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RECENT EXPERIMENTAL RESULTS ON THE THERMAL BEHAVIOR OF ELECTROCHEMICAL CELLS IN THE HYDROGEN - PALLADIUM AND DEUTERIUM - PALLADIUM SYSTEMS

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Abstract

This paper reports calorimetric experiments related to the energy breakeven issue during heavy water electrolysis using a Pd cathode in thermodynamically closed cells. A comparison with light water electrolysis under the same conditions is also given. Excess power has been observed in a number of cases in which the overall energy balance becomes positive after a short period, leading to the generation of significant amounts of excess energy. In one case, excess power was maintained over a period of ten days, and produced over 23 MJ of excess energy per mole of palladium.

1. INTRODUCTION

Since the announcement of Martin Fleischmann and Stanley Pons, and the publication of their related preliminary note [1], which reported the production of excess heat during the insertion of deuterium into palladium electrochemically, a number of laboratories have also claimed to have measured substantial rates of excess heat generation.

Nevertheless, there has been the persistent question whether the excess heat generation that has been observed might be related to some type of (perhaps chemical) energy storage mechanism, such that the magnitude of energy that had been produced in this way would be limited to an amount that had been somehow previously invested in the system.

In order to address this question one has to investigate whether one could operate a cell long enough in the excess power mode to achieve a significant positive energy balance. Our definition of the energy balance in this context is the difference between the energy produced by the system during a certain period of time and the total energy consumed for its operation during that period.

Our prior work was focused upon the direct comparison of the thermal behaviour of the hydrogen - palladium and deuterium - palladium systems. In four pairs of electrochemical experiments we observed excess power generation in the deuterium - palladium cells but not in the hydrogen - palladium cells [2-4]. Our early experiments were performed in thermodynamically open type cells, where the gases produced by the electrolysis reaction escaped from the system and the electrolyte had to be replenished constantly.

Our more recent work has concentrated on the energy breakeven issue, and all the experiments described in this paper were performed in thermodynamically closed cells, where the gases from the electrolysis process were recombined by a catalyst within the cell. This eliminates the question of a possible uncontrolled contribution to the heat production due to partial recombination in open cells. It also avoids any complications related to the enthalpy carried out of the system by evolved gases. Thus this approach is conceptually less complex, and completely eliminates several of the issues and potential problems that have been raised by some of the critics of previous calorimetric measurements.

As mentioned later, we have also designed a new type of isoperibolic calorimeter that neatly eliminates earlier questions or hypotheses related to that mode of calorimetry. These include the possibility that temperature measurements might not be indicative of the actual experimental steady state power balance because of temperature non-uniformity due to insufficient stirring, differences in the locations of the heat sources and the temperature measurement device, or that calibration was performed under non-representative conditions. A detailed discussion of this new design is presented in another paper [5], and thus will not be included here.

2. THE ENERGY BALANCE

As stated above, the energy balance can be written as

$$\text{Net Energy} = \text{Energy Produced} - \text{Energy Consumed} \quad (1)$$

The experiments reported here were conducted using isoperibolic calorimetry. This is a two - compartment steady state power balance method in which heat is generated within one compartment, and is conducted through an intermediate thermally - conducting wall into the other compartment, which is maintained at a fixed lower temperature. Under steady state conditions, a temperature distribution is established in which the temperature difference across the thermally - conducting wall between the two compartments transports heat at a rate that just balances the power generated within the first compartment. Thus, measurement of the difference in the temperature of the two compartments ($T_1 - T_2$) provides information about the thermal power generated in the first compartment, P_{therm} , that is passed out as heat flux through the thermally - conducting wall into the second compartment. This can be expressed as

$$\text{Thermal power produced} = P_{\text{therm}} = K (T_1 - T_2) \quad (2)$$

where K is the calorimeter calibration constant.

The energy produced within an isoperibolic calorimeter system is the time integral of the thermal power, which is evaluated by measurement of the time dependence of the temperature difference between the two compartments, ($T_1 - T_2$).

