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THESIS APPROVAL

The abstract and thesis of Christoph Zaczek for the Master of Science in Physics were presented July 03, 1995 and accepted by the thesis committee and the department.

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ABSTRACT

An abstract of the thesis of Christoph Zaczek for the Master of Science in Physics presented July 03, 1995.

Title: Electrolysis of Palladium in Heavy Water

Following several reports in the past few years about compositional changes on palladium used as a cathode in heavy water electrolysis, the purpose of this research project was to reproduce this results.

Two experiments were performed using two cells connected in series, an experimental cell and a control cell. Both experiments used platinum anodes, the experimental cell had a palladium cathode and the control cell had a platinum cathode. The electrolyte was D_2O with H_2SO_4 . Radiation was monitored during both experiments. Also temperature and voltage were recorded for both experiments, to allow statements about excess heat of the experimental cell in comparison to the control cell.

Both experiments had problems with unequal electrolyte loss, so that no statements about excess heat could be made.

No significant radiation was detected in either experiment.

Also no compositional changes on the palladium cathodes after electrolysis in both experiments could be detected.

Impurities in grain-shaped defects on the palladium cathode before the experiment were found in either experiment. These impurities were Si, Ca, O, and sometimes also Mg, Na and Fe.

Localized findings of Au and Pt, in a distance of 1-2 μ m to each other, were made on the palladium cathode from the second experiment before electrolysis.

Spot, grain-shaped and longitudinal defects were found on the original palladium foil used for the cathodes in either experiment

No evidence for fusion, or any other nuclear reaction in the crystal lattice of palladium, used as cathode in heavy water electrolysis, was observed.

ELECTROLYSIS OF PALLADIUM IN HEAVY WATER

by

CHRISTOPH ZACZEK

A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE
in
PHYSICS

Portland State University
1995

CONTENT

CHAPTER I

1. Introduction		1 - 2
2. Fundamentals		3 - 7

CHAPTER II

1. Experimental Setup		8 - 25
2. First Experiment		26 - 31
3. Second Experiment		32 - 44

CHAPTER III

1. Results First Experiment		45 - 69
a) Results from radiation measurements		45 - 47
b) Results from SEM and EDS examination of palladium cathode		48 - 69
2. Results Second Experiment		70 - 97
a) Results from radiation measurements		70 - 73
b) Results from SEM and EDS examination of palladium cathode		74 - 97
3. Conclusion		98 - 100
Table of tables		101
Table of figures		102 - 106
References		107

CHAPTER I

1. INTRODUCTION

In March 1989 M. Fleischmann and S. Pons published their work about palladium used as a cathode during electrolysis with heavy water. Based on excess heat as well as γ and neutron radiation measurements in their experiment, they claimed that the most probable explanation might be a deuterium fusion reaction inside the crystal lattice of palladium ¹⁾.

World wide efforts to reproduce the results of the so called cold fusion experiment, were often unsuccessful. Sometimes researchers were successful, but mostly they found no effects at all which could support the theory of a fusion reaction in a heavy water electrolysis experiment, with palladium as cathode.

Since then, further experiments were made to investigate more thoroughly the effects described by Fleischmann and Pons, as well as other researchers who were successful in reproducing the experiment. These further experiments led to greater consistency in results. For example, excess heat in sufficiently large amounts, which could not be explained by chemical effects alone, was now observed almost in every experiment. In

addition, observations of compositional changes in the palladium cathodes after the experiment were reported more frequently . In spite of the achieved progress there are still problems unsolved. The reproducibility of the experiments is not satisfying, the problem of missing radiation, or only of sporadic radiation, hardly over the background and the lack of a theoretical understanding of the observed effects are still unsolved. Because of these problems there were and are strong efforts in all these named fields to obtain better understanding and reproducible experimental data.

In following on the recent work on composition changes in palladium cathodes after electrolysis in heavy water from this lab, the main interest in this research was further investigation of compositional changes in palladium after electrolysis in heavy water. Also radiation during the experiment, especially neutrons, was monitored. And finally temperature and voltage during the experiment were also taken.

2. FUNDAMENTALS

As mentioned above the main purpose of this research and thesis project was further investigation of compositional changes in the palladium cathode after electrolysis in heavy water, in correlation with detection of radiation. Following several published reports in the past few years, mainly by scientists in Russia and Japan, but also by our own lab, it was observed that palladium shows changes in the composition after electrolysis in heavy water. In case of the Russian researchers, it was glow discharge in deuterium gas with palladium as cathode²⁾. The probable mechanisms to explain these changes were assumed as transmutations caused by multibody fusion and fusion-fission reactions. Following these assumptions, one will immediately expect that changes in the elemental composition on the palladium cathode should be correlated with activation in the material, which might lead to the emission of all kinds of radiation.

For this reason it was decided to investigate both changes in the elemental composition of palladium cathode surfaces and emission of radiation, especially neutron.

The choice for a proper detection method would presuppose the knowledge of the radiation type that could be expected, as well as its energy range, but this was exactly the problem. By the assumption of multibody fusion reactions and fusion-fission reactions, not only neutrons, but all kinds of radiation with a wide energy distribution could be expected. By considering also the fact that the electrolyte consists mainly of D_2O , which is a good moderator, often used in nuclear power plants, it was necessary to find a detector which was capable of detecting thermal neutrons and also was small enough to fit inside the cells.

The choice fell on LiF Thermo Luminescence Detectors (TLD), in the form of small chips (3mm by 3mm). The TLD 600 contains 95.62% Li-6 and the TLD 700, contains 99.93% Li-7. Both, TLD 600 and TLD 700 can detect α -, β - and γ -radiation but TLD 600 can additionally detect thermal neutrons. So the thermal neutron radiation can be obtained simply by subtracting the TLD 700 ^{137}Cs equivalent from the TLD 600 ^{137}Cs equivalent and by multiplying the result with a factor depending on the neutron energy spectrum.

The process of thermoluminescence can be described by a simple model³⁾. The energy levels of outer electrons in an inorganic perfect crystal lattice are broadened into a series of continuous regions, the so called energy bands, which are separated by forbidden regions. The highest filled energy band is the valence band, which is separated by a region of several electron volts from the lowest unfilled band above, the conduction band. Electrons from the valence band can be excited by ionizing radiation into the conduction band, leaving a positively charged hole behind. The excited electrons and holes can move independently from each other in their respective bands. With impurities in the crystal lattice, in case of LiF they are Mg and Ti, more discrete local energy levels can form in the forbidden region, so that the electrons in the conduction band can be “trapped” in these discrete energy levels. The amount of excited and “trapped” electrons is dependent on the amount of ionizing radiation, of a certain range. Light emission occurs as a result of the recombination of “trapped” electrons and holes which is stimulated by heating the chips. The light output is not absolute, therefore it must be calibrated against an absolute dosimetry system in a standard reference radiation field, which is in our case the

exposure of 10 Roentgen of ^{137}Cs . This method gives an error of $\pm 10\%$ and limits the measurable exposure to a minimum of at least 10mrem. Additionally Geiger-Mueller counters were chosen to monitor any radiation outside the cell, but also to double check the results obtained from the TLD chips.

Another problem was that compositional changes were limited to small areas (range of some μm^2) on the cathode surface (range of $\sim 0.5\text{ cm}^2$). Therefore the experiment had to be very clean. Knowledge about the impurities of the palladium cathode and the amount relative to palladium, as well as impurities in the platinum anode was important due to the fact that during the experiment, the palladium cathode would be plated to some extent by material dissolved from the anode. Finally, knowledge about the elemental compositions of all materials used inside the cells, as well as liquids (for example D_2O and H_2SO_4) and their impurity levels was required. Unfortunately, as was recognized early on, these requirements represented an insoluble problem. A method for minimizing contamination was, to observe maximum cleanness during the whole procedure, then to precisely examine the electrodes, especially the palladium cathode, before

the experiment and after the electrolysis to examine exactly the same areas. Furthermore it was necessary to recognize when contamination might occur. For example the observation of Cu was due to the possible contamination of heavy water by Cu during production. "Things" which seemed to stick to the surface mechanically should be examined with greatest care. Because of the fact, that the palladium foil used was not 100% pure, it was important to know the exact location and elemental composition of the impurities on the palladium cathode before electrolysis. Then not only changes of palladium after electrolysis could be studied, but also the changes in the impurity elements.

