PRIMARY CALORIMETRIC RESULTS ON CLOSED PD|D₂O ELECTROLYSIS SYSTEMS BY CALVET CALORIMETRY

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ABSTRACT

Anomalous heat absorption was observed in a closed Pd|D₂O electrolysis system by Calvet calorimetry. The average excess power was – 14.6 mW over 105 hours period, which corresponds to a volume excess power of – 10.3 W/cm³ Pd and heat absorption of 3.81 MJ/cm³ Pd or 350 eV/atom Pd.

1. INTRODUCTION

In previous works, we reported excess heat in open Pd|D₂O electrolysis system using a Calvet calorimeter.[1] Strictly speaking, the anomalous heat effect must be obtained from closed systems, which avoid the consideration of dissociation of heavy water, the $D_2 + O_2$ combination, the mass transfers between the system and atmospheres.[2] On the other hand, the calorimetric method has troubled the community of cold fusion research for a long time. The Calvet calorimeter is one of standard equipments in thermokinetic studies; it not only provides a high sensitivity but also depends weakly on the thermal homogeneity (the isoperibolic assumption) in the measuring vessel. Therefore, it is necessary to carry out power measurements in closed Pd|D₂O electrolysis systems using the Calvet calorimeter. In this paper, we will report some of these results obtained in our laboratory.

2. EXPERIMENTAL

The electrolysis cell consisted of a glass vessel (inner ϕ 13 × 50 mm) and electrodes in the LiOD heavy water solution as shown in Fig. 1. The cathode was made of a palladium wire (ϕ 0.2 × 45 mm, Institute of Aeronautical Materials, Beijing, 3N) bent to the shape of letter U for convenience of measuring its resistance to determine the D/Pd ratio; each cathode end was clamped by a platinum lead (ϕ 1 × 50 mm). The anode was made of a long platinum wire (ϕ 0.02 × 1400 mm) wound round a PTFE tube (outer ϕ 9 mm, inner ϕ 7 mm, 40 mm high) with dense holes (ϕ 2 mm) in its wall. The 1 M LiOD heavy water solution was prepared by dissolving metallic lithium (General Research Institute for Nonferrous Metals, 99.98%) into D₂O (Beijing Chemical Reagent Company, 99.8% isotopic purity), 4.3 ml of solution was filled in the cell. Some recombiner catalysts were used to recombine the D₂ and O₂ gas into heavy water; they were collected in a PTFE chamber (ϕ 13 × 15 mm) with some holes in its wall for gas flow. The PTFE chamber was stocked by a PTFE screw cap (the trapezoid in Fig. 1) on another PTFE tube (ϕ 6 × 35 mm), the screw cap also prevented pollution of catalyst from the sputter of solution in electrolysis processes, and the PTFE tube acted as the

channel of leads. Each lead was covered by a PVC tube and sealed by epoxy resin on a stainless steel (SS) screw top.
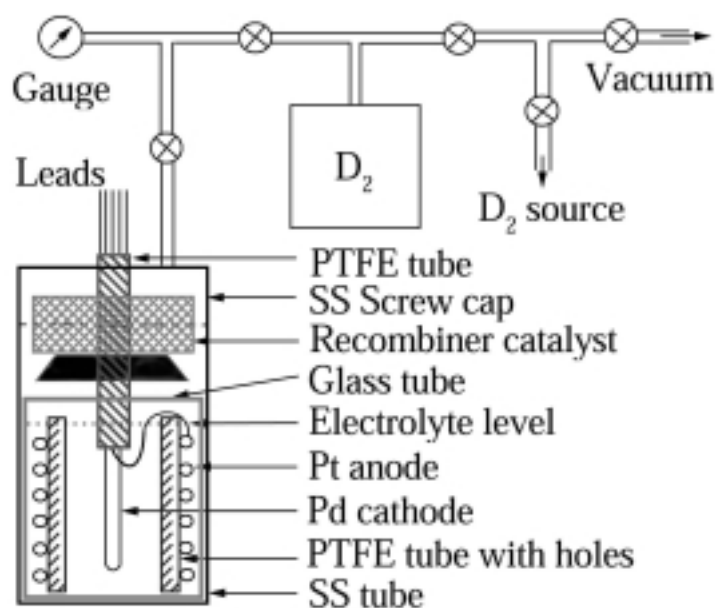

Fig. 1. Schematic diagram of the electrolytic cell and gas systems.