In an electrochemical cell undergoing electrolysis with an applied voltage E_{appl} producing a current I_{appl} the power consumed is simply the product $E_{\text{appl}} I_{\text{appl}}$. In a thermodynamically open system under steady state conditions one divides the applied power into two terms, one a chemical term related to the thermodynamic properties of the electrolysis reaction, and the other a Joule heating term related to the passage of current across the several impedances in the system. This can be expressed as

$$P_{\text{consumed}} = E_{\text{appl}} I_{\text{appl}} = I_{\text{appl}} E^\circ + I_{\text{appl}}^2 (Z_c + Z_a + Z_g) \quad (3)$$

The value of E° is related to the standard Gibbs free energy change per mole ΔG° of the electrolytic reaction, by

$$E^\circ = \Delta G^\circ / 2 F \quad (4)$$

where F is the Faraday constant. Z_c , Z_a , and Z_e are the impedances at the cathode/electrolyte interface, the anode/electrolyte interface, and in the bulk of the electrolyte, respectively.

On the other hand, in a thermodynamically closed system in which the products of the electrolysis reaction are catalytically recombined within the cell, there is no net power invested in the chemical process, and the chemical term $I_{\text{appl}} E^\circ$ is eliminated.

The energy consumed under these steady state conditions is thus simply the time integral of the product $E_{\text{appl}} I_{\text{appl}}$, or of $I_{\text{appl}}^2 (Z_c + Z_a + Z_e)$.

However, in order to determine a proper total energy balance for the whole experiment, we also have to consider several other factors. As a result of the application of the electrical power to the system and the establishment of a new temperature distribution, an investment of sensible energy proportional to the heat capacity of the electrochemical cell and calorimeter is required. Therefore an additional term must be added to the total amount of energy consumed related to the heating of the electrochemical cell and calorimeter up to the temperature of operation. Likewise, any other process that causes a positive change in the cell and calorimeter temperature will consume sensible energy.

There also are additional processes whereby thermal energy is produced when electrolysis takes place upon a palladium cathode. These include the heat of solution when hydrogen or deuterium is inserted into the palladium, and if the concentration is sufficiently high, the enthalpy change related to the $\alpha - \beta$ phase transformation.

The magnitudes of these effects are relatively small, for example, 9.55 kcal/mole for the $\alpha - \beta$ transformation in the H-Pd case, and 8.55 kcal/mole in the D-Pd case [6], and they only contribute to the observed behavior when these particular processes are under way. As the diffusion of the guest species into the interior is relatively slow in the time span of a particular measurement, and the rate of this insertion reaction decreases with time (being approximately proportional to $t^{-1/2}$) this contribution to the power production becomes less and less important the longer the cell has been in operation.

If, in addition to these processes, there is some other phenomenon within the system (presumably within the cathode or upon its surface) that produces excess heat, it will provide an extra contribution to the thermal power, and thus to the production term in the energy balance.

$$Net\ Energy = \int_{t_1}^{t_2} K(T_1 - T_2)dt - \int_{t_1}^{t_2} (I_{appl} E_{appl})dt \quad (5)$$

3. EXPERIMENTAL ASPECTS

The electrochemical cell used in these experiments had a Pd cathode and either a Pt or Pd anode. The electrolyte was 0.1 molar LiOD or LiOH, and a dispersed platinum recombination catalyst was present to recombine the produced gases (Figure 1).

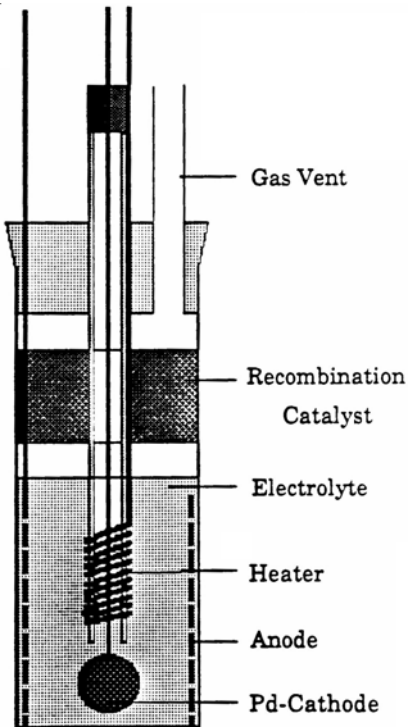


Figure 1. Electrochemical cell

This cell was mounted inside the concentric cylinder isoperibolic calorimeter described elsewhere [5] that was equipped with three redundant sets of differential thermocouple pairs for the measurement of $(T_1 - T_2)$. The calorimeter was imbedded in a large water bath in order to dissipate the power generated.

