EXPERIMENTAL EVIDENCE OF EXCESS HEAT OUTPUT DURING DEUTERIUM SORPTION-DESORPTION IN PALLADIUM DEUTERIDE

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ABSTRACT

Thermal effects have been studied in the course of sorption-desorption of hydrogen isotopes by a finely powdered palladium deuteride using a conventional differential scanning calorimeter SETARAM DSC-111. During α-β transition an excess heat release is observed in palladium deuteride of about one watt per gram of deuteride. In similar experiments with palladium hydride no anomalous effects have been observed. On the basis of earlier computer modelling, relevant publications and our experimental results the excess heat release during deuterium sorption-desorption by palladium deuteride is attributed to the nuclear reactions of deuterium atoms yielding helium.

1. INTRODUCTION

Unusual thermal effects of electrolysis on Pd cathode in the solution with D_2O solvent are described in many reports (see reviews [1-5]). About one third of the works reported that detected heat production exceeds the electric energy expended in the electrolysis. The nuclear fusion of deuterium producing tritium and helium isotopes was suggested as a probable reason of the anomalous energy production. Such an explanation met with considerable opposition. The reliability of experimental results was questioned because the technique of calorimetric measurements in electrochemical cells is sometimes not free from serious flaws. Recently, new results have been published (*e.g.* a series of publications [6-8]) but whether any excess energy is released under the deuterium interaction inside a palladium cathode along with the energy output due to usual physical and chemical processes remains an open question.

According to the earlier theoretical computations [9,10] and the analysis of the available experimental data, phase transitions in palladium deuteride must be accompanied by measurable energy generation due to the nuclear fusion reactions.

The objective of this report was to perform the experiments, which demonstrate evidently that the anomalous heat production exists. For this purpose the dry cell with palladium deuteride was treated by cycling heating that activates the phase transition. The experiment was planed especially to exclude the disadvantages of electrolytic cells. We have developed a special method for the comparison of thermal effects during hydrogen isotopes sorption-desorption by palladium employing the conventional scanning calorimeter SETARAM DSC-111. Conceptually, the method is based on the different dependence of the signal recorded by the calorimeter on the heat input in the presence or absence of additional sources of energy release in a sample. If only reversible processes occur in the sample, the heat registered by the calorimeter will practically linearly depend on the applied electric pulse and the released Joule heat. When the application of the pulses leads to the excess heat production due to internal sources, the signal dependence on the heat released on the heater must be non-linear.

2. MEASUREMENT METHODS

A hermetically sealed steel ampoule with the studied substance was placed into the measuring channel of the calorimeter; an identical ampoule with the finely powdered palladium was placed symmetrically in a reference channel (see fig. 1). Finely powdered palladium was prepared making use of $PdCl_2$ solution reduction by sodium formiate $Na(HCOO)_2H_2O$. The precipitate was filtered off on an ashless filter, washed by alcohol and then ignited. The readings on a scanning electronic microscope JSM-35 showed that Pd particles sizes vary in the range of 100-800 nm whereas over 70% of them have the size of 300-500 nm and are isometrically shaped.
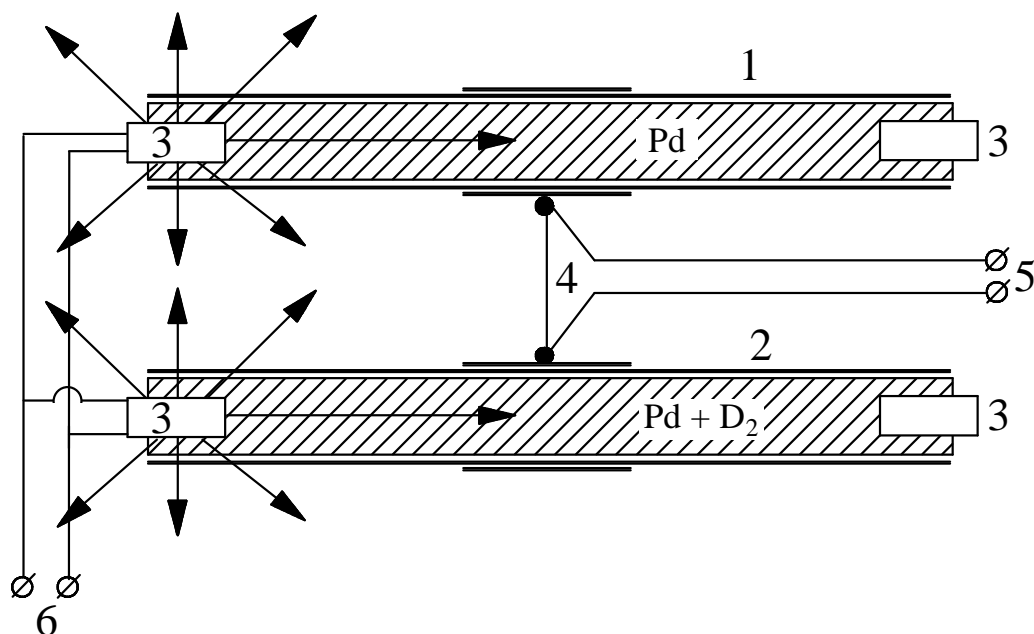

