

Two Fast Mixed-Conductor Systems: Deuterium and Hydrogen in Palladium—Thermal Measurements and Experimental Considerations¹

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1. INTRODUCTION

Martin Fleischmann and Stanley Pons announced on March 23, 1989 that they had performed electrochemical experiments involving the insertion of deuterium into palladium that produced excess heat generation, neutrons, gamma rays, and tritium. They claimed that these experimental observations could not be explained by any known chemical or electrochemical effect, and must be due to some previously unrecognized form of atomic fusion. This announcement, made after receiving confirmation of the acceptance of a reviewed paper, which appeared in the *Journal of Electroanalytical Chemistry* roughly two and a half weeks later,⁽¹⁾ received an immense amount of attention, for if found to be correct, it might represent a very important breakthrough in the search for a source of energy that is widely available, relatively inexpensive, and not accompanied by severe radiation hazards or environmental pollution.

Activities were quickly undertaken in a large number of laboratories throughout the world, and reports soon appeared that similar phenomena had been observed by some, whereas a number of other laboratories indicated that they could not reproduce the Fleischmann-Pons experiments. The result has been a good measure of skepticism in parts of the scientific community, par-

ticularly among those who had long been pursuing entirely different, difficult, and expensive alternative approaches to the possibility of generating usable power through atomic fusion processes.

There are three major questions to be resolved. The first is the existence question. Is anything unusual actually happening when deuterium is inserted into palladium at very high negative potentials by the use of electrochemical methods, or were the Fleischmann-Pons experiments or interpretation somehow flawed?

The second is the reproducibility question. Why do some people apparently observe one or another of these effects, and some evidently do not, and why do some samples and experiments seem to produce different results from others, even in the same laboratory?

The third major question is related to the satisfactory resolution of the first two, and has to do with the matter of mechanism. What is causing these observed effects, and is the relevant phenomenon related to some nuclear fusion reaction?

The experiments reported in this paper were designed to provide a direct comparison of the thermal behavior during electrolysis of the deuterium-palladium system with that of the chemically and metallurgically similar hydrogen-palladium system under comparable experimental conditions, by the careful use of conventional calorimetric methods.

Except for neutron and gamma ray monitors used for safety purposes, no radiation detection or reaction product measurements were undertaken in this work.

In addition to reporting the results of these experiments, some comments will be made concerning some

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of the experimental issues that may have an influence upon the problem of reproducibility among various laboratories.

2. EXPERIMENTAL ASPECTS

Experiments 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 will be 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

$$\text{Thermal power generated} = P_{\text{therm}} = K_{\text{clr}} (T_1 - T_2) \quad (1)$$

where K_{clr} is the calorimeter calibration constant. As will be shown later, the thermal power generated P_{therm} is not equal to the applied electrical power P_{appl} in the case of a reaction involving a change in the enthalpy of the system.

Our experiments were conducted such that the first compartment consisted of an electrochemical cell that was operated at a sufficient voltage that electrolysis of the D_2O , in the one case, or H_2O in the other, took place. This involved the passage of electric current through these cells, and the generation or absorption of heat related to the various effects that occurred within them. The major effect is the joule heating due to the passage of ionic current through the electrolyte as well as across the two electrode/electrolyte interfaces, which each have impedances related to the various microscopic processes that occur at them. There are also other possible endothermic and exothermic phenomena which can occur and contribute to the overall power balance, as will be discussed later.

The electrochemical cell was placed inside a large cold water bath that was well stirred in order to maintain its temperature relatively constant, and which acted as the second compartment. The intermediate thermally-

conducting wall thus was the glass container surrounding the electrochemical cell.

Two closely comparable electrochemical cells were employed, one containing a 0.1-M solution of LiOH in light water (H_2O), and the other a 0.1-M solution of LiOD in D_2O as electrolytes. Each also contained a resistance heater for calibration purposes, and a protected thermocouple for temperature measurements. There was also a thermocouple to measure the temperature of the surrounding water bath.