CHAPTER II

1. EXPERIMENTAL SETUP

Two experiments were performed, for the same purposes. These were the observation of radiation, especially neutron, during the experiment and examination of changes in the elemental composition on the Pd cathode after the experiment. Both experiments had two cells, an experimental cell, the D cell, with palladium as cathode and a control cell, the C cell, with platinum as cathode. The purity of the palladium foil, thickness originally 0.05 cm, used as cathode, as given by Johnson Matthey certificate of analysis stock #11514, lot #D12E06, was 99.9%. Unfortunately the lot number of the used palladium foil, lot#19652, was different and although efforts were made to get the correct certificate of analysis, it was impossible to get the desired certificate from the vendor. But according to the vendor's information the composition should be the same as the one given. The purity of the platinum foil used as cathode, as given by Johnson Matthey certificate of analysis stock #00261, lot #B24E24, was 99.9%. The purity of the platinum wire used as anodes in both cells, as given by Johnson Matthey certificate of analysis stock #10959, lot #9820, was 99.998%.

Certificate of Analysis

Palladium foil, 0.5mm thick, 99.9% (metals basis)

Stock Number: 11514

Lot Number: D12E06

Analysis

Pt	43	Cd	ND	Sn	ND	Ti	ND
Pd	M	As	ND	Cr	ND	Co	ND
Rh	2	Te	ND	Si	ND	Ni	26
Ir	ND	B	ND	Fe	42	Al	ND
Ru	ND	Sb	ND	Bi	ND	Ca	ND
Os	ND	Mn	ND	Mo	ND	Zr	ND
Au	10	Mg	ND	Cu	7	Ag	3
Pb	ND	Zn	ND				

ND = Not Detected

Analysis is in ppm

Figure 1. Certificate of analysis palladium foil (lot#D12E06 and stock#11514).

CERTIFICATE OF ANALYSIS

Platinum foil, 0.127mm (0.005in) thick, 99.9%

Stock number: 00261

Lot number: B24E24

Cd	1 ppm
Fe	13 ppm
Cu	18 ppm
Zn	1 ppm
Ca	1 ppm
Zr	60 ppm

Others checked for but not detected

Figure 2 Certificate of analysis platinum foil (lot#B24E24 and stock#00261).

Material : Platinum Wire 0.1mm dia Batch No. 9820

In any reference to this material the above batch number should be quoted.

Elements sought and limits of detection :

Below is a list of limits of detection of impurity elements appropriate to the matrix, analytical standards, and methods of analysis used.

Ag	1	Al	1	As	3	Au	1	B	1	Ba	1
Be	...	Bi	1	Ca	2	Cd	1	Co	1	Cr	1
Cs	...	Cu	1	Fe	1	Ga	3	Ge	1	Hg	...
In	1	Ir	3	K	1	Li	1	Mg	1	Mn	1
Mo	1	Na	10	Nb	1	Ni	1	Os	1	P	50
Pb	1	Pd	1	Pt	...	Rb	...	Re	...	Rh	2
Ru	3	Sb	1	Si	5	Sn	7	Sr	1	Ta	...
Te	1	Ti	1	Tl	2	V	6	W	20	Zn	10
Zr	5										

Elements detected :

Ca	<1	Cu	<1	Fe	<1	Mg	<1	Si	<1	Ag	<1
Pd	<1										

Figure 3. Certificate of analysis platinum wire (lot#9820 and stock#10959).

Both experiments and cells used the same type of glass bottles, KIMBLE OPTICLEAR (Art. No. 60975-L), as well as the same type of Teflon electrode holders. For the first experiment the diameter of the bottles opening had to be widened by heating the glass to its softening point, because the diameters of the Teflon electrode holders were too large. For the second, the diameters of the Teflon electrode holders was decreased, simply by cutting with a lathe a thin layer from their surface so they could fit into the glass bottles. Furthermore, the electrolyte which was used for both experiments and both cells, was a mixture of heavy water, D₂O with 99.9 atom % D, and sulfuric acid, H₂SO₄ 94-95%, Bakers Reagent Sp.G. 1.84. Only the concentrations of H₂SO₄ by volume in the electrolyte varied in both experiments.

		H ₂ SO ₄ (94-95%) by volume in Electrolyte	Electrolyte [ml] C cell	Electrolyte [ml] D cell
Experiment 1		14.9%	9.4	9.4
Experiment 2	1st start	7.6%	15.0	15.0
	2nd start	7.6%	15.0	15.0
	3rd start	7.6%	-	~15.0

Table 1. Volume of H₂SO₄ in the electrolyte.

The current was provided in both cases by a constant current source.

Experiment 1: HEWLETT PACKARD DC-Power Supply

Model: Harrison 6202B (max. current: 0.75A)

Experiment 2: LAMDA DC-Power Supply

Model: LH 122FM (max. current: 5.7A)

The radiation measurements, on the outside of the cells were made separately for each cell by Geiger-Mueller counters, which were connected to IBM-compatible computers. Inside the cell TLD chips were sealed in a polybag (one TLD 600 and one TLD 700 chip). For the first experiment one polybag for each cell was used containing one TLD 600 and one TLD 700 chip. Additionally one polybag with TLD chips was used to monitor the background outside the cells. For the second experiment two polybags were used for each cell. The inner polybag contained, just as in the first experiment, one TLD 600 and one TLD 700 chip and this polybag was then additionally put into another polybag to prevent wetting of the chips. This time no background measurements were done by TLD chips.

	Geiger-Mueller Counter	Computer C cell	Computer D cell
Experiment 1	Pasco Scientific Model: SE7985	DFI (CPU 80486 DX2/66MHz)	AST (CPU 80286 10MHz)
Experiment 2	Pasco Scientific Model: SE7985	DFI (CPU 80486 DX2/66MHz)	AST (CPU 80286 10MHz)

Table 2. Devices for radiation measurement outside the cells.

The cells in both experiments were surrounded by lead blocks (see Figure 4.) and the cells in the first experiment were additionally covered with a styrofoam case and stood on a styrofoam base. The cells in both experiments were placed on a piece of foam, while in the second experiment the foam was additionally covered with aluminum foil.

Aluminum can be activated by capturing thermal neutrons. The radiation emitted following an activation of Aluminum would be β^- and γ -radiation according to ⁴⁾:

The half life of the activated aluminum is 2.3 minutes.

This radiation could be detected by the Geiger-Mueller counters, as well as the TLD-chips, especially the TLD 700, inside the cell.

Figure 4. Schematic placement of cells, lead blocks, background TLD chips and Geiger-Mueller counters for first and second experiment (top view).

Although the main interest was to detect radiation and observe changes in composition of elements on the cathode material, it was also of interest to record temperature and voltage data. This would provide information about possible heat effects. This temperature and voltage data could be used also to compare the cell temperatures to each other, so that, according to earlier results, a higher D cell temperature could indicate a

successful experiment. The temperature and voltage during the experiments were recorded separately for each cell. In the first experiment two plotters to record the temperature and voltage data were used and each cell had only one single thermocouple. The second experiment used a computer, with a customized interface and program, which was capable of recording voltage and temperature data. Six thermocouples were used for each cell. The thermocouples were fixed to the glass bottle by using an insulating tape.

Figure 5. Thermocouple placement for the first experiment.

Figure 6. Thermocouple placement for the second experiment

The thermocouples used were OMEGA TYPE T (copper-constantan), with a maximum useful temperature range of -200°C to 350°C . The first experiment used standard connectors, OMEGA OST-T (copper-constantan), to connect the thermocouples to a cold junction compensator, OMEGA CJ-T (copper-constantan), which set the reference temperature to 0°C . The two cold junction compensators, one for each cell, were then connected to the first two-pen plotter, an OMEGA 0585 11/13, which recorded the temperature for each cell separately. The voltage was recorded by the

second two-pen plotter, a HOUSTON INSTRUMENT 3000 RECORDER.

The cells were connected in series.

Figure 7. Circuit used in the first experiment.

Temperature and voltage readings in the second experiment were recorded by a computer, ZENITH (CPU 8088 4MHz), equipped with a customized interface, so that the thermocouples could be connected directly

to this interface. A basic program was used to process the temperature and voltage data collected by the interface. The cells were connected in series, also in the second experiment .

Figure 8. Circuit used in the second experiment.

