Reproduction of Fleischmann and Pons experiments

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Abstract

The objective of this work is to check the reliability of the initial Fleischmann and Pons calorimeter for studying cold fusion from ambient to boiling temperature. After describing our experimental set up, the assessment of excess heat from the enthalpy balance is discussed. We have observed deposits on the electrodes after electrolysis, which, in our opinion, have a determining role in the excess heat generation. We show raw data from three runs. It is concluded that this calorimeter is well adapted for such cold fusion investigation.

1- Introduction

Since the announcement of the cold fusion phenomenon by Fleischmann and Pons [1] in 1989, various techniques have been utilized to produce excess heat. Numerous results have been obtained seem random, and even sometimes contradictory with each other.

Being aware of that, we have decided to "simply" reproduce the exact experiments of M. Fleischmann and S. Pons as described in their 1993 article 2. The purpose of our work is to ascertain the various phenomena involved and the conditions of their appearance in order to master the experiments.

2- Experimental

2.1 Description of the experiment

The cell we use is identical to the one used by M. Fleischmann and S. Pons [2]. It is described in figure 1. It is a Pyrex Dewar with the upper part sliver coated to prevent heat radiation losses in this area, and to make the heat losses by radiation insensitive to the water level. The various parameters are as follows:

- the electrolyte: LiOD, 0.1 M l^{-1},
- the cathode: palladium cylinder (platinum for blanks), diameter 2 mm, length 12.5 mm is spot welded on a platinum wire,
- the anode: platinum wire, diameter 0.2 mm,
- a thermistor for temperature measurement of the electrolyte, with a precision of ±0.01°C at 20°C and of 0.1°C at 100°C,
- a resistor for heat pulses generation,
- a Kel-F plug for electrical connections, and a duct for replacing the water eliminated by electrolysis and by water vapor carried away in the electrolysis gases.

The cell is immersed in a constant temperature bath (20°C), as shown in Figure 2. Electrolysis is performed at constant current, with a high accuracy power supply, having a maximum voltage of 150 Volts. Current, voltage, temperature and atmospheric pressure are recorded by computer, with an AOIP interface box. Water is added automatically every time 1 cm^3 is consumed. Data are collected every 6 seconds, and averaged every minute.
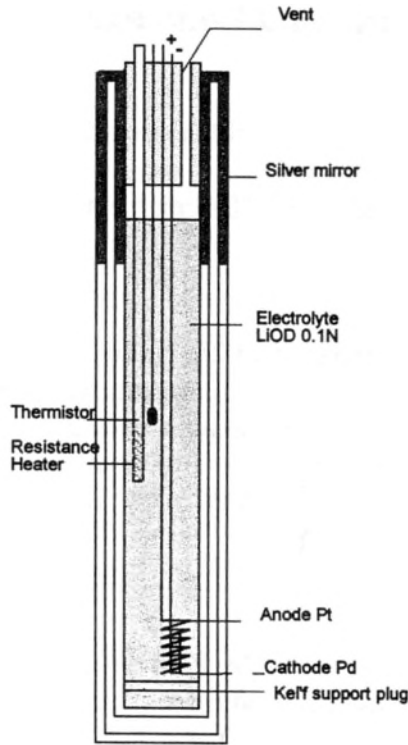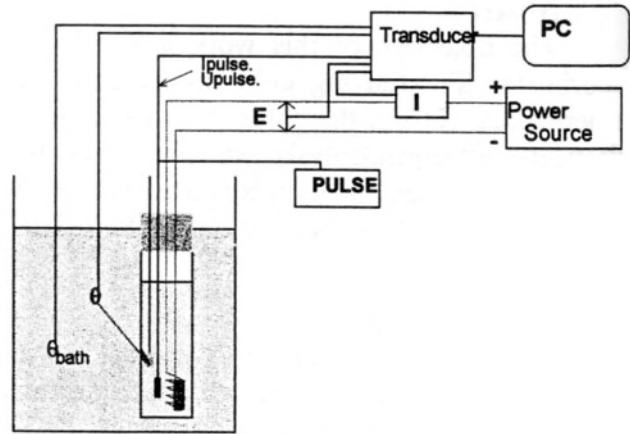
Figure 1. Fleischmann and Pons type cell   **Figure 2. Experimental stand**