The electrochemical cells were completely immersed under the surface of the waterbath in order to reduce the possibility of heat escaping directly into the atmosphere, rather than through the cell wall into the bath, the second compartment in this arrangement.

Voltages in the range 3–15 V were applied to the cells, and the observed currents varied between 10–1000 mA. The temperature differences between the cells and the surrounding water bath ranged up to about 10°C.

The palladium that was used for these experiments was obtained by arc melting pieces cut from a palladium crucible that had previously been used as a hydrogen-transporting membrane in a molten salt environment (LiCl-KCl-LiH) at approximately 400°C for a long period of time. This material surely contained an appreciable amount of hydrogen, and possibly other species, such as lithium, as well. In order to get rid of such species, the samples were re-melted at least 10 times, using an arc-melting apparatus with a water-cooled tungsten electrode. The samples sat on a water-cooled copper hearth, and 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 no longer caused visible changes in arc color.

The resulting palladium, in the form of a distorted sphere, was then mechanically converted into coin-shaped disks 2–4 mm thick and roughly 1 cm in diameter, with weights in the range of 1–2 grams each. Fine gold wire was employed as the current collector.

The anodes were made from approximately 2 meters of fine platinum wire, and were coiled just inside the cell periphery in order to be as far away as possible from the palladium samples, which were attached by gold wire to the calibration heater in the center of the cell. The separation of anode and cathode was deliber-

ate, so that there would be little direct mixing of the evolved gases as they were emitted from the electrode surfaces.

Hydrogen acts as a poison in a system of this type because of its rapid ion exchange and preferential absorption inside palladium, as discussed later. Therefore precautions were taken to prevent contact between the palladium 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 nitrogen-filled glove box in order to reduce contact with the air and to make sure that there was no residual air within the cell after assembly. Gases were allowed to exhaust from the cell through a simple one-way bubbler system containing silicone oil.

Initial calibration of each of the electrochemical cell-calorimeter configurations was done by supplying different amounts of electrical power to the internal heaters within each of the cells, and observing the difference in temperature between the cells and the external waterbath ($T_1 - T_2$) under steady-state conditions at each of the heater power values. It was found that the characteristic relaxation time of this type of calorimeter design was of the order of 15–20 minutes, both when the power was increased and when it was decreased.

A number of people have pointed out possible errors that might occur when doing this type of calorimetry, and special attention was made to be sure that these were not present in this work. One of the issues that was raised is the possibility that insufficient stirring may occur within the electrochemical cell, so that there is a non-reproducible temperature distribution within it, leading to a non-reproducible value of T_1 , and thus of ($T_1 - T_2$) across the thermally-conducting wall separating the two compartments. This might lead to problems with calibration.

In an electrolysis experiment of this type, the rate of electrolysis is directly proportional to the current, and at appreciable currents, such as those involved in these experiments, there is a large amount of gas evolution. The gas bubbles provide vigorous gas pumping of the liquid electrolyte, and therefore rapid convective mixing. The impressive magnitude of this was demonstrated by Fleischmann and Pons in a videotape that they showed at the Los Angeles meeting of the Electrochemical Society in May, 1989.⁽²⁾

In order to be sure that there was sufficient stirring in the experiments reported here, this gas pumping mechanism was supplemented by the use of mechanical stirring. This was accomplished by mounting both cells, the one containing heavy water and the other containing light water, in a gyrotary waterbath shaker of the type

commonly used in biological laboratories. This provided additional mechanical motion, and therefore stirring, both within the cell and in the external waterbath.

The rate of motion in such devices can be varied over an appreciable range. Measurements were made with different levels of this additional mechanical stirring. Data were taken under conditions where no additional stirring had any significant effect upon the measured temperatures.

