas was analyzed in a high-resolution mass spectrometer system that was specially designed and prepared [3]. Off gas collected in bottles was also analyzed, but results were only preliminary. After these analyses the Pd samples were carefully observed and photographed through microscope. Although 3 months had already passed after the heat burst phenomenon, γ ray radiation from the sample VI05(941016) was measured by the use of a Ge(Li)-spectrometer. Chemical analyses of the solution or the solid precipitates in the cell after electrolysis were also done by ion chromatography, X-ray diffraction, X-ray fluorescence method and so on.

4. Results and Discussions

Under the constant current conditions the cell potential and the cell temperature increased gradually. Owing to improved heat insulation, electrolysis continued at relatively higher cell temperatures, even the higher as the addition of D_2O repeated. At the early stage of high current density up to $920mA/cm^2$ (VI05 cell) or $663mA/cm^2$ (VI06 cell), the electrolysis was rather calm, but after a few weeks it became astable and fluctuating. Cell resistance measured across reference electrode and anode showed similar but asynchronous fluctuations.

In case of VI05 cell sudden rise-up and fall-down of cell potential were found as the first symptom. At the next stage sudden step-ups like **A** and **B** in Fig.2 appeared. Decrease of liquid conductance due to Li escape, however, cannot account for these effects, as it should be more gradual, if any. All of a sudden the cell potential sharply increased and thus the cell temperature reached to boiling at **C** [4]. Due to voltage limitation of the power supply used, the current is lowered and boiling stopped again all of a sudden at a point **D** owing to some unknown delicate factors.

It was just during the calm period about 6 hours after the first boiling that an enormous heat release was observed (between **E** and **F**). The temperature of the cell, about 100 ml in volume, increased by 7.5 K (from 83.4°C to 90.9°C) in 13 minutes. The cell potential showed a dip correspondingly. Enlarged view is shown in Fig.3. As two cells were made almost identically, they obey the same calibration curves (see Fig.4 and Fig.5). By applying an electric current to a heater in a twin cell, VI06, we could simulate the heat burst phenomenon as shown in Fig.6. From this simulation, assuming no stored energy is released, the excess heat can be estimated to be 6.8 W, about 110% as compared with the input electric power. It amounts to 360 W per 1 cm^3 Pd bulk. Although a mechanism of heat generation is still uncertain, the cathode can be assumed to be a heat source due to following reasons. First the cell potential showed an abrupt partial recovery as shown by **B→ C** in Fig.3, when the heat release stopped. It can be assumed to be caused by fast cooling of the Brunner-Nemst layer bearing a large potion of potential drop near the cathode. Secondly the Pyrex glass was found to be cracked near the end of the cathode due to heat, which may justify the sudden stoppage of the heat release phenomenon at **B**.

Boiling occurred 3 times the last of which continued for about 16 hours, in the former period violent but in the prolonged later period rather gentle, and the cell was driven to almost dryness. No *heat after death* [5] was observed in this case. During the whole period of this run the heat burst phenomenon took place only once. In case of the cell VI06, boiling due to sharp increase of cell potential also occurred but only once. A large number of candidates of small heat release were, however, observed in this cell. This is why the calibration curve shows a wider spread than in the cell VI05 (see Fig.5).

No increase of neutron emission as observed before [2] has been detected during whole process of D_2 gas charging and electrolysis (see Fig.7). Only one exception was an accidental increase up to 19 counts/30min of ^3He type detector at time t_1 (see Fig.3), but it was not coincidental in BF_3 ones. No abnormal increase of tritium has been found either as shown in Table I. Measurement of γ during electrolysis after boiling and heat burst has shown no anomalies in counting rate and energy spectrum up to 32 MeV.

Owing to possible contamination from air (5.24ppm) as well as from standard gas used before, whether ^4He exists in the off gas or not could not be conclusively determined this time. According to the mass analysis of gases dissolved in Pd samples, not only ^4He but also any traces of D_2 could not be detected in case of VI05. ^4He was not detected for the sample VI06, either. In this case, however, a smaller amount of D_2 which is equivalent to $PdD_{0.1}$ was found. VI06 cell was not dried as VI05 cell during electrolysis. This means all occluded gases removed from Pd bulk during the violent boiling process. The heat burst in VI05 might happen in the deuteron reoccluding stage.

The heat of combustion of hydrogen, assuming $PdH_{0.9}$, is equal to about 232J for 0.227g of Pd. Furthermore the heat of absorption of deuterium in $PdD_{0.9}$ only amounts to about 16J. These values from chemical reactions can never account for the excess enthalpy of 5300J that comes from 6.8W lasting for 13min. Observation through microscope clarified that Pt as well as Pd, near their interface in particular, had been seriously eroded. No such erosion could be found in case of another sample that had been electrolyzed for 4 months without showing any heat excess and was degassed up to 500°C. Pt anodes were both covered with much white brittle material abundant in Si mainly composing of $Li(Al)SiO_4 \cdot D_2O$. Dark brittle scab was found on Pd surface that also consists of Si > Pt > Zr and so on. On the other hand, no special γ ray radiation except the natural one was observed in the γ spectroscopy performed on the Pt/Pd cathode sample of VI05 although peaks of ^{228}Ac (338.4keV) and ^{214}Bi (1764.5keV) were enhanced a little in a sample run (see Tables II and III).

The low intensity of neutrons and the poor enrichment of tritium in so-called cold fusion experiments have prompted proposals of nuclear processes that yield only heat and helium as products. If the nuclear reactions were assumed as: 1) $D + D \rightarrow {}^4He + \gamma$ (23.8MeV), 2) $D + D + D \rightarrow D + {}^4He + \gamma$ (23.8MeV), the number of nuclear products should be 2.62×10^{11} s^{-1} per Watt, that is, totally 1.39×10^{15} in case of the heat excess of VI05(941016) cell. Although many difficulties are met with in ^{4}He detection [6, 7], measurements of these products should be accomplished coincidentally with the heat burst as we observed. Detection of γ ray emission as well as ^{3}He and ^{4}He in off gas during or just after release of excess power would be ardently pursued further.

Acknowledgments

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