The palladium was obtained by arc melting pieces cut from a palladium crucible that contained an appreciable amount of hydrogen, and other possible impurities. In order to get rid

of such contaminants, the samples were re-melted at least 10 times, using an arc-melting apparatus with a water cooled tungsten electrode and a water cooled copper hearth, which acted as the other electrode. The environment was argon, and the procedure consisted of first melting some titanium sponge in order to getter species from the argon, such as oxygen, just prior to melting the palladium. After melting the palladium, the argon atmosphere was replaced, and the procedure repeated again. It was quite obvious from the change in the color of the arc during repeated melting that the impurity content of the palladium was gradually being changed. This process was repeated until re-melting caused no further visible change in the arc color.

The resulting palladium, in the form of a distorted sphere, was then mechanically converted into coin - shaped disks 2 - 3 mm thick and roughly 1 cm in diameter, with weights in the range of 2 to 3 grams each. Fine palladium wire was employed to hold the sample and act as the current collector.

The anodes were made either from approximately 2 meters of fine platinum wire or from a spiral length of thin Pd ribbon of equivalent surface area, and were coiled just inside the cell periphery.

Heavy water is a getter for light water, and therefore precautions were taken to prevent contact between the electrolyte and (moist) air or water, both during assembly and operation of the cells. The cell components were stored, as well as assembled and loaded into the cells, inside a dry nitrogen - filled glove box. All cells were connected to a one-way gas bubbler system containing silicone oil to allow the escape of unrecombined oxygen during the charging period without back flow of atmospheric gas.

Questions have been raised about possible errors in calorimetric measurements upon electrochemical cells in which electrolysis is taking place. The key issues have involved the calibration process whereby the value of K is determined, and the comparability of the measurements of T_1 and T_2 during the calibration and during the actual experiments.

Of special concern have been questions such as the influence of the physical locations at which heat is produced and at which the temperatures are measured in the two cases, and the magnitude of the stirring of the electrolyte fluid, which should have some influence upon thermal homogeneity.

In order to avoid these potential problems a new type of isoperibolic calorimeter was designed in which, under steady state conditions, essentially all the heat generated within the electrochemical cell passes to the external environment radially through a pair of concentric heavy aluminum cylinders that are separated by a well - defined thermal conduction layer. As a result, it is not necessary to measure the temperature either inside the electrochemical cell itself, or in a surrounding water bath. Instead, temperature measurements are made inside the two aluminum cylinders. Detailed information about the performance of this new calorimeter design, as well as documentation of the calibration procedure, are the subject of a separate paper [5].

The electrochemical cell, with an outer diameter of about 1.16 inches and a length of 4 inches. was placed into the calorimeter as shown in Figure 2. The inner (T_1) aluminum cylinder is 4 inches long, and the outer (T_2) cylinder is 7 inches long. The inner diameter of the T_1 cylinder is about 1.16 inches, and its outer diameter 2.0 inches. The inner diameter of the T_2 cylinder is 2.25

inches and its outer diameter is 3.0 inches. Thus the gap across which the heat conduction takes place, and the temperature difference measured, is 0.125 inches.

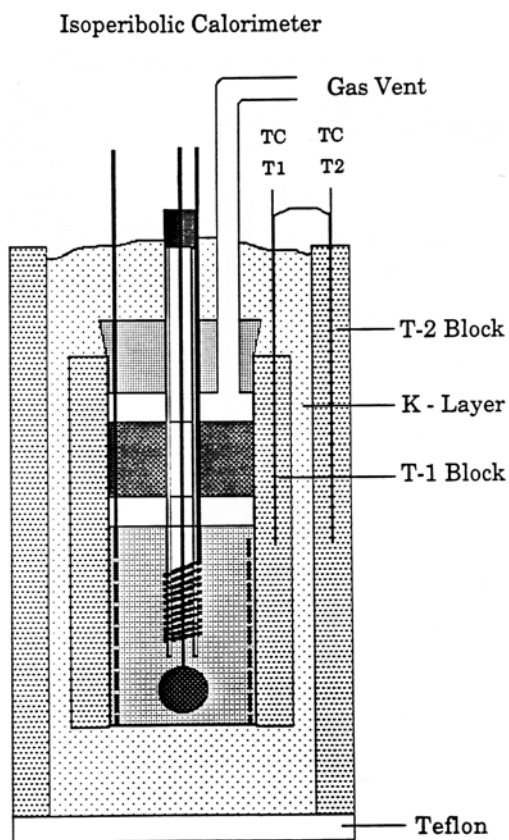


Figure 2. Electrochemical cell mounted in the concentric cylinder calorimeter.