It has also been pointed out by others that it is possible that the calorimeter calibration constant may vary with the magnitude of the heat flux. In order to avoid this possible problem, calibration measurements were made over the whole range of electrolysis power level. This was accomplished by adding to the electrolysis power three different values of additional heater power for each data point. By measuring the change in ($T_1 - T_2$) as a function of the additional electrical power supplied to the heater, one can determine the calibration constant over a specified range of total input power in the presence of the convective stirring. Thus, every data point that was obtained was accompanied by a direct calibration of the calorimeter.

During electrolysis experiments, in addition to the exothermic dissipative losses (joule heating) due to the electrolyte and interface impedances mentioned earlier, there are other phenomena which can occur, some of which are endothermic, and some of which are exothermic.

If we introduce power to the cell electrically by passing current I_{appl} at voltage E_{appl} , the power applied to compartment 1, the cell, is

$$P_{\text{appl}} = E_{\text{appl}} I_{\text{appl}} \quad (2)$$

If we have only a simple resistive impedance Z_R in the cell,

$$E_{\text{appl}} = I_{\text{appl}} Z_R \quad (3)$$

and the applied electrical power is all converted to thermal power

$$P_{\text{appl}} = P_{\text{therm}} = I_{\text{appl}}^2 Z_R. \quad (4)$$

Under steady-state conditions, this thermal power generated in the cell passes across the thermally-conducting wall, and from Eq. (1)

$$P_{\text{appl}} = P_{\text{therm}} = I_{\text{appl}}^2 Z_R = K_{\text{clr}} (T_1 - T_2) \quad (5)$$

However, in an electrochemical cell passing current so that electrolysis is taking place, we must take cognizance of the thermal effects of that process. We can divide the externally applied voltage across the cell into

several parts, a chemical term, and a purely resistive term

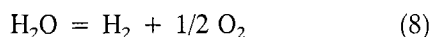
$$E_{\text{appl}} = E^{\circ} + I_{\text{appl}} (Z_c + Z_a + Z_e) \quad (6)$$

where E° is the equilibrium thermodynamic voltage due to any difference in the chemical potentials at the two electrodes, and 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. The products I_{appl} , Z_c , and $I_{\text{appl}} Z_a$ are often called overvoltages in the electrochemical literature.

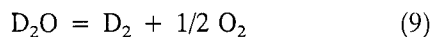
The applied electrical power can therefore be written as

$$P_{\text{appl}} = I_{\text{appl}} E^{\circ} + I_{\text{appl}}^2 (Z_c + Z_a + Z_e) \quad (7)$$

In experiments that involve the electrolysis of H_2O or D_2O , the values of E° are related to the reactions



and



respectively, and each can be related to the respective standard Gibbs free energy change per mole ΔG° , following the convention that E° is positive in an electrolytic reaction, by

$$E^{\circ} = \Delta G^{\circ} / 2 F \quad (10)$$

where F is the Faraday constant. Furthermore, the Gibbs free energies can be divided into their enthalpic and entropic components:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \quad (11)$$

where ΔG° , ΔH° , and ΔS° are all positive. We can thus write from Eq. (7) that

$$P_{\text{appl}} = I_{\text{appl}} (\Delta H^{\circ} - T \Delta S^{\circ}) / 2 F + I_{\text{appl}}^2 (Z_c + Z_a + Z_e) \quad (12)$$

The enthalpy change can be converted to an associated voltage, the thermoneutral voltage E_{in} , which is the voltage that can be applied across the electrochemical cell that causes no heat evolution, and thus neither generates nor consumes heat as a result of the chemical reaction taking place. It is also the open circuit voltage of the electrochemical cell at 0 K.

$$\Delta H^{\circ} = 2 F E_{\text{in}} \quad (13)$$

Thus, we can rewrite Eq. (12) as

$$P_{\text{appl}} = I_{\text{appl}} E_{\text{in}} - I_{\text{appl}} (T \Delta S^{\circ}) / 2 F + I_{\text{appl}}^2 (Z_c + Z_a + Z_e) \quad (14)$$