The preparation of both cathodes, platinum and palladium, in both experiments was similar. First the originally 0.050cm thick palladium foil was ultrasonically cleaned in deionized water and then cold rolled to a thickness of:

Experiment 1: 0.003cm

Experiment 2: 0.035cm

After another ultrasonic cleaning for 5 minutes in deionized water, the palladium cathode, as well as the platinum cathode, were spot welded to a platinum wire (chemical analysis not available), and then carefully cleaned, first with concentrated hydrochloric acid, HCL, to remove the Cu impurities due to the spot welding followed by a second ultrasonic cleaning in deionized water. Afterwards, they were examined with the scanning electron microscope (SEM) and the energy dispersive spectrometer (EDS), using an ISI-SS40 SEM equipped with a LINK AN10000 EDS. The results of these examinations can be found in *chapter III* in the results. The next step, after EDS and SEM examination and an additional ultrasonic cleaning for 5 minutes in deionized water, was to partly cover the cathodes' areas with Teflon tape, to obtain the area which would be exposed to the electrolyte. This area was dependent on the minimum current density, which was required to be $j = 1.75 \text{ Acm}^{-2}$, and the maximum current which was provided by the constant current sources. In the case of the first experiment,

the maximum current was $I_{\max} = 0.5$ A and for the second experiment it was about $I_{\max} = 1.1$ A. Therefore the uncovered areas were:

	AREA [cm ²] Pd and Pt	CURRENT $I_{\min}$ [A]	CURRENT $I_{\max}$ [A]	CURRENT DENSITY $j_{\min}$ [Acm ⁻²]	CURRENT DENSITY $j_{\max}$ [Acm ⁻²]
EXP. 1	0.22 ± 0.02	0.50 ± 0.00	0.50 ± 0.00	2.27 ± 0.21	2.27 ± 0.21
EXP. 2	0.40 ± 0.02	0.69 ± 0.05	1.10 ± 0.05	1.73 ± 0.21	2.75 ± 0.26

Table 3. Cathodes areas and current densities for both experiments

Figure 9. Pd and Pt cathodes from the first experiment; magnification 2 times

Figure 10. Pd and Pt cathodes from the second experiment; magnification 2 times

The anodes were made of the above mentioned Pt wire and had a spiral shape with 17 turns for the C cell and 25 turns for the D cell.

After completing all necessary preparations, which included all the steps mentioned above, as well as weighing every single part of the cells, both cells were put together. Then the entire cells were weighed to ensure, that the D cell was heavier than the C cell. The objective behind this, was to perform a conservative experiment regarding the energy. This meant that greater energy was required to heat up the D cell to the same temperature as the C cell.

	D cell [g]	C cell [g]	Pd cathode with Pt wire [g]	Pt cathode with Pt wire [g]
Experiment 1	67.281 ± 0.001	66.815 ± 0.001	0.314 ± 0.001	0.314 ± 0.001
Experiment 2	64.926 ± 0.001	63.851 ± 0.001	0.531 ± 0.001	0.376 ± 0.001

Table 4. D and C cell weight before the experiments.

The main difference between the two experiments was that the first experiment used tightly sealed cells to prevent, or at least minimize electrolyte loss caused by evaporation, and the cells were covered by a styrofoam case. The second experiment used “open cells”, so that evaporated electrolyte or gas could escape unhindered without using a

styrofoam case. The idea behind tightly sealed cells was to prevent larger electrolyte loss, which if it were successful, would give the possibility to determine more exactly, if excess heat was obtained from the D cell in comparison to the C cell. Another important issue, which would be necessary to compare in both cells, regarding excess heat, is, that the amount of electrolyte loss had to be almost equal in both cells. Electrolyte loss means also energy loss. How much energy is lost in this way, is dependent on how the electrolyte vanishes. One possibility would be loss of heavy water vapor D_2O . Another one would be the loss of D_2 and O_2 gas created by electrolysis. But as long as the exact quantities of both or even other possibilities are not measured, the electrolyte lost has to be equal to allow statements regarding excess heat. The sealing of the cells in the first experiment was done with Teflon tape which was covered with APIEZON Q sealing wax. The Teflon tape was necessary to prevent a contamination of the cells inside by APIEZON Q during the experiment, when the cell's temperature increased. Figure 11 and 12 show the cell setup for the first and second experiment.

Cell setup for first and second experiment

Figure 11. Setup C and D cell for the first experiment.

Figure 12. Setup C and D cell for the second experiment.

Pictures - First experiment

Figure 13. First experiment setup

Figure 14. First experiment setup

Pictures - Second experiment

Figure 15. Second experiment setup

Figure 16. Second experiment setup

2. FIRST EXPERIMENT

The first experiment was supposed to run for at least 24 hours. After 11 hours and 50 minutes the current at the constant current source dropped automatically. The reason was, that the D cell voltage reached the maximum value of 12V, which was set at the DC power supply. The drastic voltage increase in the D cell was due to its great electrolyte loss. Figures 17 and 18 show the temperature and voltage as a function of time during the first experiment. Figures 19 and 20 show the temperature difference and voltage difference as a function of time.

The power input into the cells can be directly calculated from the voltage, because power input and voltage are, in this case where the current is constant, directly proportional to each other.

$$dP = I \cdot dV, \quad \text{with } I = 0.5A \dots \text{constant current}$$

dP ... change in power

dV ... change in voltage

So Figure 18 can also be regarded as power input in both cells and Figure 20 as the difference in power input to the cells.

Figure 17. Temperature first experiment.

Figure 18. Voltage first experiment.

Figure 19. Temperature difference C - D first experiment.

Figure 20. Voltage difference C - D first experiment.

In Figure 17 and 18 one can see:

- for the first 70 minutes, that as the temperature increases, due to the power input, the voltage decreases. The voltage decrease is due to the increase in temperature, which also increases the diffusion rates of the ions and so their mobility in the solution and therefore the conductivity of the solution ^{9,10)} increases;
- for the period between 70 to 570 minutes, the system reached a sort of “steady state condition”, where voltage and temperature do not change very much.
- for the period from 570 minutes to the end, especially the D cell voltage and temperature start to increase dramatically. This was because the electrolyte loss in the D cell reached a critical level, where the Pd cathode and Pt anode were no longer completely covered by the electrolyte. On the one hand the voltage and power input increased, due to the smaller electrode area in the electrolyte .

$$V \propto 1/A$$

V ... voltage

A ... cross sectional area

On the other hand, the higher power input resulted in a temperature increase and therefore in an expansion of the electrolyte, so that the electrodes were again completely immersed in the electrolyte. At this point the voltage started to decrease. Consequently the temperature also decreased and so the electrolyte volume got smaller, so that the electrodes were again not completely immersed in the electrolyte etc.

This sort of growing oscillations went on until the D cell voltage reached a value where the current of the constant current source dropped automatically.

The reason for the higher electrolyte loss in the D cell, was a crack in the glass bottle.

Figure 21. Location of the crack in glass bottle of D cell.

This crack was caused by the greater expansion of Teflon in comparison to glass, with increasing temperature. The temperature of the D cell was smaller than that of the C cell most of time, see Figure 19. The reason might be that the greater loss of electrolyte caused greater energy loss in the D cell. On the other hand it was recognized that it was not possible to conclude about the cell's temperature by measuring at one single point. It is rather necessary to use several thermocouples to conclude about the cells temperature. This means that more temperature measurements might have given a higher D cell average temperature. Table 5 gives the weight and electrolyte loss data of the cells after the experiment.

	weight change entire cell [g]	electrolyte loss [ml]	weight change cathodes [g]
D cell	-2.976 ± 0.002	2.43 ± 0.01	0.000 ± 0.001
C cell	-2.594 ± 0.002	2.12 ± 0.01	0.000 ± 0.001

Table 5. Electrolyte loss and weight change first experiment.

So from table 5 it can be seen, that the D cell lost (0.31 ± 0.01) ml more electrolyte than the C cell.

3. SECOND EXPERIMENT

The second experiment ran, with interruptions, for 46 hours and 09 minutes. One major problem throughout the experiment was an unstable current. The current, provided by the DC power supply, was supposed to be constant, as long as no manual changes were made, but in reality the current source had an instability of about $\pm 0.06\text{A}$. The voltage at the DC power supply was set to its maximum of 20 V. This should on the one hand stabilize the current and on the other hand limit the possible cell voltage to 20 V, so that in case of, for example explosions, the current at the power supply would drop automatically.

The first uninterrupted period had a duration of 17 hours. The current was set at the beginning to $I = 0.75\text{A}$. Three hours later it was increased to $I = 0.8\text{A}$ and finally forty minutes later to $I = 0.9\text{A}$. See the according temperature and power input graphs below, as well as the graphs for temperature and power input difference between the cells.

Figure 22. Temperature (0 - 1h 10min) second experiment.