Fig. 1. - Schematic diagram of calorimetric measurements: 1 - reference ampoule; 2 - measured ampoule with the substance; 3 - heaters; 4 - calorimetric detector (thermocouples batteries); 5 - calorimetric signal measurement amplifier; 6 - power supply for the heaters. Arrows designate a heat flow from heaters on the left side of the ampoules in the "on" condition.

Palladium deuteride β-PdD_x was obtained by charging 5 μm-thick palladium foil (99.9% pure) with deuterium in the course of electrolysis of heavy water containing 0.1 M LiOH at the current density of $50mA/cm^2$ for 70-100 hours. The heavy water (99.9% D_2O) had been produced by the Experimental Plant of the State Institute of Applied Chemistry, St.-Petersburg. The completeness of transfer to the β-phase and its composition was controlled by the weight and X-ray methods using a diffractometer. The composition of the obtained palladium corresponded to $PdD_{0.60\pm0.01}$. Making use of lithium hydroxide resulted in the presence of the insignificant amount of light hydrogen isotope in proportion H/D ~ 1:300. Palladium hydride was obtained by the similar technique but using of doubly distilled H_2O.

Equal masses of palladium deuteride (or hydride) foil and finely powdered palladium were placed in the measured ampoules. The ampoules were hermetically sealed by press-fitted copper ring and held at 650K for 30 minutes and then cooled. Meanwhile, the desorption took place of hydrogen isotopes from the foil and cooling resulted in the sorption into finely powdered palladium deuteride whose surface was much greater. The weight method was used to control the absence of gaseous hydrogen isotopes losses. The calorimeter measurements showed that the sorption-desorption of hydrogen isotopes resulted in the temperature range of 400-500K. One and the same reference ampoule with pure palladium powder was used in all experiments produced so that its thermal effect was a little lower than that of the measured ampoule.

At the ends of the ampoules platinum wire resistive heaters were placed with an approximately equal resistance of ~2.7 Ohm. Power from a.c. generator was alternately supplied to the right and left resistive heaters. The Ohmic heat released on the heaters was calculated from the readings of voltmeter and amperemeter. Prior to starting the measurements, the ampoules were centred one at a time in the channels so that the heat flows from equal electric pulses of the left and right resistive heaters were equal. At constant temperature and when the heaters were switched off the calorimetric signal is constant. On measurements taken at elevated temperature, the temperatures at the centre and at the ends of the channel and, therefore, of the ampoule, are different.

The heat flow measured by the calorimeter is only a part of the supplied electric power: $\Delta W = I \cdot V \cdot \alpha$, where I is the current, V is the voltage and α is the calibration coefficient measured by us as a function of a distance between the ampoule heater and the calorimeter detector.