The electrolysis cell was placed in a SS container (inner ϕ 15 × 80 mm), which was sealed by the top screw cap. A SS tube (ϕ 2 mm) was welded to the cap and connected to a SS bottle (capacity = 530 cm^3) filled with D_2 gas, whose pressure was measured by a transducer. The pressure was typically 0.12 MPa; the leakage rate of gas was less than 0.58 mPa s^{-1}. The Pd electrode also acted as a heater for calibration of the calorimeter. The Pd resistance was measured by a Keithley Model 2000 Multimeter and using an alternating current (100 mA, 50 Hz) to avoid the problems caused by direct currents [3]. The detailed description of Calvet type calorimeter can be found in Ref. [1]. The atmosphere temperature was maintained at 17.0 ± 0.5 °C or 20.0 ± 0.5 °C.

The Pd and Pt electrodes, the electrolysis cell, D_2 gas bottle and pipelines involved in experiments were washed by acetone or petroleum ether. In addition, the Pd electrode was etched in aqua regia for about 15 s. All electrolysis was carried out under galvanostatic conditions, the applied current was 3 − 100 mA, which was measured as a voltage drop across a standard resistor.

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

A number of calibration experiments were performed with Joule heating before, after and in the interval of electrolysis; each calibration was carried out after the experimental zero was stable. It was found that the device constant did not change within the error of 0.6%.

3. RESULTS AND DISCUSSION

A run of calorimetric experiment on the Pd|D_2O electrolysis system was always carried out over several days. The excess power is calculated from the input and output powers, and other correction factors:

$$P_{ex} = P_{out} - IV - I_{Pd}V_{Pd} - c\frac{dp}{dt} \tag{1}$$

where P_{out} is the output power measured by the calorimeter; I is the applied electrolysis current; V is the measured potential drop across the cell; I_{Pd} and V_{Pd} are the current and potential drop for measuring the Pd resistance, respectively; $c = 43.1$ mJ Pa^{-1} for our system, $- c dp/dt$ is the contribution of $D_2 + O_2$ gases evolved in electrolysis, which has not combine into heavy water due to the catalysis deactivated, although the corresponding power loss is usually very small.

There have been three runs of calorimetry on closed Pd|D_2O electrolysis systems being conducted. Former two runs gave no excess energy within errors of 0.18% and 0.0034%. The latter one gave energy absorption but not excess heat. Two runs of results are shown in Figs. 2 and 3.
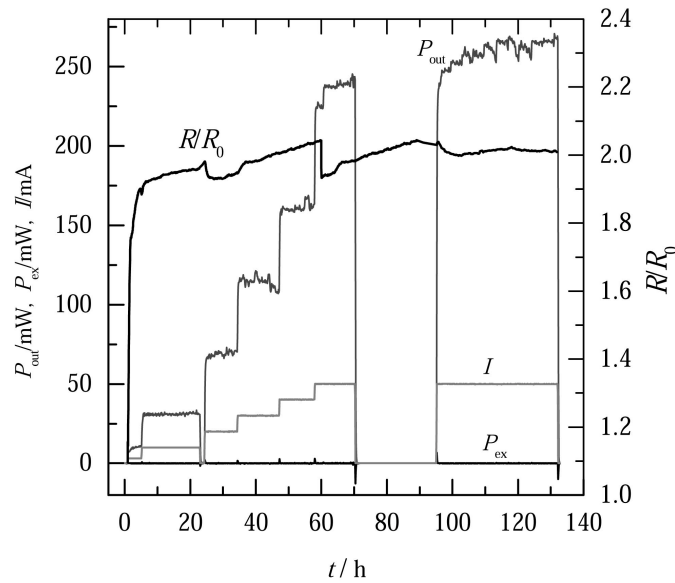

Fig. 2. Calorimetric results of a closed Pd|D_2O system, $T = 17$ °C.

