Measurements of Excess Heat in the Open Pd|D₂O Electrolytic System by the Calvet Calorimetry


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Abstract

Excess heat was observed in the Pd|D₂O electrolytic system using a Calvet type microcalorimeter. It was found that the average excess power was 0.025 W over 79 hours period. This result corresponds to a volume excess power of 8.75 W/cm³ Pd or a surface excess power of 0.044 W/cm² Pd, and a specific excess heat of 2.48 MJ/cm³ Pd or 228 eV/atom Pd. The current density and D/Pd ratio for excess power production were lower than the recognized ‘threshold’ values 100–150 mA/cm² and 0.83–0.92 D/Pd, this indicates that the critical requirement for reproduction of the anomalous heat can be ‘cut down’ using high sensitivity calorimetry. By comparison with that of the Pd|D₂O system, no anomalous excess heat was measured in the Pd|H₂O electrolytic system within the experimental uncertainty.

1. Introduction

Since the discovery of the anomalous excess heat in the Pd|D₂O electrolytic system [1], there have been continuing controversies on this result in the scientific community; one of the problems is the calorimetric method. As predicted by Storms in an extensive review [2], the isoperibolic calorimetry used by Fleischmann and other researchers introduces some uncertainty and complexity, e.g. the problems of inhomogeneous distribution of temperature in the electrolyte, recombination of D₂ and O₂ gas in the cell and effect of the stagnant water layer at the cell wall on the thermal conductivity of the wall etc. Strictly speaking, the isoperibolic calorimeter usually measures overall heat but not power at any time in a process. Another widely using method in cold fusion experiments, the mass-flow calorimetry, is adapted but not preferred means in power measurement at present. On the other hand, the Calvet calorimetry has been used in thermokinetics for more than a half century. It not only provides a high sensitivity but also depends weakly on the thermal homogeneity (the isoperibolic assumption) in the measuring vessel. The great differences between these three methods can be demonstrated by the magnitudes of the minimum
value of current density for excess heat production in the Pd\(\text{D}_2\text{O}\) electrolytic system. Based on the results measured by the isoperibolic and mass-flow calorimetry, Fleischmann et al [1], McKubre et al [3] and other researchers all mentioned that the minimum current density (known as the ‘threshold value’) is 100–150 mA/cm\(^2\). Nevertheless, Bush and Lagowski [4], and our results showed that 10–50 mA/cm\(^2\) is enough to produce excess heat using the Calvet calorimetry. This fact indicates that the anomalous excess heat can be easily detected, in other words the critical requirement for reproducibility of the anomalous excess heat can be ‘cut down’, by using high sensitivity calorimetry.

Starting in 1989, our group has been continually involved in studying the anomalous excess heat in the Pd\(\text{D}_2\text{O}\) (\(\text{H}_2\text{O}\)) electrolytic system by the Calvet calorimetry [5] as well as some material and electrochemical characteristics of Pd\(\text{D}\) (\(\text{H}\)) electrode [6]. In the present paper, we report some of the result obtained in the last experiment.

2. Experimental

The electrolytic cell consisted of a glass vessel (inner \(\phi 12 \times 40\) mm) and electrodes in the \(\text{LiNO}_3 + \text{D}_2\text{O}\) solution as shown in Fig. 1. The cathode was made of a palladium wire (\(\phi 0.2 \times 50–90\) mm, 99.9\% purity) wound round a PTFE rod, each cathode end was spot welded to two platinum leads (\(\phi 0.2 \times 50\) mm) for measuring atomic ratio of D/Pd by the resistance method. The anode was made of a platinum wire (\(\phi 0.02 \times 100\) mm) wound round another PTFE rod. All platinum wire leads were covered with thin-walled PTFE tubes to minimize their contact with electrolyte and catalysis of \(\text{D}_2 + \text{O}_2\) combination. Both the cathode and anode were partially inserted in an appropriately machined PTFE piece, which ensured good permanent positioning of the electrodes and fixed distance (ca. 2 mm) between them. A diaphragm made of a PTFE plate with thin holes in it was used in the cell to separate the cathode and anode compartments and to prevent from \(\text{D}_2\) and \(\text{O}_2\) gas bubbles mixing. The 5 M \(\text{LiNO}_3\) heavy water solution was prepared by dissolving \(\text{LiNO}_3\) (No. 3 reagent plant of Shanghai, AR) in \(\text{D}_2\text{O}\) (Beijing chemical plant, 99.8\% isotopic purity). The cell was filled with about 2 ml of the electrolyte solution.

The electrolytic cell was coiled with an isolated resistance wire as a calibration heater and placed in a stainless steel container (inner \(\phi 16.9 \times 60\) mm). An appropriate amount of silicon oil was filled in the space between the glass vessel and stainless steel wall for good heat conductivity.

Figure 2 shows the experimental apparatus. A microcalorimeter, LKB 2107 made in Sweden, was employed in our work, it is a kind of instrument used to determine the heat flow evolved or absorbed in a process undergoing in a system and it is used widely in thermokinetic studies. The overall thermal flux produced in the system converts to electromotive force, and has a simple linear relationship to the output signal in voltage. This sort of calorimetry avoids the problem of inhomogeneous distribution of temperature in the isoperibolic calorimetry, and has much more sensitivity than the mass-flow calorimetry. The effect of slight temperature fluctuation around the calorimeter is eliminated by the twin cell design. The temperature in the air bath in which the calorimeter
is mounted was maintained at 40.00 ± 0.02 °C.