Figure 23. Power input (0 - 1h 10min) second experiment.

Figure 24. Temperature difference C - D (0 - 1h 10min) second experiment.

Figure 25. Difference in power input (0 - 1h 10min) second experiment.

Figure 26. Temperature (1h 10min - 17h) second experiment.

Figure 27. Power input (1h 10min - 17h) second experiment.

Figure 28. Temperature difference C-D (1h 10min-17h) second experiment.

Figure 29. Difference in power input (1h 10min - 17h) second experiment.

After 17 hours the experiment was switched off, to refill the lost electrolyte. The temperature drop of the D cell after ~ 24 minutes, was due to the replacement of a defective thermocouple. In Figure 22 to 29 one can see:

- for most of the time the power input into the C cell was greater than into the D cell. As mentioned before, the C cell anode had 17 turns and the D cell had 25 turns, so the C cell anode had 8 turns less. Therefore the cross sectional area between the electrodes was smaller and so the voltage and power input was higher in the C cell.
- for the first ~33 minutes the D cell temperature was higher than the C cell. Then for the next ~860 minutes the C cell temperature was higher. And again for the remaining time, the D cell temperature was higher. One reason for a, most of the time, higher C cell temperature was the greater electrolyte loss from the D cell. Another reason was, of course, that most of the time there was greater power input to the C cell. The higher temperature of the D cell in the last ~127 minutes was due to the higher power input (voltage) into the D cell, because of the lost electrolyte. See also the first experiment.

Table 6 gives the weight and electrolyte loss after the first 17 hours.

	Weight change of cells [g]	Electrolyte loss [ml]
D cell	-9.771 ± 0.001	8.36 ± 0.01
C cell	-7.870 ± 0.001	6.73 ± 0.01

Table 6. Electrolyte loss and weight change second experiment (0 - 17h).

As can be seen from Table 6 the D cell lost about 1.63ml more electrolyte than the C cell. This was because the D cell Teflon electrode holder did not fit as tightly into the glass bottle opening as the C cell Teflon electrode holder, so the electrolyte could escape much easier from the D cell. To fix this problem of unequal electrolyte loss, the D cell Teflon electrode holder was made to fit tighter into the glass opening, by using a Teflon tape. Afterwards the lost electrolyte was refilled and the cells were prepared for a restart of the experiment. The total time of break was three hours. After restarting the current was set to $I = 1.2A$, because the so far collected temperature data did not show the expected excess heat from the D cell in comparison to the C cell. After only 10 minutes and 30 seconds the C cell exploded.

Through the high current of $I = 1.2\text{A}$ the production of D_2 and H_2 gas at the cathode and O_2 at the anode reached a critical level, so that probably the following exothermic chemical reactions were initiated:

or/and

Below are the graphs of temperature and power input for this period, as well as their differences.

Figure 30. Temperature (17h - 17h 12min) second experiment.

Figure 31. Power input (17h - 17h 12min) second experiment.

Figure 32. Temperature difference C - D (17h - 17h 12min) second experiment.

Figure 33. Difference in power input C - D (17h - 17h 12min) second experiment.

After an interruption of 15 minutes, due to the explosion of the C cell, the experiment was continued only with the D cell. The current was set first to $I = 1.10\text{A}$, but as the gas production seemed still to be too large, the current was set after 30 minutes of operation to $I = 1.00\text{A}$. Finally 5 hours and 20 minutes later the current was set to $I = 0.85\text{A}$. That was to minimize possible explosions, due to gas production, for the remaining operating time.

The last period was 28 hours and 57 minutes, before the experiment was switched off. At this time the electrolyte loss reached a critical level, where the electrodes were not completely in the electrolyte anymore. Below are the graphs of temperature and voltage data for the last period.

Figure 34. Temperature D cell (17h 12min - 46h 09min) second experiment.

Figure 35. Power input D cell (17h 12min - 46h 09min) second experiment.

Table 7 gives the weight and electrolyte loss data for the D cell after 29 hours and 9 minutes operation and for the C cell after 17 hours and 12 minutes operation .

	Weight change entire cell [g]	electrolyte loss [ml]	Weight change cathodes [g]
D cell	-12.176 ± 0.002	~ 10.5	0.000 ± 0.002
C cell	-	-	0.000 ± 0.002

Table 7. Weight and electrolyte loss for C and D cell second experiment.

As can be seen from Figure 35, there are three peaks at ~150 minutes, ~375 minutes and at ~1600 minutes. These peaks were due to a voltage decrease, which was probably caused by current decrease. As mentioned before the constant current source was not as stable as required, so this would explain the occurrences of these three power drop peaks.

There are also temperature drops, see Figure 34, which corresponds to the power input drops in Figure 35.

CHAPTER III

1. RESULTS FIRST EXPERIMENT

1a. RESULTS FROM RADIATION MEASUREMENTS

No significant radiation was measured, whether with the TLD chips, or with Geiger-Mueller counters. The light output from the TLD chips was read by the vendor, below are the results:

	Chip	Net Light Output	Net ^{137}Cs equivalent [mrem]
Background	TLD 600	15	9
	TLD 700	0	0
C Cell	TLD 600	8	5
	TLD 700	0	0
D Cell	TLD 600	10	6
	TLD 700	2	2

Table 8. Radiation by TLD chips; first experiment

Net doses under 10 mrem ^{137}Cs equivalent are not statistically significant.

The count rates from the Geiger-Mueller counters were:

	Average Counts Per 1h	Average Background Counts Per 1h	Resultant Counts Per 1h
C Cell	685 ± 26	669 ± 26	16 ± 37
D Cell	667 ± 26	650 ± 25	17 ± 36

Table 9. Radiation by Geiger-Mueller counters; first experiment.

The background for the Geiger-Mueller data, as can be seen in Table 9, was measured after the experiment. Background measurements were done at exactly the same location as the experiment and were performed for 20 hours.

	Maximum Count Rate Per 1h In 12 h	Minimum Count Rate Per 1h In 12h	Resultant Maximum Count Rate Per 1h In 12 h	Resultant Minimum Count Rate Per 1h In 12h
C Cell	727 ± 26	643 ± 26	58 ± 37	-26 ± 37
D Cell	708 ± 26	627 ± 26	58 ± 36	-23 ± 36

Table 10. Maximum and minimum counts by Geiger-Mueller counter; first experiment

No unusual radiation burst was detected during the electrolysis, as can be seen from the maximum count rate per one hour in Table 10. The maximum and minimum count rate per one hour gives the highest and the lowest count rate that was recorded during the experiment. The deviations of the count rates in Table 9 and 10 were obtained by:

$$\delta = \sqrt{x_{av}} ; \quad \delta \dots \text{deviation}$$

x_{av} ... average count rate per 1 hour

This is the standard deviation of the poisson distribution. For time evaluation of the Geiger-Mueller count rates see Figure 36 below.

Figure 36. Radiation data obtained with two Geiger-Mueller counters; first experiment.

1b. RESULTS FROM SEM AND EDS EXAMINATIONS OF PALLADIUM CATHODE

No change in the elemental composition on the surface of the Pd cathode was observed. From now on the side on the Pd cathode with the Pt wire welded to it will be called side A and the opposite side will be side B.

Figure 37. Definition of names for the Pd cathode.

The cathodes surface analysis was done by an ISI-SS40 SEM using an electron beam with an acceleration voltage of 20 kV. The spectra were taken with a LINK AN10000 EDS x-ray analyzer using the “thin” window for the detector. Below are the pictures and spectra taken from the Pd cathode before the experiment (Figures 38, 39 and 41 from side A and Figures 43 and 44 from side B).

Side A:

Figure 38. Pd cathode before electrolysis; side A
(magnification: 10 times; working distance: 38mm; tilt: 0°).

Figure 39. Pd cathode before electrolysis; side A; magnification of area 1 in Figure 38
(magnification: 760 times; working distance: 10 mm; tilt: 45°).

This “thing” sticking to the cathodes surface, in Figure 39, is probably a piece of a kimwipe tissue, on which the cathode was placed to dry after ultrasonic cleaning .

Below are the spectra taken from specified locations in this area.

Spectrum c2101/area/a

Spectrum c2104/spot/b

Figure 40. EDS spectra from Figure 39; first experiment; before electrolysis.

Figure 41. Pd cathode before electrolysis; side A; magnification of area 2 in Figure 38 (magnification: 1530 times; working distance: 10 mm; tilt: 45°).

Below are the spectra from the specified areas in Figure 41.