The general calibration procedure involved the introduction of several levels of electrical power and the measurement of the temperature difference between the two aluminum cylinders ($T_1 - T_2$) in each case. Two different methods were employed in the experiments reported here. One involved the introduction of Joule heat by use of a resistive heater immersed within the cell electrolyte. The second made use of an internal electrolysis method and a three - electrode cell configuration.

The latter method was used in order to simulate the electrolysis process, with its attendant gas evolution and recombination during calibration. A special cell was designed that allowed electrolysis of the heavy water electrolyte at an additional cathode made of Pt wire and of equal surface area to the Pd cathode. This three electrode arrangement is shown in Figure 1. Our results confirmed those of Appleby et al. [7], based on microcalorimeter measurements, that heavy water electrolysis using a Pt cathode does not produce excess power. Therefore, conducting electrolysis with such an electrode within the cell itself serves as a blank and can be used for calibration of the calorimetric system.

This three electrode arrangement has a further advantage. The Pt cathode serves as a collector for impurities in the heavy water electrolyte, and may be especially useful if the calibration procedure is done before starting electrolysis on the Pd cathode.

Observation of the time behavior of the gas evolution through the bubbler system provided confirmation that there was no insertion of deuterium into the Pt, as would be indicated by the evolution of uncombined oxygen. When current was passed through the Pd cathode, gas was evolved, and observations showed that the rate decreased with time as the Pd cathode became saturated with deuterium.

Electrolysis was performed under controlled voltage, and all electrical and thermal measurements were monitored using a Macintosh data acquisition system controlled by Lab View software.

In total, eleven samples of palladium were prepared and measured in the way described above, but the results from only three will be reported here. One, designated as P2, was operated in an H₂O, rather than D₂O, electrolyte, and produced no excess energy. A second, P9, was operated in a D₂O electrolyte for 10 days, and produced a large amount of excess energy under quasi - steady state conditions. The third, P11, was prepared in a different way, and demonstrates a substantial “heat burst”. The sample history and specific data relating to these are shown in Tables 1-3.

TABLE 1: SAMPLE P2; HISTORY AND SPECIFIC DATA

Source	Engelhard*
Processing	Arc Melted in Argon 5-10 Times
Shaping	Deformed by Hammer Blows into “Fat Dime”
Weight	2.39 g
Pretreatment	-
Electrolyte	0.1M LiOH(Li ₂ O in H ₂ O)
Anode	Pt-Wire
Anode/Cathode Surface Area	7
Heater for Calibration	Resistive J-Tube Heater
Calibration	Before and During Electrolysis
Operation Mode	Constant Voltage
Cell Current	
Cell Power	2W
Excess Power	-
Excess Energy	-
Duration of Experiment	106 Hours or 4.4 Days

*Crucible used for Hydrogen Permeation Measurements in LiCl-KCl-LiH Molten Salt

TABLE 2: SAMPLE P9; HISTORY AND SPECIFIC DATA

Source	Engelhard 3.125 mm Wire
Processing	Arc Melted in Argon 5-10 Times
Shaping	Deformed by Hammer Blows into "Fat Dime"
Weight	3.055 g
Pretreatment	Precharged with D2 electrochemically
Electrolyte	0.1 M LiOD (Li ₂ O in D ₂ O)
Anode	Pd Ribbon
Anode/Cathode Surface Area	10
Heater for Calibration	Pt Wire Electrode (0.01", 24 cm)
Calibration	Before and During Electrolysis
Operation Mode	Constant Voltage 14 - 23 V
Cell Current	1-1.3 A
Cell Power	14, 20, 23, 25, 30 W
Excess Power	6-7%
Excess Energy	22,500 kJ / mole Pd 2,537 kJ / cm ³ Pd
Duration of Experiment	240 Hours or 10 Days

TABLE 3: SAMPLE P11; HISTORY AND SPECIFIC DATA

Source	Engelhard 3.125 mm Wire
Processing	Arc Melted in Argon 5- 10 Times
Shaping	Deformed by Hammer Blows into "Fat Dime"
Weight	3.29 g
Pretreatment	Precharged in D ₂ Gas
Electrolyte	0.1M LiOD (Li ₂ O in D ₂ O)
Anode	Pd Ribbon
Anode/Cathode Surface Area	14
Heater for Calibration	Pt Wire Electrode (0.01", 24 cm)
Calibration	During Electrolysis
Operation Mode	Constant Power: 2, 10, 20 W
Cell Voltage	10 - 30V
Excess Power	1 - 3 %, 56 % burst (30 min)
Excess Energy	7, 200 kJ / mole Pd 812 kJ/ cm ³ Pd
Duration of Experiment	210 Hours or 8.75 Days

4. EXPERIMENTAL RESULTS

The time dependence of the energy balance of the cell that contained sample P2 and had a light water electrolyte is shown in Figure 3. It is seen that, after the initial transient period the energy input and output remained essentially balanced over a period of 106 hours.