From elementary thermodynamics, one can relate the enthalpy change of a system ΔH to the difference between electrical work done on it and the heat evolved. Thus, in the presence of electrolysis, the thermal power generated will be less than the electrical power introduced. This can be expressed as

$$P_{\text{therm}} = P_{\text{appl}} - I_{\text{appl}} E_{\text{in}} \quad (15)$$

or

$$P_{\text{therm}} = I_{\text{appl}} (E_{\text{appl}} - E_{\text{in}}) \quad (16)$$

The values of ΔH° for such reactions are essentially independent of temperature, and are reported to be + 286 kJ/mol for the electrolysis of H_2O , and + 297 kJ/mol for the electrolysis of D_2O .⁽³⁾ Thus, the values of E_{in} are 1.48 V and 1.54 V, respectively.

Thus, we see that the positive values of ΔH° in the reactions of Eq. (8) and (9) mean that a cell in which such reactions are occurring should be generating less heat than an identical cell containing only resistive components by an amount corresponding to the value of $I_{\text{appl}} E_{\text{in}}$, and

$$P_{\text{therm}} = - I_{\text{appl}} (T \Delta S^{\circ}) / 2 F + I_{\text{appl}}^2 (Z_c + Z_a + Z_e) \quad (17)$$

The thermal power generated is thus the result of entropic cooling and joule heating. It is important to note that the latter is related to the sum of the impedances in the cell, and the distribution between them is of no consequence.

If, in addition to the endothermic electrolysis phenomenon and the exothermic resistive behavior included in equation (17), there were some other phenomenon present in the cell that produced thermal power, P_{int} , it would add an additional term, giving

$$P_{\text{therm}} = - I_{\text{appl}} (T \Delta S^{\circ}) / 2 F + I_{\text{appl}}^2 (Z_c + Z_a + Z_e) + P_{\text{int}} \quad (18)$$

and therefore an increase in $(T_1 - T_2)$ over that for the case of only endothermic electrolysis and exothermic resistive behavior given in Eq. (17) for any level of P_{appl} , in accordance with Eq. (1).

Additional endothermic phenomena will, of course, provide a negative value of P_{int} , and decrease the measured temperature in the electrochemical cell, and therefore $(T_1 - T_2)$. Any heat leakage that does not go through the thermally-conducting wall into the second compartment (the external waterbath) will also lead to a reduction in the temperature of the electrochemical cell compartment relative to what would be the case if only resistive phenomena were present. This could include

heat transport up wires, tubing, electrical connectors, etc. In addition, any sensible heat carried out of the cell by the gases evolved, entrained liquid, and the evaporation of the solvent (H_2O or D_2O) could contribute endothermically to the observed behavior.

In addition to the resistive components in Eq. (17), other exothermic phenomena can also be present related to chemical phenomenon taking place within the cell, and contribute positively to P_{int} . One of these is the heat of solution when hydrogen or deuterium is inserted into the palladium, and the enthalpy change related to the α - β phase transformation. The magnitudes of these effects are relatively small, 9.55 kcal/mole for the α - β transformation in the H-Pd case, and 8.55 kcal/mole in the D-Pd case⁽⁴⁾ and only contribute to the observed behavior when these particular processes are underway. As the insertion into the interior is relatively slow in the time span of a particular measurement these produce only relatively small effects in comparison to the large thermal effects of the electrolysis phenomenon itself. In addition, the rate of the insertion reaction decreases with time (approximately proportional to $t^{-1/2}$) and so this effect becomes less and less important the longer the cell has been in operation.

Any corrosion reactions that are present and operate at appreciable rates will also contribute exothermically to the system, as will the mechanical energy input through the stirring mechanism. Both of these were of essentially no consequence in the experiments described here.

Any recombination of the hydrogen (or deuterium) and oxygen gases that are formed by the electrolysis reaction, either within the electrolyte or in the adjacent gas phase, would contribute exothermally. As will be mentioned shortly, the experimental evidence is very strong that the amount of recombination that occurs in cells of this type operated in this manner is trivial.