Spectrum c2106/area/d

Spectrum c2109/spot/c

Figure 42. EDS spectra from Figure 41; first experiment; before electrolysis.

EDS spectrum	Figure #	Elements
c2101/area/a	39	Pd
c2104/spot/b	39	Pd, Si and probably Ca
c2106/area/d	41	Pd compare to c2101/area/A
c2109/spot/c	41	Pd, Si, Ca and probably O

Table 11. EDS results Pd cathode before electrolysis; side A; first experiment.

Significant amounts of silicon and calcium were found. At the beginning it was suspected that these were impurities due to a not completely clean preparation of the experiment. Later on it will be shown that these impurities were probably due to the production procedure of palladium. Also pieces probably from the kimwipe tissue were found sticking to the surface. See Figure 41 and Figure 39. The “thing” sticking to the surface seems to be a piece of the kimwipe tissue. Their EDS analysis showed just a palladium peak, the expected low energy (0.282 keV) carbon peak could not be resolved by the EDS.

Side B:

Figure 43. Pd cathode before electrolysis; side B; first experiment
(magnification: 11 times; working distance: 38 mm; tilt: 0°).

Figure 44. Pd cathode before electrolysis; side B; first experiment; magnification of area
1 in Figure 43 (magnification: 770 times; working distance: 10 mm; tilt: 45°).

Below are the spectra from the location specified in Figure 44.

Spectrum c2163/spot/a

Spectrum c2164/spot/b

Spectrum c2165/area/c

Figure 45. EDS spectra from Figure 44; first experiment; before electrolysis

EDS spectrum	Figure #	Elements
c2163/spot/a	44	Pd, Si and Ca
c2164/spot/b	44	Pd and Pt
c2165/area/c	44	Pd

Table 12. EDS results Pd cathode before electrolysis; side B; first experiment.

Silicon and Calcium impurities were also found on side B and in similar locations as on side A. These were grain-shaped defects on the surface of palladium. Again pieces probably of the kimwipe tissue used were found sticking to the surface. After the experiment the Pd cathode was cleaned with deionized water before examination with SEM and EDS. Below are the results from the SEM and EDS examination from the palladium cathode after the experiment.

Side A:

Figure 46. Pd cathode after electrolysis; side A; first experiment; compare to Figure 38 (magnification: 10 times; working distance: 38 mm; tilt: 0°).

From Figure 46, it can be seen, which area was exposed to the electrolyte, the bright (white) area, and which area was covered by the Teflon tape, the darker area. The area exposed to the electrolyte was plated with platinum.

Figure 47. Pd cathode after electrolysis; side A; first experiment; magnification of area 1 on Figure 46 (magnification: 510 times; working distance: 10 mm; tilt: 45°).

The lines which can be seen in Figure 47 are due to the cold rolling before the experiment, the white “stuff” is platinum plating and the grain-shaped defects in the center of the picture are magnified below in Figure 48.

Figure 48. Pd cathode after electrolysis; side A; first experiment; magnification of area 1 in Figure 47 (magnification: 2004 times; working distance: 10 mm; tilt: 45°).

Figure 49. below shows a further magnification of one of these grain-shaped defects in 48.

Figure 49. Pd cathode after electrolysis; side A; first experiment; magnification of area 1 in Figure 48 (magnification: 11800 times; working distance: 10 mm; tilt: 45°).

As can be seen in Figure 49, the grain-shaped defects contain a sort of crystal. Below are the spectra obtained.

Spectrum c42101/spot/a

Spectrum c42102/area/b

Spectrum c42103/spot/c

Figure 50. EDS spectra from Figure 49; first experiment; after electrolysis.

The occurrence of these grain-shaped defects with grains inside are assumed not to be due to the electrolysis, because they also can be found on the original palladium foil (see Figure 57). Below are pictures of “ball-shaped” structural changes which are due to the electrolysis. These “ball-shaped” structures were found on both sides of the Pd cathode and are similar to the observations made by I. Savvatimova and A. Karabut⁵⁾. This research group used palladium as a cathode in a glow discharge experiment in deuterium gas. Contrary to the compositional results from I. Savvatimova and A. Karabut, where they found the elemental composition of this “ball” to be also Mo and Ag, no elements like the mentioned nor other unexpected elements were found. See Figure 51 and resulting spectra below.

Figure 51. Pd cathode after electrolysis; side A; first experiment; magnification of area 2 in Figure 46; example of “ball-shaped” structural change (magnification: 2400 times; working distance: 10 mm; tilt:45°).

Spectrum c42401/area/a

Spectrum c42402/spot/b

Figure 52. EDS spectra from Figure 51; first experiment; after electrolysis.

Spectrum c42403/area/c

Spectrum c42404/spot/d

Figure 53. EDS spectra from Figure 51; first experiment; after electrolysis.

EDS spectrum	Figure #	Elements
c42101/spot/a	49	Pd, Si, Ca, Pt and O
c42102/area/b	49	Pd, Pt, Si, Ca, O and Cu
c42103/spot/c	49	Pt, Pd, Cu, Si, Ca and O
c42401/area/a	51	Pd, Pt and Cu
c42402/spot/b	51	Pd, Pt and Cu
c42403/spot/c	51	Pd, Pt and Cu
c42404/spot/d	51	Pd, Pt and Cu

Table 13. Results spectra Figure 49 and 51; first experiment.

The main elemental composition of the grain inside the grain-shaped defect in Figure 49 is (see Table 13): Pd, Si, Ca and O .

The results of spectrum c42101/spot/a and c42102/area/b (Figure 49) are similar to the results from the spectrum c2109/spot/c (Figure 41) and spectrum c2163/spot/a (Figure 44). So it can be concluded, that the occurrence of silicon, calcium and oxygen can be probably explained as impurities in the palladium cathode. The results of the spectral examination of the “ball-shaped” structures in Figure 51 (spectra c42403/area/c and c42404/spot/d) show no unexpected elements. The occurrence of platinum is due to the plating during the electrolysis and that of copper is probably due to the copper impurities in heavy water.

Side B:

Figure 54. Pd cathode after electrolysis; side B; first experiment; compare to Figure 43; (magnification: 10 times; working distance: 38 mm; tilt: 0°)

Figure 55. Pd cathode after electrolysis; side B; first experiment; magnification of area 1 in Figure 54 (magnification: 1500 times; working distance: 10 mm; tilt: 45°).

Below are the spectra obtained from an EDS examination of the area in Figure 55.

Spectrum c3151/area/a

Spectrum c3152/spot/b

Spectrum c3159/spot/c

Figure 56. EDS spectra from Figure 55; first experiment; after electrolysis.

EDS spectrum	Picture	Elements
c3151/spot/a	55	Pd, Pt and Cu
c3152/area/b	55	Pd, Pt and Cu
c3159/spot/c	55	Pt, Pd, and Cu

Table 14. EDS results Figure 55; first experiment.

The SEM and EDS examination showed no unexpected results. No new elements were found after the electrolysis. The occurrence of grain-shaped defects with grains inside, which contains Si, Ca and O, also before electrolysis, is most probably due to impurities which came from the production of palladium. See Figure 57.

Figure 57. Magnification of impurity on original palladium foil (magnification: 3900 times; working distance: 10 mm; tilt: 45°).

Below are the spectra from specified area in Figure 57.

Spectrum c52721/area/a

Spectrum 52722/spot/b

Figure 58. EDS spectra from Figure 57; original palladium.

EDS spectrum	Picture	Elements
c52721/area/a	57	Pd, Ca, Si and O
c52722/spot/b	57	Pd, Ca, Si, Fe and O

Table 15. Results spectra Figure 57; original palladium.

By the comparison of spectra c42101/area/a and c42102/spot/b (Figure 49) to the spectra c52721/area/a and c52722/spot/b (Figure 57), c2109/spot/c (Figure 41) and c2163/spot/a (Figure 44), one can see a main difference in the relative peak height of silicon to calcium. In c42101/area/a and c42102/spot/b the height and therefore amount of silicon is always greater than that of calcium. But in c52721/area/a, c52722/spot/b, c2109/spot/c and c2163/spot/a the heights and amounts seem to be vice versa or at least equal. The reason for the change, as was recognized, is due to the x-ray detector. The spectra where the height of silicon is greater than that of calcium were taken right after the detector was de-iced, “cleaned”. This sort of cleaning the detector had the effect, that lower energy x-rays could pass into the detector more easily and were not absorbed as much as when ice

was on the detector. So the difference was not due to any experimental effects, but to the x-ray detector.