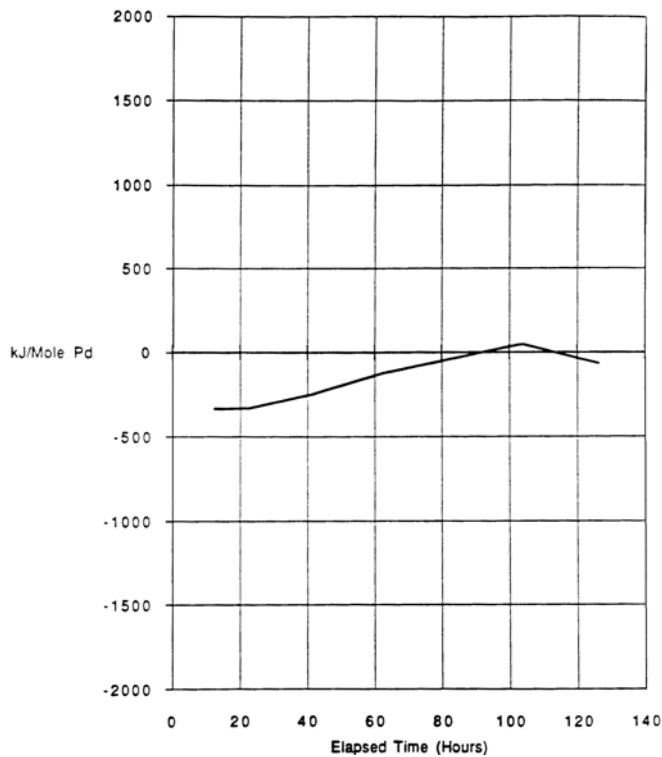


Figure 3. Time dependence on the net energy in a light water cell.

Sample P9, which was run in the D_2O electrolyte, showed very different behavior, with the production of a large amount of excess energy over a period of 10 days.

Figure 4 shows both the power and energy balances during the early part of the electrolysis. It is seen that there is an initial energy investment or deficit of roughly 500 kJ/mole of Pd during the first hour of operation. This resulted mostly from the energy consumption necessary to heat the cell and calorimeter mass to the equilibrium operating temperature. There are also two other contributions at the start. One is due to the insertion of deuterium into the palladium cathode, which is exothermic, and the other is an endothermic effect due to the loss of enthalpy in the cell due to the evolution of unrecombined oxygen. This unbalanced oxygen, which amounted to about 100 ml at a D/Pd ratio of 0.6 for this 3.055 gm sample, escaped from the system through the bubbler.

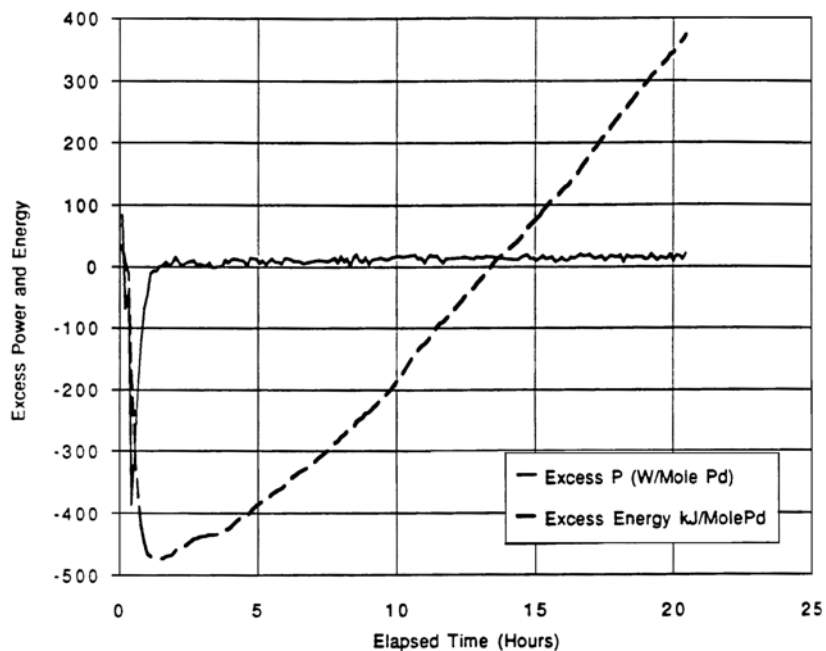


Figure 4. Time dependence of the excess power and net energy for sample P9 during the early stages of electrolysis.