It is important to remember that no exothermic effects related to the reversal of the primary electrolysis cell reaction can be larger than the endothermic effects of the reaction itself. Therefore, one cannot get more heat from recombination than that which was absorbed by the electrolysis reaction. It is thus impossible for any recombination reaction related to the electrolysis phenomenon to give a thermal power output greater than that which would be obtained by passing current through a simple resistive heater.

One can readily predict the difference between a cell that only has simple joule heating, and one in which endothermic electrolysis is taking place, as indicated, and compare the results with experimental measurements. This has been done in a number of cases and it has been found that the measured endothermic effect

related to the electrolysis is within a few percent of that which is calculated from Eq. (15).

In the experiments reported here, the lack of appreciable recombination has been verified for both the light water cells and those containing heavy water. In the latter case, measurements were made immediately upon the introduction of a fresh palladium cathode into the cell, so that there would be no confusion from any phenomenon that might relate to the presence of appreciable amounts of deuterium in the palladium.

The good correspondence between the measured and predicted differences in behavior of these cells during electrolysis from what was observed with power put in through the calibration heaters means that the amount of recombination, or any other exothermic phenomenon present, must be very small in comparison with the major processes that are occurring.

The assumption made by a number of critics of calorimetric experiments that a significant amount of recombination must be occurring, and providing false indications of exothermic behavior, is just not born out by the experimental results.

3. EXPERIMENTAL RESULTS

Figure 1 shows the relation between the thermal power out through the calorimeter system as a function of the amount of applied electrical power for a cell containing light water. The top curve represents the data obtained when the power was put into the electrochemical cell by the use of only the calibration heater. The lower curve shows data obtained when the power was put into the electrochemical cell by passing current between the electrodes. The output thermal power can be seen to be lower in the latter case because, superimposed upon the joule heating related to the passage of the electrical current through the system, there is the associated endothermic electrolysis cooling. The lower curve has data points taken at two different times, when the experiment was first initiated, and approximately 30 hours later. It is seen that there is essentially no time dependence to this behavior.

On the other hand, in experiments in which heavy water was present, the thermal behavior under electrolysis conditions was found to vary with time. This is illustrated in Fig. 2, which shows the temperature difference between the two compartments of the calorimeter system with the heavy water cell as a function of applied electrical power for three situations. The data on the middle line are those obtained when the electrical power was applied to the calibration heater. The data on

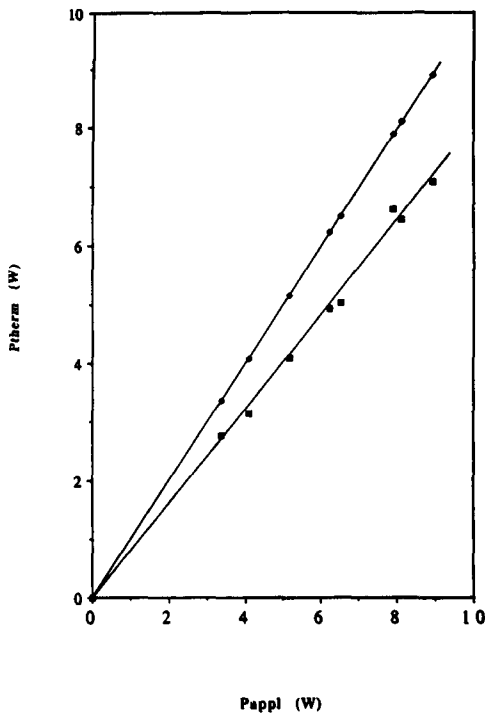


Fig. 1. Data showing the time-independence of the endothermic influence of electrolysis in an H - Pd cell. The upper data were from heater calibrations, and the lower data, obtained under electrolysis conditions, were from two experiments 30 hours apart.

the lower line are those which were obtained initially when a fresh piece of palladium not containing deuterium was inserted into the cell and the electrolysis reaction was made to occur. One sees that the endothermic behavior related to electrolysis was initially present in this case, as was the situation with the light water illustrated earlier.