2. RESULTS SECOND EXPERIMENT

2a. RESULTS FROM RADIATION MEASUREMENTS

No significant high radiation was measured, whether with TLD chips, or with Geiger-Mueller counters. The light output from the TLD chips was read by the vendor, below are the results:

	Chip	Net Light Output	Net ¹³⁷ Cs equivalent [mrem]
C Cell	TLD 600	7	4
	TLD 700	5	3
D Cell	TLD 600	0	0
	TLD 700	1	1

Table 16. Radiation by TLD chips; second experiment

Net doses under 10 mrem ¹³⁷Cs equivalent are not statistically significant.

The count rates from the Geiger-Mueller counters were:

	Average Counts Per 1h	Average Background Counts Per 1h	Resultant Counts Per 1h
C Cell	618 ± 25	605 ± 25	13 ± 35
D Cell	613 ± 25	592 ± 24	21 ± 35

Table 17. Radiation by Geiger-Mueller counters; second experiment

The background for the Geiger-Mueller data, as can be seen in Table 17, was measured after the experiment. Background measurement for the C cell was for 82 hours and for the D cell 60 hours, at exactly the same location as the experiment.

	Maximum Count Rate Per 1h In 46h	Minimum Count Rate Per 1h In 46h	Resultant Maximum Count Rate Per 1h In 46h	Resultant Minimum Count Rate Per 1h In 46h
C Cell	668 $\pm$ 25	572 $\pm$ 26	63 $\pm$ 35	-33 $\pm$ 35
D Cell	673 $\pm$ 25	530 $\pm$ 26	81 $\pm$ 35	-62 $\pm$ 35

Table 18. Maximum and minimum counts in 46 hours and 9 minutes by Geiger-Mueller counters; second experiment

No radiation bursts were monitored during the experiment. See Table 18 for maximum count rate per one hour. For time evaluation of the Geiger-Mueller count rates see Figure 59 below.

Figure 59. Radiation data obtained with two Geiger-Mueller counters; second experiment.

Although the above graph seems to indicate a small net radiation above background, this result is not significant, particularly because just the cell radiation without electrodes is higher than the background. Below is the result of cell radiation with 10 ml electrolyte, containing 14.9% H_2SO_4 by volume:

Cell radiation without electrodes: (755 ± 27) average counts per 1 hour

Background for this measurement: (707 ± 27) average counts per 1 hour.

In Figure 60 below is the setup for this measurement.

Figure 60. Setup for the cell radiation measurement

The cell radiation was recorded for 16 hours. The background was recorded for 17 hours after the cell radiation measurement, at the same place and with the same equipment.

2.b RESULTS FROM SEM AND EDS EXAMINATIONS OF

PALLADIUM CATHODE

No change in the elemental composition on the surface of the palladium cathode was observed. The cathode surface analysis was done with an ISI-SS40 SEM using an electron acceleration voltage of 20 kV. The spectra were taken with a LINK AN10000 EDS x-ray analyzer, using the “thin” window of the detector. Below are the pictures and results of the Pd cathode before and after the electrolysis. This time pictures and spectra before and after the electrolysis will be compared directly. The comparison of the spectra before and after electrolysis is difficult and can only be done qualitatively. One problem is the reason mentioned in chapter III 1b with the icing of the x-ray detector. Another problem is that spectra taken from a certain spot can differ from each other, because the placing of the electron beam at the same location is not very precise, and therefore just a small deviation can result in a different spectrum. As can be seen from Figure 69 below, but also from the other pictures that will follow, all areas from which EDS spectra were taken before the experiment, are not plated with platinum during electrolysis or are just a bit plated. This was due to contamination by

oil. The contamination of these particular areas was due to backstreaming of oil from the vacuum pumps. This can be seen in particular in Figure 71 below. The column of the SEM is held under high vacuum. This vacuum is reached by using first a forepump and afterwards a diffusion pump. A fraction of the evaporated oil from the diffusion pump reaches the column, where the high intensity electron beam reacts with the oil so that the examined surface gets contaminated. The contamination is stronger on areas where EDS spectra were taken, because the intensity of the electron beam was increased and so the reaction with oil was enhanced.

Side A:

Figure 61. Pd cathode before electrolysis; side A ; second experiment (magnification: 14 times; working distance: 38 mm; tilt: 0°).

Figure 62. Pd cathode after electrolysis; side A; second experiment (magnification: 14 times; working distance: 38 mm; tilt: 0°).

Figure 62 shows strong plating with platinum, which comes from the Pt anode. Figure 63 below shows area 1 magnified.

Figure 63. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure 62; (magnification: 390 times; working distance: 10 mm; tilt: 45°).

Below are the spectra for Figure 63.

Spectrum c42201/area/a

Spectrum 42202/area/b

Figure 64. EDS spectra from Figure 63; second experiment; after electrolysis.

Spectrum 42203/area/c

Figure 65. EDS spectra from Figure 63; second experiment; after electrolysis.

EDS spectrum	Figure #	Elements
c42201/area/a	63	Pt, Pd and Cu
c42202/area/b	63	Pt, Pd and Cu
c42203/area/c	63	Pt, Pd and Cu

Table 19. EDS results Pd cathode after electrolysis; side A;
second experiment

The EDS results show, that the plating is so strong, that almost no palladium was detected. To remove the plating the Pd cathode was

ultrasonically cleaned for 150 minutes. Figure 66 shows the Pd cathode after the cleaning.

Figure 66. Pd cathode after electrolysis and 150 minutes of ultrasonic cleaning in deionized water; side A; second experiment (magnification: 14 times; working distance: 38 mm; tilt: 0°).

As can be seen from Figure 66 the Pt plating did not fall off during ultrasonic cleaning. But more precise examination showed small areas, which were not plated. See figures below.

Figure 67. Pd cathode before electrolysis; side A; second experiment; magnification of area 1 in Figure 61 (magnification: 530 times; working distance: 10 mm; tilt: 45°).

Spectrum c40401/spot/a

Spectrum c40402/spot/b

Figure 68. EDS spectra from Figure 67; second experiment; before electrolysis.

Figure 69. Pd cathode after electrolysis; side A; second experiment; magnification of area 2 in Figure 62 (magnification: 530 times; working distance: 10 mm; tilt: 45°).

Spectrum c42814/spot/a

Spectrum c42815/spot/b

Figure 70. EDS spectra from Figure 69; second experiment; after electrolysis.

Before electrolysis			After electrolysis		
EDS spectrum	Figure #	Elements	EDS spectrum	Figure #	Elements
c40401/spot /a	67	Au, Si, Pd, Ca, C, O, Pt, Na and Mg	c42814/spot /a	69	Ca, Pd, Si, Pt, Na and O
c40402/spot /b	67	Pd, Si, Ca, C, O, Na and Mg	c42815/spot /b	69	Pd, Ca, Si and Pt

Table 20. Comparison of EDS results Figure 67 and 69; second experiment

Below are the specified areas in Figures 67 and 69 magnified.

Figure 71. Pd cathode before electrolysis; side A; second experiment; magnification of area 1 in Figure 67 (magnification: 2300 times; working distance: 10 mm; tilt: 45°).

Spectrum c41701/spot/a

Spectrum c41702/spot/b

Spectrum c40707/spot/c

Figure 72. EDS spectra from Figure 71; second experiment; before electrolysis.

Figure 73. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure 69 (magnification: 2300 times; working distance: 10 mm; tilt: 45°).

Spectrum c52710/spot/a

Spectrum c52711/spot/b

Figure 74. EDS spectra from Figure 73; second experiment; after electrolysis.

Spectrum c52709/spot/c

Figure 75. EDS spectra from Figure 73; second experiment; after electrolysis.

Before electrolysis			After electrolysis		
EDS spectrum	Figure #	Elements	EDS spectrum	Figure #	Elements
c40707/spot /c	71	Pt and Pd	c52709/spot /c	73	Pd, Pt, Fe and Mg
c41701/spot /a	71	Pd and Pt	c52710/spot /a	73	Pd and Pt
c41702/spot /b	71	Pd and Pt	c52711/spot /b	73	Pd and Pt

Table 21. Comparison of EDS results Figure 71 and 73; second experiment

Figure 76. Pd cathode before electrolysis; side A; second experiment; magnification of area 1 in Figure 71 (magnification: 5700 times; working distance: 10 mm; tilt: 45°).

Spectrum c40703/spot/a

Spectrum c40704/spot/b

Figure 77. EDS spectra from Figure 76; second experiment; before electrolysis.