After this initial energy investment, the cell began producing excess power at a low, but gradually increasing rate, and reached energy breakeven after about 13 hours. Thereafter, the energy balance became increasingly positive.

As shown in Figure 5, this cell produced a total of 22.5 MJ/mole of Pd excess energy in a quasi - steady state reaction over the following 10 days. If one compares this total excess energy output to the initial investment of about 0.5 MJ/mole, we see that it indicates a factor of 45 over energy breakeven.

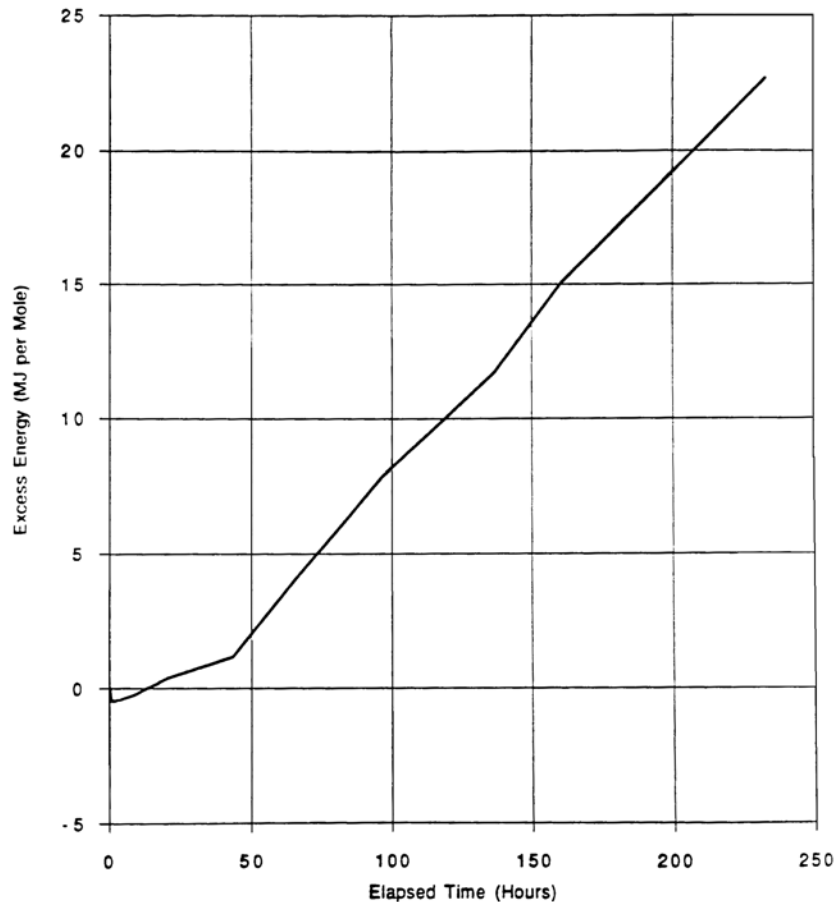


Figure 5. Time dependence of the net energy for sample P9.

The other sample, P11, was treated in about 1 atm. D_2 gas at 400 °C for several hours and cooled in this D_2 atmosphere to room temperature. It was then inserted into a heavy water electrochemical cell with a Pd anode and a Pt cathode heater and put into the calorimeter. The calibration was done using the Pt wire cathode, and was performed during electrolysis on the Pd cathode, so the sample did not sit in the electrolyte without a negative potential applied for any appreciable time.

The energy balance profile of sample P11 is shown in Figure 6. The initial energy investment is similar to that of sample P9, but the level of excess power production was much lower. It took about 17 hours to reach energy breakeven. Somewhat later, after about 18.5 hours of operation, there was a sudden increase in excess power, giving rise to a sharp increase in the slope of the energy balance profile, as shown in Figure 6. This “thermal excursion” is shown in more detail in Figure 7, in which the excess power, as indicated by two sets of differential thermocouples (whose data were so close that they are shown on top of each other), and the applied power are plotted versus the elapsed time.