With multiplexed computer data acquisition, the data associated with the input power, output power and D/Pd ratio were displayed in real time on the computer monitor and also stored on disc using a software package.

Finally, all electrolysis was carried out under the galvanostatic condition, the applied current was typically between 25 and 30 mA, which was measured as a voltage drop across a standard resistor. The light water solution was used in blank experiments for comparison.

![Schematic diagram of the electrolytic cell.](image)

![Schematic diagram of the experimental apparatus.](image)

### 3. Results and discussion

In order to verify the accuracy and reliability of the calorimeter, a number of calibration
experiments were performed with Joule heating after the temperature in the air bath and calorimetric experimental zero were stable. It was found that the precision was better than ± 2% with the applied power being just about that of the electrolysis and the device constant did not change within the error 1% before and after the electrolysis.

A run of calorimetric experiment on the Pd|D\(_2\)O (H\(_2\)O) electrolytic system was always carried out over several days. In general, the calorimetry on the electrolytic system lasted about 20 hours. Between two calorimetric experiments, the calorimeter was calibrated and heavy water (light water) was added into the electrolytic cell to compensate the D\(_2\)O (H\(_2\)O) consumption in electrolysis and the evaporation in the gas stream escaping from the cell although the latter was very small.

The excess power is calculated from the input, output and water electrolysis powers:

\[ P_{\text{ex}} = P_{\text{out}} + IV_{\text{th}} - IV \]  

where \( P_{\text{out}} \) is the output power measured by the calorimeter; \( I \) is the applied current; \( V \) is the measured potential drop across the electrolytic cell; \( V_{\text{th}} \) is the thermoneutral potential in the water electrolysis, \( V_{\text{th}} = 1.524 \) and \( 1.478 \) V at 40 °C for D\(_2\)O and H\(_2\)O, respectively.

Fig. 3. Calorimetric results of Pd|(5M LiNO\(_3\) + D\(_2\)O) system, T = 40 °C, sizes of Pd cathode: φ0.2 x 91 mm.
There have been seven runs of calorimetric experiment on Pd|D$_2$O (H$_2$O) electrolytic systems being performed in two months period. Most of Pd|D$_2$O systems exhibited excess heat in different magnitudes of excess power and sustaining time. Two runs of calorimetric results throughout the experiments for Pd + D$_2$O and Pd + H$_2$O systems are shown in Figs. 3 and 4, respectively. Each figure shows the output power and excess power calculated according to Eq. (1) in less than one-day period. The applied current, resistance ratio of PdH$_x$ to Pd (R/R$_0$) and loading ratio of D/Pd are noted in each figure.

By Figs. 3 and 4, we find that both the D$_2$O and H$_2$O systems exhibit excess heat (ca. 500–800 J) at the beginning of electrolysis. Because it is greater than the enthalpy of palladium deuteride (hydride) formation (≤ 5 J) and any chemical process associated with LiNO$_3$ is endothermic, so we only attribute it to unknown chemical process, which needs further research in future. Subsequently, both these two systems experience the trivial time of no excess heat. The distinction between them appears at the latter time, we find the excess heat is produced in the Pd|D$_2$O system on the third day and it lasts for 4 days; otherwise, the Pd|H$_2$O system exhibits no any excess heat during the rest time and it also provides a calibration for the calorimeter in some sense. These results clearly indicate that the Pd|D$_2$O electrolytic system produces anomalous excess power.
For result in Fig. 3, the average excess power over 79 hours is 0.025 W which corresponds to a volume excess power of 8.75 W/cm³ Pd or a surface power of 0.044 W/cm² Pd. The maximum excess power shown in Fig. 3 is 0.035 W, the ratio of excess power to input power ranged from 48% to 83%. The overall excess heat corresponds to 2.48 MJ/cm³ Pd or 228 eV/atom Pd which appears to be well beyond any chemical process can be expected to release.

Our calorimetric results showed an excess power that was quite in line with other positive results reported up to now. In particular, if we consider the excess power per unit electrode surface area as a function of the current density, our result is beyond the general behavior pointed out by Storms [2] by considering many calorimetric measurements on the Pd/D₂O system in various laboratories. The applied current density for production of the excess heat in Fig. 3, 44–53 mA/cm², is lower than the ‘threshold’ value 100–150 mA/cm² mentioned by Fleischmann, McKubre and other researchers [1,3,7]. However, it is consistent with the result of Bush and Lagowski [4] who found 10–30 mA/cm² is enough to produce excess heat using the Calvet calorimetry. At the same time, the loading ratios accompanying the excess heat production in Fig. 3 are between 0.51–0.68 D/Pd which are lower than the ‘threshold’ value, 0.83–0.92 D/Pd, first mentioned by McKubre et al [3] and Kunimatsu et al [7]. Both results indicate the ‘threshold’ current density and D/Pd ratio for anomalous heat production may be ‘cut down’ using a high sensitivity calorimeter. Of course, our experiment was performed at a higher temperature (40 °C) than before used (20–30 °C), this difference may cause the triggering condition of the excess heat being modified. On the other hand, these results are qualitative and the quantitative relation of excess power vs. current density and loading ratio needs further research in future works.

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References