Spectrum c40705/spot/c

Spectrum c40706/spot/d

Figure 78. EDS spectra from Figure 76; second experiment; before electrolysis.

Figure 79. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure 69 (magnification: 5700 times; working distance: 10 mm; tilt: 45°).

Spectrum c52703/spot/a

Spectrum c52704/spot/b

Spectrum c52701/spot/c

Spectrum c52702/spot/d

Figure 80. EDS spectra from Figure 79; second experiment; after electrolysis.

Before electrolysis			After electrolysis		
EDS spectrum	Figure #	Elements	EDS spectrum	Figure #	Elements
c40703/spot /a	76	Pd, Au, Si and Ca	c52703/spot/ a	79	Pd, Pt, Au, Si and Ca
c40704/spot /b	76	Au and Pd	c52704/spot/ b	79	Pd, Pt and Au
c40705/spot /c	76	Au and Pd	c52701/spot/ c	79	Pd and Pt
c40706/spot /d	76	Au and Pd	c52702/spot/ d	79	Pd and Pt

Table 22. Comparison of EDS results Figure 76 and 79; second experiment

Pt and Au were found on the surface of the Pd cathode before electrolysis, in a distance of about $\sim 2 \mu\text{m}$ from each other, see Figure 76 with corresponding EDS. The amount of Au decreased after the electrolysis. This was probably because Au fell off the surface (compare Figure 76 and 79) due to the ultrasonic cleaning for 150 minutes of the Pd cathode. Observations of Au were also reported by G. Noble, J. Dash and D. Diman⁶⁾, but according to their results Au was found after electrolysis. The

palladium specimen used in their experiment was the same as the one that was used for this experiment.

Also observations of grain-shaped defects, caused by hydrogen charging, cold fusion or by a combination of both processes, with grains inside were recently reported by T. Matsumoto ⁷⁾. The shape of these defects has similarity to the defects which can be seen in Figures 67, 69, 71, 73, 76 and 79 and in other following figures, and also in Figures 47 to 49 and Figure 57 in chapter III 1b. Additionally observations of longitudinal cracks were made by T. Matsumoto in the same paper. It was assumed that these longitudinal cracks can develop by the growth of grain-shaped defects, when they connect with each other. In Figure 67, 69, 71, 73, 76 and 79, as well as in Figure 57 chapter III 1b observations of similar longitudinal cracks were made. These cracks were observed before and after the experiment, with no significant growth. A slight growth of grain-shaped defects after the experiment was observed. Compare especially Figure 71 and 73.

Furthermore T. Matsumoto reported in another paper ⁸⁾ about observations of unexpected elements after a cold fusion experiment in grain-shaped defects. Elements like Na, Mg, Si, Ca and also other elements

were observed. These observations are also similar to the results of the spectral analysis of the grain-shaped defects in this experiment. See for example the spectra c40401/spot/a, c40402/spot/b (Figure 67) above and spectrum c41007/spot/b (Figure 83) below. But in contrast to T. Matsumoto, these observations were made before the experiment.

Side B:

Figure 81. Pd cathode before electrolysis; side B; second experiment
(magnification: 14 times; working distance: 38 mm; tilt: 0°)

Figure 82. Pd cathode after electrolysis; side B; second experiment
(magnification: 14 times; working distance: 38 mm; tilt: 0°)

Below are magnified areas from side B.

Figure 83. Pd cathode before electrolysis; side B; second experiment; magnification of area 1 in Figure 81 (magnification: 390 times; working distance: 10 mm; tilt: 45°).

Spectrum c41006/spot/a

Spectrum c41007/spot/b

Figure 84. EDS spectra from Figure 83; second experiment; before electrolysis

Spectrum c41008/area/c

Spectrum c41009/area/d

Figure 85. EDS spectra from Figure 83; second experiment; before electrolysis

Figure 86. Pd cathode after electrolysis; side B; second experiment; magnification of area 1 in Figure 82 (magnification: 390 times; working distance: 10 mm; tilt: 45°).

Figure 87. Pd cathode after electrolysis; side B; second experiment; magnification of area 2 in Figure 82 (magnification: 390 times; working distance: 10 mm; tilt: 45°).

Spectrum c42806/spot/a

Spectrum c42804/spot/b

Figure 88. EDS spectra from Figure 86; second experiment; after electrolysis

Spectrum c42807/area/a

Spectrum c42808/area/c

Figure 89. EDS spectra from Figure 87 and 86; second experiment; after electrolysis.

Additionally a magnified picture was made from area 1 in Figure 86.

Figure 90. Pd cathode after electrolysis; side B; second experiment; magnification of area 1 in Figure 86 (magnification: 5900 times; working distance: 10 mm; tilt: 45°).

Spectrum c42805/area/a

Figure 91. EDS spectra from Figure 90; second experiment; after electrolysis.

Before electrolysis			After electrolysis		
EDS spectrum	Figure #	Elements	EDS spectrum	Figure #	Elements
c41006/spot/a	83	Pd, C	c42806/spot/a	86	Pt, Pd and Fe
c41007/spot/b	83	Si, O, Ca, Pd, Fe, Mg and Na	c42804/spot/b	86	Si, Ca, O, Pd, Pt and Fe
c41008/area/c	83	Pd, Si, Ca and O	c42807/area/a	87	Pd, Pt, Si and Ca
c41009/area/d	83	Pd, Si, Ca and O	c42808/area/c	86	Pd, Pt, Si and Ca
			c42805/area/a	90	Si, Ca, O, Pt, Pd and Fe

Table 23. Comparison of EDS results Figure 83, 86, 87 and 90; second experiment.

3. CONCLUSION

Two experiments on electrolysis of palladium in heavy water were performed. First, the emission of radiation during the experiment was recorded and second, the change in the composition of elements on the surface of the palladium cathode after the experiment was examined. No significant high radiation was measured during either experiment. Small changes in the surface morphology, like the growth of grain-shaped defects, were detected in the second experiment. But, no unexpected change in the elemental composition on the surface of the palladium cathodes after the experiment was found.

Unexpected elements were found before the electrolysis, which can probably be explained as impurities due to the production of the palladium foil used. So for example Au was found close ($\sim 2\mu\text{m}$ distance) to Pt localized on the palladium cathode of the second experiment. According to the phase diagrams¹⁰⁾ of Pd - Au alloys and Pd - Pt alloys, these elements should mix homogeneously. The finding of Pt and Au localized gives reason to believe that these are impurities. According to the vendor the localized contamination of the palladium foil by Au and Pt, could happen,

when the palladium is finally cold rolled to the foil of 0.5 cm thickness which was used by us. This cold roll device is also used for rolling Au and Pt to foils. Despite the fact, that the rolls are cleaned carefully after each use, there can not be an absolute guarantee for 100% clean rolls. But besides this, it is unusual that the contamination of the used palladium foil by Au and Pt is within a diameter of $\sim 2\mu\text{m}$. Therefore one can think of two possible explanations. First, it is possible, that the roll used for cold rolling the palladium to a foil, had a tiny defect on the surface which can collect material and by chance this material, in this case Au and Pt, stuck to the palladium. Second, by assuming that the impurity was first Pt which, if slow neutrons were around, partly transmuted to Au, as suggested by G.Noble, J. Dash and D. Diman⁶⁾.

Another unexpected finding on the Pd cathode before the experiment, as well as on the original palladium foil, was that of grain-shaped defects on the surface with grains inside, which contain Si, Ca, O, Pd and also often Na, Mg and Fe. On the one hand, their occurrence could not be explained by the vendor. On the other hand, T. Matsumoto reported about finding similar grain-shaped defects after cold fusion experiments. Some of these grain-

shaped defects in T. Matsumotos work contained also grains with a similar elemental composition as the one found in these experiments. If these grains found in the grain-shaped defects are really impurities or if they developed while the palladium foil was stored for now almost 6 years in our lab is not clear. Further examinations of the original palladium foil over a longer period of time would be necessary to investigate, if changes in the elemental composition and surface morphology occur, even without an electrolysis experiment.