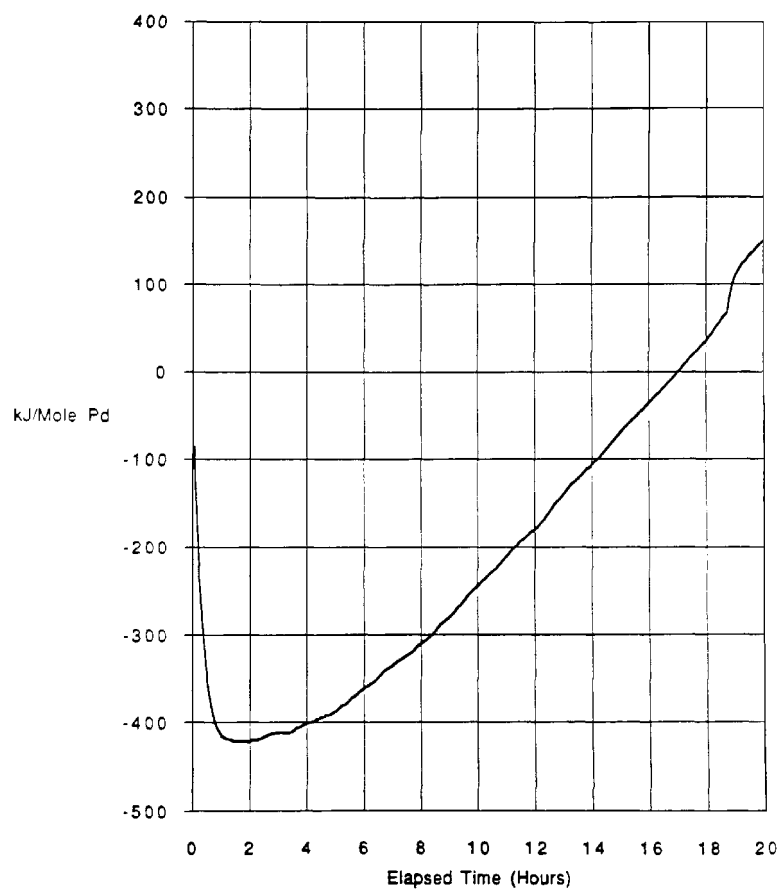


Figure 6. Time dependence of the net energy for sample P11 during the early stages of electrolysis.

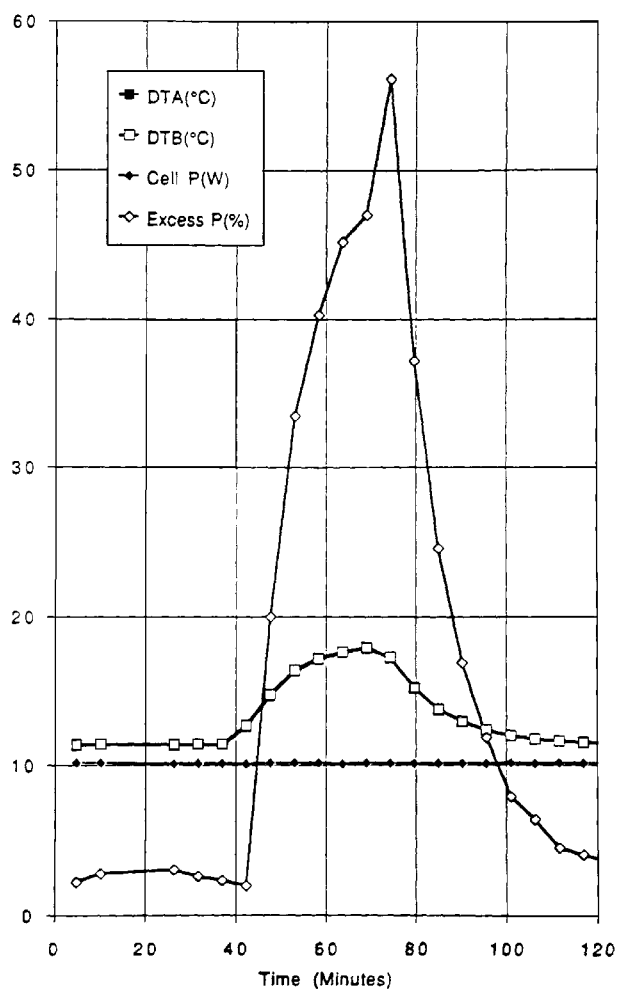


Figure 7. Time dependence of the temperature, applied cell power, and apparent excess power during a thermal excursion in sample P11.