After the both ampoules have been centred, the heaters are switched on. When the current is on, the calorimeter measures the difference between the signals from the measured and reference ampoules. The measurements are performed in the following way. At the initial stationary state, at constant heat flow, the resistive heaters are turned on for 300 seconds. The current and voltage are measured at the 100th and 200th seconds. The heat flow attains a new constant value. In 300 seconds, the heaters are turned off. This brings the heat flow back to its original state in 250-400 seconds (depending on the pulse power). Then the heaters at the opposite side of the ampoule are switched on and the procedure is repeated. After the signal has been brought into its original state, a new cycle begins. The voltage is increased by about 50%.

3. EXPERIMENTAL RESULTS

Eight series of experiments with four different ampoules have been carried out. The data for series with palladium hydride are presented on fig. 2 and 3. It is evident that the recorded signal retains its form and increases practically linearly with the increase in pulse power. The similar linear signal dependence on the applied pulse power of the heaters has been observed in other series with palladium hydride and pure palladium.
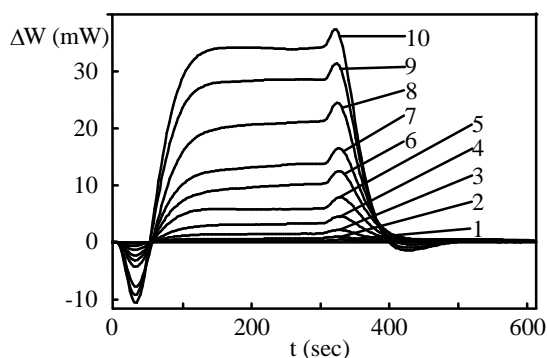

Fig. 2. - Heat flux at various values of power supply for palladium hydride at the initial temperature 440 K (Watt): 1 - 0.13; 2 - 0.28; 3 - 0.64; 4 - 1.30; 5 - 2.3; 6 - 3.2; 7 - 4.3; 8 - 7.1, 9 - 8.8; 10 - 10.2.
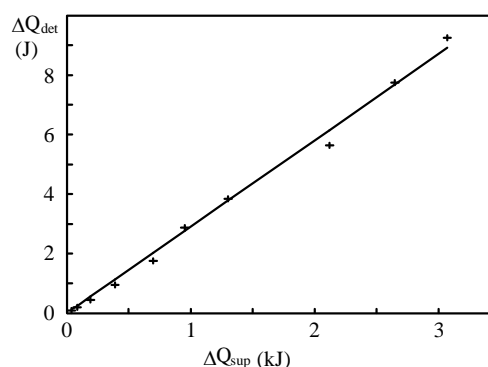
Fig. 3. - Heat measured with the calorimeter (ΔQ_{det}) on the ampoule containing the palladium hydride vs. the power supply (ΔQ_{sup}), expended on the heater.

A completely different type of dependence occurs when palladium deuteride is used. On power increase to 3 W, the measured signal increases. As the power is increased further, the measured signal falls and even its sign is changed. The experimental results for all the eight series are shown in fig. 4 and 5. Anomalous dependence of the calorimetric signal value on the applied pulse was observed using the ampoule with the same sample after a lapse of two months at the temperatures of 440 and 520 K.
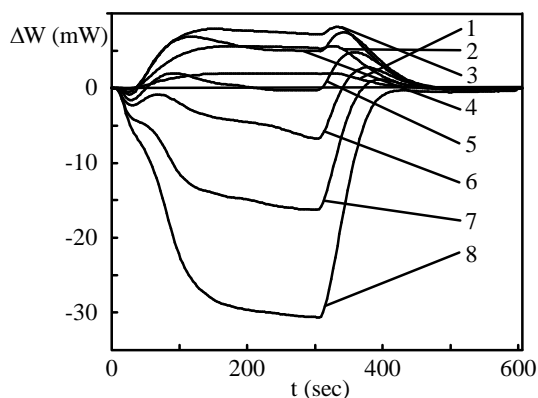