Table of tables

	page
Table 1. Volume of H ₂ SO ₄ in the electrolyte	11
Table 2. Devices for radiation measurement outside the cells	13
Table 3. Cathodes areas and current densities for both experiments	20
Table 4. D and C cell weight before the experiments	21
Table 5. Electrolyte loss and weight change first experiment	31
Table 6. Electrolyte loss and weight change second experiment (0 - 17h)	38
Table 7. Weight and electrolyte loss for C and D cell second experiment	43
Table 8. Radiation by TLD chips; first experiment	45
Table 9. Radiation by Geiger-Mueller counters; first experiment	45
Table 10. Maximum and minimum counts by Geiger-Mueller counter; first experiment	46
Table 11. EDS results Pd cathode before electrolysis side A first experiment	52
Table 12. EDS results Pd cathode before electrolysis side B; first experiment	55
Table 13. Results spectra Figure 49 and 51; first experiment	62
Table 14. EDS results Figure 55; first experiment	66
Table 15. Results spectra Figure 57; original palladium	68
Table 16. Radiation by TLD chips; second experiment	69
Table 17. Radiation by Geiger-Mueller counters; second experiment	69
Table 18. Maximum and minimum counts in 46 hours and 9 minutes by Geiger-Mueller counters; second experiment	70
Table 19. EDS results Pd cathode before electrolysis side A; second experiment	77
Table 20. Comparison of EDS results picture 22 and 23; second experiment	81
Table 21. Comparison of EDS results Figures 67 and 69; second experiment	84
Table 22. Comparison of EDS results Figure 76 and 79; second experiment	88
Table 23. Comparison of EDS results Figure 83, 86, 87 and 90; second experiment	96

Table of figures

	page
Figure 1. Certificate of analysis palladium foil (lot#D12E06 and stock#11514)	9
Figure 2. Certificate of analysis platinum foil (lot#B24E24 and stock#00261)	10
Figure 3. Certificate of analysis platinum wire (lot#9820 and stock#10959)	10
Figure 4. Schematic placement of cells, lead blocks, background TLD chips and Geiger-Mueller counters for first and second experiment (top view)	14
Figure 5. Thermocouple placement for the first experiment	15
Figure 6. Thermocouple placing for the second experiment	16
Figure 7. Circuit used in the first experiment.	17
Figure 8. Circuit used in the second experiment	18
Figure 9. Pd and Pt cathodes from the first experiment; magnification 2 times	20
Figure 10. Pd and Pt cathodes from the second experiment; magnification 2 times	20
Figure 11. Setup C and D cell for the first experiment	23
Figure 12. Setup C and D cell for the second experiment	23
Figure 13. First experiment setup	24
Figure 14. First experiment setup	24
Figure 15. Second experiment setup	25
Figure 16. Second experiment setup	25
Figure 17. Temperature first experiment	27
Figure 18. Voltage first experiment	27
Figure 19. Temperature difference C - D first experiment	28
Figure 20. Voltage difference C - D first experiment	28
Figure 21. Location of the crack in glass bottle of D cell	30
Figure 22. Temperature (0 - 1h 10min) second experiment	32
Figure 23. Power input (0 - 1h 10min) second experiment	32

	page
Figure 24. Temperature difference C - D (0 - 1h 10min) second experiment	33
Figure 25. Difference in power input (0 - 1h 10min) second experiment	33
Figure 26. Temperature (1h 10min - 17h) second experiment	34
Figure 27. Power input (1h 10min - 17h) second experiment	34
Figure 28. Temperature difference C - D (1h 10min - 17h) second experiment	35
Figure 29. Difference in power input (1h 10min - 17h) second experiment	35
Figure 30. Temperature (17h - 17h 12min) second experiment	38
Figure 31. Power input (17h - 17h 12min) second experiment	39
Figure 32. Temperature difference C - D (17h - 17h 12min) second. Experiment	39
Figure 33. Difference in power input C - D (17h - 17h 12min) second experiment	40
Figure 34. Temperature D cell (17h 12min - 46h 09min) second experiment	41
Figure 35. Power input D cell (17h 12min - 46h 09min) second experiment	42
Figure 36. Radiation data obtained with two Geiger-Mueller counters; first experiment	47
Figure 37. Definition of names for the Pd cathode	48
Figure 38. Pd cathode before electrolysis; side A; first experiment	49
Figure 39. Pd cathode before electrolysis; side A; first experiment; magnification of area 1 in Figure 38	49
Figure 40. EDS spectra from Figure 39; first experiment; before electrolysis	50
Figure 41. Pd cathode before electrolysis; side A; first experiment; magnification of area 2 in Figure 38	51
Figure 42. EDS spectra from Figure 41; first experiment; before electrolysis	51
Figure 43. Pd cathode before electrolysis; side B; first experiment	53
Figure 44. Pd cathode before electrolysis; side B; first experiment; magnification of area 1 in Figure 43	53
Figure 45. EDS spectra from Figure 44; first experiment; before electrolysis	54

Figure 46. Pd cathode after electrolysis; side A; first experiment; compare to Figure 38	56
Figure 47. Pd cathode after electrolysis; side A; first experiment; magnification of area 1 in Figure 46	57
Figure 48. Pd cathode after electrolysis; side A; first experiment; magnification of area 1 in Figure 47	58
Figure 49. Pd cathode after electrolysis; side A; first experiment; magnification of area 1 in Figure 48	58
Figure 50. EDS spectra from Figure 49; first experiment; after electrolysis	59
Figure 51. Pd cathode after electrolysis; side A; first experiment; magnification of area 2 in Figure 46	61
Figure 52. EDS spectra from Figure 51; first experiment; after electrolysis	61
Figure 53. EDS spectra from Figure 51; first experiment; after electrolysis	62
Figure 54. Pd cathode after electrolysis; side B; first experiment; compare to Figure 48	64
Figure 55. Pd cathode after electrolysis; side B; first experiment; magnification of area 1 in Figure 54	64
Figure 56. EDS spectra from Figure 55; first experiment; after electrolysis	65
Figure 57. Magnification of impurity on original palladium foil	67
Figure 58. EDS spectra from Figure 57; original palladium	67
Figure 59. Radiation data obtained with two Geiger-Mueller counters; second experiment	71
Figure 60. Setup for the cell radiation measurement	72
Figure 61. Pd cathode before electrolysis; side A ; second experiment	74
Figure 62. Pd cathode after electrolysis; side A; second experiment	75

Figure 63. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure 62	76
Figure 64. EDS spectra from Figure 63; second experiment; after electrolysis	76
Figure 65. EDS spectra from Figure 63; second experiment; after electrolysis	77
Figure 66. Pd cathode after electrolysis and 150 minutes of ultrasonic cleaning in deionized water; side A; second experiment	78
Figure 67. Pd cathode before electrolysis; side A; second experiment; magnification of area 1 in Figure	79
Figure 68. EDS spectra from Figure 67; second experiment; before electrolysis	79
Figure 69. Pd cathode after electrolysis; side A; second experiment; magnification of area 2 in Figure 62	80
Figure 70. EDS spectra from Figure 69; second experiment; after electrolysis	80
Figure 71. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure 67	81
Figure 72. EDS spectra from Figure 71; second experiment; before electrolysis	82
Figure 73. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure	83
Figure 74. EDS spectra from Figure 63; second experiment; after electrolysis.	83
Figure 75. EDS spectra from Figure 73; second experiment; after electrolysis	84
Figure 76. Pd cathode before electrolysis; side A; second experiment; magnification of area 1 in Figure 71	85
Figure 77. EDS spectra from Figure 76; second experiment; before electrolysis.	85
Figure 78. EDS spectra from Figure 76; second experiment; before electrolysis.	86
Figure 79. Pd cathode after electrolysis; side A; second experiment; magnification of area 1 in Figure 69	86
Figure 80. EDS spectra from Figure 79; second experiment; after electrolysis.	87

Figure 81. Pd cathode before electrolysis; side B; second experiment	91
Figure 82. Pd cathode after electrolysis; side B; second experiment	91
Figure 83. Pd cathode before electrolysis; side B; second experiment; magnification of area 1 in Figure 81	92
Figure 84. EDS spectra from Figure 83; second experiment; before electrolysis	92
Figure 85. EDS spectra from Figure 83; second experiment; before electrolysis	93
Figure 86. Pd cathode after electrolysis; side B; second experiment; magnification of area 1 in Figure 82	93
Figure 87. Pd cathode after electrolysis; side B; second experiment; magnification of area 1 in Figure 82	94
Figure 88. EDS spectra from Figure 86; second experiment; after electrolysis	94
Figure 89. EDS spectra from Figure 87 and 86; second experiment; after electrolysis	95
Figure 90. Pd cathode after electrolysis; side B; second experiment; magnification of area 1 in Figure 86	95
Figure 91. EDS spectra from Figure 90; second experiment; after electrolysis	96

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