However, it was found that over a period of time the temperature in the electrolysis cell rose relative to its initial value when heavy water was present, in contrast to the light water case. The data on the upper line are those which were obtained after electrolysis had been under way for 66 hours. This indicates that there was some other process taking place, generating heat, and giving P_{int} a positive value.

In this case, at any applied electrical power level, the thermal power out had increased beyond that observed when electrical power was applied to the resistive calibration heater. This means that under these conditions, P_{int} was greater than $I_{appl} E_{int}$, and the electrochemical cell was producing excess power P_{exc} above

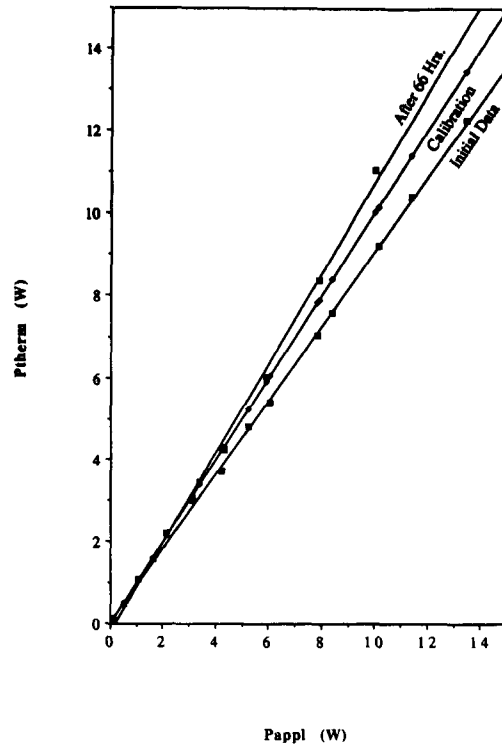


Fig. 2. Variation of the relation between the thermal power output P_{therm} and the applied electrical power P_{appl} of a D - Pd cell with time. The data on the middle line were from the heater calibrations, those on the lower line were obtained shortly after the introduction of a fresh sample of palladium, and those on the top line were measured 66 hours later.

and beyond that which was being input electrically, P_{appl} . That is,

$$P_{exc} = P_{therm} - P_{appl} = P_{int} - I_{appl} E_{int} \quad (19)$$

was greater than zero.

Thus, the cell in which an appreciable amount of deuterium had diffused into the palladium had an additional exothermic phenomenon present producing P_{int} that was not observed in the case of the light water cell where hydrogen was inserted into the palladium.

Note that this definition of excess power is different from that which has been used by some authors, for it involves a comparison with the electrical power input. In some other cases, the value of P_{int} , which is a measure of the effect of an additional internal heat generation process, is described by the term "excess power."

Measurements have been taken of the ratio of power out P_{therm} to the power supplied electrically P_{appl} at var-

ious values of time after the insertion of a fresh palladium electrode.

$$P_{\text{therm}}/P_{\text{appl}} = (P_{\text{appl}} + P_{\text{exc}})/P_{\text{appl}} \quad (20)$$

Data are shown for two different D-Pd cells in Fig. 3. At the beginning, one sees the electrolysis cooling effect, but this is gradually overcome with time by an additional phenomenon that produces P_{int} , so that after about 60 hours we see that P_{exc} becomes greater than zero, and the thermal power evolved P_{therm} is greater than the electrical power applied P_{appl} .

To date, we have run four sets of light water/heavy water comparisons. In every case, we have seen no time dependence to the behavior of the light water cell, in which hydrogen is inserted into the palladium. In the heavy water cells, with deuterium insertion into the palladium, we always observe a time-dependent generation of additional power P_{int} above that which is due to the exothermic joule heating and the endothermic electrolysis process. Over time, the values of thermal power out of the cell come to exceed the electrical power input, so that the value of P_{exc} becomes positive.