In Fig. 2, the electrolysis currents were 3, 10, 20, 30, 40 and 50 mA, which were applied by a step-up mode. The initial low current was to prevent the crack creation in Pd electrode during the $\alpha \rightarrow \beta$ phase transformation [2]. There were two intervals at which the electrolysis was interrupted. The first interval (22.8–24.3 h) was to calibrate calorimeter when the measurement range was switched. The second one (70–95 h) was to monitor the pressure change and calibrate the calorimeter. Although there are random errors and some pulses in the P_{ex} curve caused by signal delayed in the data acquisitions, the excess power is almost zero as shown in Fig. 2. Integrating powers with respect to time, we find the total output energy is 61.193 kJ whereas the excess energy is $- 2.102$ J, which is only $- 0.0034\%$ of the total energy. The maximum current density was 177 mA cm^{-2}; the maximum D/Pd ratio was 0.85 from the resistance ratio in Fig. 2.

Another electrolysis experiment (Fig. 3) was carried out in the same system as that of Fig. 2 only with the Pd electrode being etched in aqua regia for removing impurities deposited during electrolysis previously, the atmosphere temperature was raised from 17 to 20 °C. This experiments was performed for 105 h using currents of 50, 80 and 100 mA. The maximum current density was 354 mA cm^{-2}; the maximum D/Pd ratio was 0.87. We find that V, P_{in} and P_{out} are lower than those of Fig. 2 at the same current due to the Pd surface treatment. On the other hand, we found that the catalyst had deactivated when the current of 100 mA had been applied for 3 h (at 97.5 h in Fig. 3) and the pressure increased substantially to about 0.2 MPa, then we

had to stop the experiment after some time. Different from that in Fig. 2, the excess power is less than zero prominently, especially when the current was greater than 50 mA. However, its amplitude diminished when the current decreased from 100 mA to 80 mA at 100 h. After the experiment, we calibrated the calorimeter with the power being closed to that applied before (~ 0.5 W), we found that the device constant was the same as that before experiments in error 0.6%. The average P_{ex} over 105 h is − 14.6 mW. Integrating powers with respect to time, we find the total input, output and excess energies are 94.063, 88.449 and − 5.613 kJ, respectively. The absorption excess energy is 5.97% of the input energy and its amplitude is greater than the experimental error; this energy corresponds to − 3.81 MJ/cm^3 Pd or − 350 eV/atom Pd.
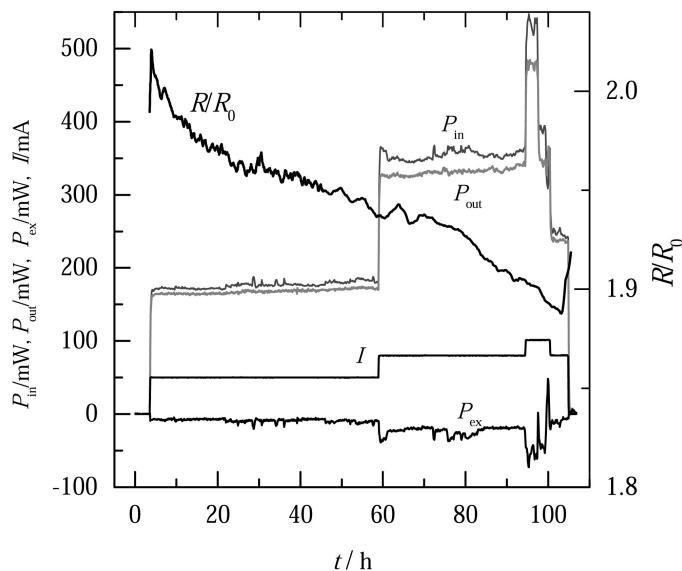

Fig. 3. Calorimetric results of a closed Pd|D$_2$O system, T = 20 °C.

Contrary to the most of calorimetric results on electrolysis Pd|D$_2$O system [1,2], we observed anomalous heat absorption but not production in it. However, similar results have also been detected in Pd|D$_2$O and Ni|H$_2$O systems [4] and La$_{0.95}$AlO$_3$ + D$_2$ system [5] before. Therefore, it should be another effects in cold fusion. Nevertheless, this phenomenon needs to be studied more detail since the related evidences and reproducibility are lacking. Currently we are organizing a new series of experiments on this study.

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