Fig. 4. - Heat flux at various values of power supply for palladium deuteride at the initial temperature 440 K (Watt): 1 - 0.37; 2 - 1.33; 3 - 2.62; 4 - 4.5; 5 - 5.5; 6 - 6.5; 7 - 8.9; 8 - 11.6.
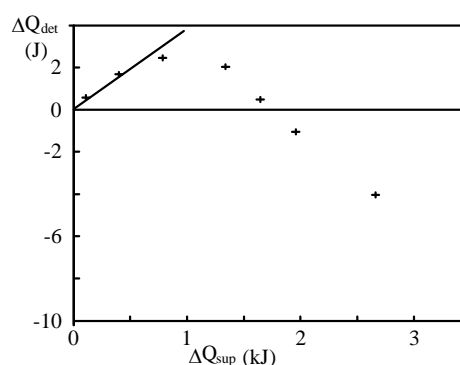
Fig. 5. - Heat measured with the calorimeter (ΔQ_{det}) on the ampoule containing the palladium deuteride vs. power supply (ΔQ_{sup}), expended on the heater.

4. DISCUSSION

The obtained results show that during deuterium sorption-desorption by finely powdered palladium deuteride, excess energy is released whereas in the analogous experiments with the light hydrogen isotope no anomalous effects have been observed. The experimental conditions (hermetically sealed ampoules with the samples inside, the ampoule mass conservation after the experiments, similarity of measurements on using deuteride and palladium hydride) make it impossible to attribute the obtained difference to any chemical grounds or various D and H diffusion rate in the palladium. The source of the excessive heat release can be mainly the nuclear reaction of the deuterium atoms yielding helium with absorption of the released energy (Q) by the palladium deuteride: $D + D \rightarrow {}^4He + Q$.

The computer modelling [9, 10] of deuterium atoms interaction in the palladium also confirmed a significant increase in the rate of the nuclear interaction of deuterons in the crystalline structure of the palladium deuteride with the rise in their mobility due to the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions. Accepting that isostructural phase transitions can activate the reaction, the method and devices were developed to proceed such a nuclear reaction [11-13].

An important factor favourable for the intensification of the nuclear reaction is making use of palladium powder with the minimum particles size. In this case the maximum D/Pd ratio in particles increases which enhances the probability of deuterons approaching closely each other. Furthermore the mass of palladium deuteride undergoing the phase transformation at a time unit increase as function of the general surface area of particles.

The maximum release of excess energy recorded by us in experiments with palladium deuteride is estimated as 10 Joules which taking into account the conditions of our experiments (mass of $PdD_{0.6}$=0.3 g, t=300 seconds and coefficient $\alpha \approx 0.1$) corresponds to ≈ 1 Watt of the excess output power per gram of the palladium deuteride. The order of magnitude of this value corresponds to the earlier performed theoretical evaluations of the nuclear reaction rate in the palladium deuteride [9, 10].

Similar results had been obtained earlier in [6] by the electrolysis of the solution on the basis of D_2O when the closed palladium ampoule with the finely powdered palladium deuteride inside served as a cathode, *i.e.* under conditions in this respect similar to our experiments. In the series of experiments performed under various modes continuously for several thousands hours, an excess heat release has been observed with the power of 1.7–3.4.W/g. The analysis of gases accumulated in the ampoule after the experiment was performed on a high-resolution mass-spectrometer and showed significant content of helium with the proportion of isotopes ${}^4He/{}^3He$ down to ≈ 4 which differs drastically from their atmospheric content equal to $7.2 \cdot 10^5$ and therefore rules out the possibility of its penetration from the atmospheric air. In experiments conducted under similar conditions using ordinary water solutions neither excess heat release nor helium generation have been observed.

In conclusion, our experiments excluding the possible sources of errors in measuring energy balance in electrochemical studies together with the results obtained in [6] are the evidence of the heat release resulting from nuclear fusion under sorption-desorption and diffusion of deuterium in finely powdered palladium deuteride in the order of magnitude of about 1 Watt per gram of palladium deuteride.

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