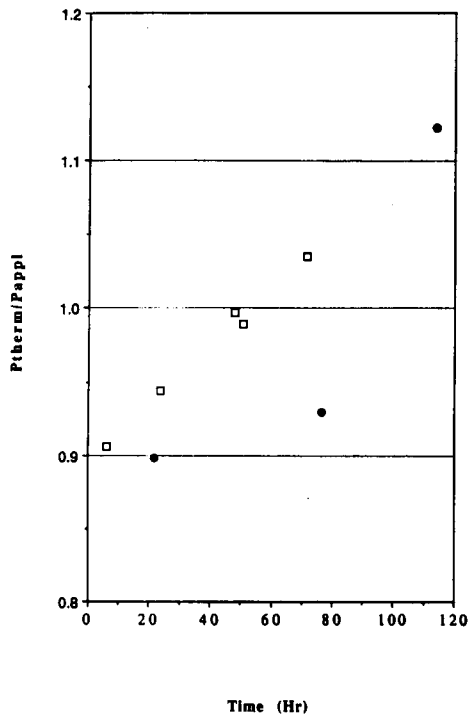


Fig. 3. Longer term time dependence of the ratio of thermal power output P_{therm} to electrical power input P_{appl} for two different D - Pd cells.

4. SOME EXPERIMENTAL CONSIDERATIONS

As mentioned at the beginning of this paper, one of the important problems with research in this area at the present time has to do with reproducibility. Not only is there a disparity between what people in various laboratories have reported but there is also a lack of consistency among different experiments in the same laboratory in some cases. We certainly do not understand the critical features that are the source of these problems at the present time. However, it may be useful to point out several features of these materials and types of experiments that might have some bearing upon such questions.

The microstructure and chemical composition of the palladium may be important. There may be important differences between palladium samples that have been prepared or treated in different ways; some have been cast, followed by various types and degrees of mechanical deformation, others have been annealed under various conditions. Perhaps the dislocation structure or grain size are important. It is well known that dislocations and grain boundaries are important traps for hydrogen in many metals. The fact that they also act as traps for other interstitial species which can competitively occupy interstitial sites in the palladium crystal structure may be important. While we have no direct evidence, it is our assumption that this may be a critical issue, and it is one of the reasons why we have repeatedly arc melted our palladium samples to reduce the initial concentration of hydrogen and other volatile impurities.

A number of species that may be in the electrolyte, either initially present, or that enter it during the operation of the electrolysis cell, may form blocking layers on the palladium surface, and a number of investigators have reported the observation of species electrodeposited on the cathode surface.

We have observed that the cell resistance increases appreciably after certain treatments, and have also noted that there are blocking species on the palladium surface under some conditions. This can be readily observed by looking at the gas evolution if the cell voltage is reduced or turned off for a short time. Since the cell voltage determines the concentration of hydrogen or deuterium in the surface of the palladium, a reduction in cell voltage allows the diffusion of these species out into the electrolyte, where they form a readily observable gas bubble cloud. If no gas evolves under such a condition, there must be a layer on the surface blocking the exit of hydrogen (or deuterium). Such a layer will, of course,

and therefore also block further ingress of them into the interior.

It is also interesting to consider the possible influence of the presence of carbon in the palladium. Palladium is prepared in various ways by different commercial producers. In some cases, it is melted in carbon or graphite crucibles; in others, it is cast into carbon or graphite molds. One sees from the palladium-carbon phase diagram that molten palladium dissolves at least 2.45 weight percent carbon. Upon cooling, there is a eutectic reaction at about 1500°C. The reaction products are palladium with a rather low carbon content, and graphite. Upon slow cooling, this graphite may be present as rather large particles, whereas with more rapid cooling, the particle size will be much smaller. This may be important, for it is known that graphite tends to react with hydrogen (or deuterium) in solid solution within a number of metals at elevated temperatures to form methane, CH₄.

The standard Gibbs free-energy change for this reaction, if the carbon is in the form of graphite, is -12.1 kcal/mole at room temperature, so that there is a driving force tending to cause it to occur. This would consume some of the hydrogen (deuterium) that enters the palladium, thus slowing down the insertion process. It would also drastically reduce their activities, influencing both the local solute concentration and the diffusion kinetics.