2.2   *Experimental procedure*

The Dewar is cleaned with acetone, and dried in air. Heavy water (85 cm^3) is filled in the cell in an argon atmosphere to avoid contamination by CO_2 and H_2O from the air. Experiments are performed in a constant temperature room $\pm$ 0.1°C at 20°C. A typical experiment starts at low current: 0.2 A (0.26 A cm^{-2}) until temperature reaches 40°C. This period lasts typically one to two weeks. This "loading" period does not show any excess heat production. Current is then raised at 0.5 A (0.66 A cm^{-2}) until the cell reaches boiling temperature.

3- Assessment of excess heat

Excess heat is evaluated two ways. At temperatures below boiling we calculate excess heat on a continuous mode, while the experiment is being performed. At boiling the excess heat is calculated once all the water of the cell has been evaporated without addition of water.

3.1   *Excess heat calculation below boiling temperature*

In this regime, the excess heat is calculated from the energy balance[2] as detailed below.

Excess heat = A + B + C – D   (1)

Enthalpy flux evaluation formulae

Enthalpy losses (by radiation) to the water bath:

$$K_R\left(\theta^4 - \theta^4{}_{bath}\right)$$ (2)

Enthalpy content of the gas stream: [2]

$$\frac{3I}{4F}\frac{P}{P^*-P}L \tag{3}$$

Where "I" is the electrolysis current, "F" is the Faraday constant, "P", the water pressure at the temperature of the bath, and "P*", the atmospheric pressure. "L" is the enthalpy of vaporization of the water (41,000 J.mol^{-1}).

The variation in the enthalpy content of the calorimeter:

$$C_{pD_2O,l}M_o\frac{d\theta}{dt} \tag{4}$$

$C_{pD20,l}$ is is the heat capacity of liquid D_2O. The thermal mass of the calorimeter can be converted to an equivalent mass of D_2O, which is given as M_0.

The input electrical enthalpy:

$$(E-E_{th})I \tag{5}$$

Relation (1) is valid when there is no calibration pulses, and not at boiling, where the analysis using this approach becomes difficult because the denominator of (3) is close to zero as the temperature approaches boiling and water vapor pressure is close to the atmospheric pressure. At boiling, a different analysis is made which is described below. The only unknown parameter that needs to be calibrated is K_R. All other variables can be measured independently. K_R is determined by calibration with a platinum cathode.

3.2 Excess heat calculation at boiling temperature

When temperature reaches a value close to boiling, i.e. typically 99 to 101°C, we stop adding water to the cell, and we measure the total enthalpy necessary to evaporate the contents of the cell. The excess enthalpy is therefore given by the formula:

Excess heat = A + L – D (6)

Where "A", "D" and "L" have the same definition as above. It is difficult to follow accurately the level of water during this period because of the formation of foam, so it is only at the end of the experiment, when the cell is dry that the excess heat can be calculated with precision.

3.3 The various experimental regimes

a) Low temperature regime: $\theta < 70$°C

In this region relation, (1) becomes:

Excess heat = A - D (7)

Since temperature is low, the water vapor pressure is negligible; therefore "B" can be ignored. In this region, temperature varies slowly with time, hence "C" can be neglected.