Also shown is the apparent percent excess power during this period. However, one should not literally believe the time dependence of the excess power shown in this figure as a true measure of what was occurring, because of the thermal mass of the cell and calorimeter system, and the associated sensible heat absorption and time delay.

The magnitudes of these observations are substantial. The cell temperature went through an excursion over a period of about an hour, with a maximum temperature rise of about 7 °C. The apparent excess power rose to over 50 % of the input power. The energy released during this “heat burst” amounted to about 290 kJ/mole or 32 kJ/cm³ Pd. During the first 9 days of operation P11 produced a total of about 7 MJ/mole Pd excess energy.

5. SUMMARY AND DISCUSSION

A direct comparison has been made, using careful calorimetric techniques, of the behavior of the light water (H₂O) - palladium system and the heavy water (D₂O) - palladium system under conditions in which electrolysis was taking place at high rates and the gases produced were internally recombined within the cell.

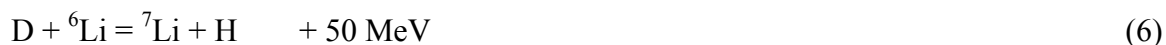
Experimental results demonstrate that it is possible to obtain substantial amounts of excess energy production as well as excess power generation in such thermodynamically “closed” electrochemical cells when deuterium is inserted into palladium. Similar experiments with light water and hydrogen insertion do not produce either excess energy or excess power. These conclusions are similar to those reached earlier [2-4] with similar, but thermodynamically “open” cells.

Of equal, or perhaps greater importance, these experiments have also demonstrated that it is possible to generate large amounts of excess energy, far above breakeven, in the deuterium - palladium case.

Our calorimetric measurements give no information about the mechanism causing the generation of this excess power.

One of the major problems in this “cold fusion” area at the present time is the apparent lack of evidence for some product that could verify that there is a process taking place that causes the production of the experimentally observed large values of excess power and energy, and give some guidance concerning its nature. Efforts have been undertaken in many laboratories to look for either radiation products or chemical products.

Because of the limitations of analytical methods, the observation of chemical products is especially difficult. Let us consider two possible examples to illustrate this. For example, if the important reaction were either of the following:



one might look for decreases in the amount of ⁶Li or enhancements in the amounts of ⁷Li or ⁴He.

If we recall that 1 MeV is 1.603 x 10⁻¹³ Joules, we can calculate the number of events that would have been necessary to produce the 22.5 MJ per mole of excess energy observed from sample P9. In the case of reaction (6) this would require about 2.8 x 10¹⁹ events per mole of Pd, whereas if reaction (7) were relevant, it would require about 6.27 x 10¹⁸ events per mole of Pd. If we convert these numbers to events per cm³ of Pd, we have 3.167 x 10¹⁸ events per cm³ for reaction (6), and 7.066 x 10¹⁷ events per cm³ for reaction (7).

The natural abundance of ⁶Li in Li is about 7.5 %, and measurements of the ratio of ⁶Li to ⁷Li generally have an accuracy of 5 to 10 %, or 0.75 % of the total lithium present. Thus if a sample of palladium had a total lithium concentration of 1 %, or 6.79 x 10²⁰ Li atoms per cm³, the ⁶Li analysis would have an accuracy of about 5.1 x 10¹⁸ ⁶Li atoms per cm³.

Compare this with the estimated ${}^6\text{Li}$ atom concentration in sample P9 if reaction (6) were occurring, of 3.167×10^{18} ${}^6\text{Li}$ atoms per cm^3 . If reaction (7) were occurring, the resulting ${}^6\text{Li}$ concentration would be 7.066×10^{17} ${}^6\text{Li}$ atoms per cm^3 .

Thus we see that if ${}^6\text{Li}$ were a major reactant, the detection of a change in its concentration would be quite difficult.

Measurements were undertaken to evaluate the content of ${}^4\text{He}$ in sample P9, and concentrations well below the values discussed here were found. Therefore, we tentatively conclude that reaction (7) did not play a substantial role in the heat generation process taking place in that case.

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