This phenomenon is directly analogous to the well-known process of internal oxidation of solutes with a high affinity for oxygen, another relatively mobile species. If the phenomenon that produces the excess power within the palladium requires high local concentrations of deuterium, the presence of carbon may be deleterious.

Another feature of these experiments that is probably important is the fact that pure heavy water is hygroscopic. It reacts irreversibly with light water under the conditions employed here to form HDO.⁽⁵⁾ H₂O is readily extracted from the humidity in the atmosphere.

It is also well known that hydrogen, rather than deuterium, is preferentially evolved during the electrolysis of D₂O/HDO/H₂O solutions.⁽⁶⁾ This is the basis for the use of electrolytic methods to concentrate D₂O. Likewise, hydrogen, rather than deuterium, is preferentially absorbed into palladium.⁽⁷⁾ Thus, the presence of hydrogen-containing impurities in the heavy water-based electrolyte will lead to the formation of hydrogenated, rather than deuterated, palladium.

Consequently, care must be taken at all times to prevent the cell contents from coming into contact with atmospheric moisture, both during cell assembly and subsequent operation. As mentioned earlier, we assembled our cells in a dry nitrogen-filled glove box, and

prevented atmospheric contact during operation by the use of an oil-filled bubbler system.

We have observed the disappearance of excess power from an electrochemical cell containing heavy water after about 1 day of inadvertent exposure to a moist air atmosphere. Infrared spectroscopy of the electrolyte subsequently showed large concentrations of both H₂O and HDO to be present.

5. DISCUSSION

The main thrust of the work discussed here has been the direct comparison, 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. Under such conditions, hydrogen and deuterium are caused to enter the palladium crystal structure at high activities.

It was found that these two systems behaved quite differently. In the light water case, the electrochemical cell temperature was lower than that expected from joule heating alone, because of the endothermic electrolysis reaction taking place. This behavior was found to be independent of time.

On the other hand, the electrochemical system containing heavy water that was carefully protected against the presence of light water, showed different behavior. Initially, such electrochemical cells behave in a manner directly analogous to the light water case, showing the combination of joule heating and electrolysis cooling. However, with time, the cell thermal power output gradually increases, and after a number of days reaches values greater than the input electrical power.

These experiments thus demonstrate not only a different behavior in the case of the hydrogen-palladium system and the deuterium-palladium system, but also the generation of true excess power in the deuterium case. They are consistent with the claim of Fleischmann and Pons⁽¹⁾ of the observation of excess power generation in the deuterium-palladium system under electrolytic conditions. The magnitude of the effects observed here, of the order of 1-2 watts of excess power per gram of palladium, are comparable to those which they reported.

We have no information from our calorimetric measurements concerning the mechanism that is causing the internal generation of this excess power upon the electrolytic insertion of deuterium into palladium. However, the observations which have now come from several different laboratories of the generation of tritium in such

cells seem to be especially interesting, and deserve further consideration. If, indeed, tritium is an important product of the reaction occurring in these electrochemical systems that is producing P_{int} , it is an indication that some type of nuclear process must be taking place.

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REFERENCES

1. M. Fleischmann and S. Pons (1989). *J. Electroanal. Chem.* **261**, 301.
2. M. Fleischmann and S. Pons (1989). Presented at the meeting of the Electrochemical Society, Los Angeles, May.
3. I. Barin, O. Knacke, and O. Kubaschewski (1973/1977). *Thermochemical Properties of Inorganic Substances* (Springer-Verlag).
4. A. Maeland and T. B. Flanagan, (1964). *J. Phys. Chem.* **68**, 1419.
5. Gmelin. D_2O . *Handbuch f. Anorganische Chemie*.
6. B. Dandapani and M. Fleischmann (1972). *J. Electroanal. Chem.*, **39**, 323.
7. A. Sieverts and W. Danz (1937). *Z. Phys. Chem.*, **38B**, 46, 61.