This domain is the one used during calibration to determine K_R, since during blank runs, there is, by definition, no excess heat produced, K_R is therefore given by:

$$K_R=\frac{(E-E_{th})I}{(\theta^4-\theta^4_{bath})} \tag{8}$$

b)   Intermediate temperature regime: 70°C < θ < 99°C

In this region all terms of relation (1) must be taken into account. Since the water pressure becomes high, "B" becomes important and since the temperature varies rapidly "C" cannot be neglected.

c)   Boiling θ > 99°C

The boiling temperature is only progressively reached as the bubbles, here initiated by electrolysis incorporate more and more water vapor. In this region, the full calculation using equation (1) gives wrong positive excess heat measurements, and therefore cannot be applied. This is probably due to an erroneous estimation of "B" which is very sensitive to pressure and temperature measurements. Up until now we have not been able to get a good blank experiment with platinum in this region using the full equation. Therefore, instead, we use the measurement of the enthalpy produced to evaporate the total amount of water contained in the cell, as described in section 3.2.

4- Basic phenomena occurring during electrolysis

The main effect of electrolysis is generation of deuterium and oxygen gas at the electrodes. However in this type of cell, other side reactions occur which possibly have major importance in the production of excess heat. The basic phenomenon discussed here is the formation of an overvoltage on the electrodes. Table 1 shows a synthetic view of what we believe is happening:
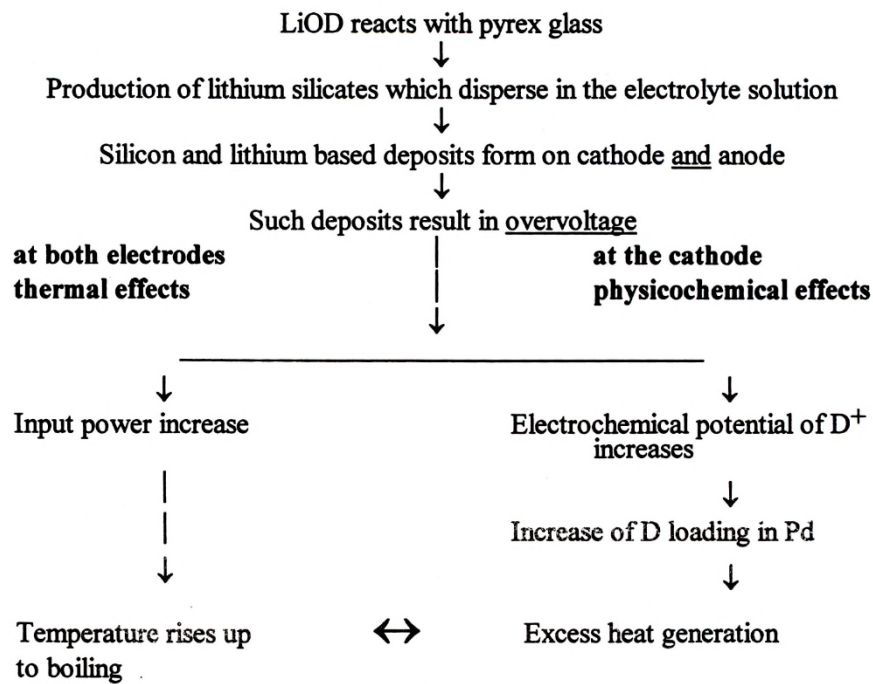
LiOD reacts with pyrex glass
↓
Production of lithium silicates which disperse in the electrolyte solution
↓
Silicon and lithium based deposits form on cathode <u>and</u> anode
↓
Such deposits result in <u>overvoltage</u>

at both electrodes | **at the cathode**
thermal effects | **physicochemical effects**
↓

────────────────────────────────

↓   ↓
Input power increase   Electrochemical potential of D^+
                                         increases
| ↓
| Increase of D loading in Pd
↓   ↓
Temperature rises up   ↔   Excess heat generation
to boiling

Table 1

5.1- Calibration experiments (platinum cathode)

As mentioned above, the two unknown parameters, M_0 and K_R, must be deduced from calibration since they cannot be calculated accurately.

K_R is deduced from blanks with platinum cathodes of the same size and positioned exactly as the palladium cathode. By definition, we assume that platinum does not produce excess heat. In the low temperature regime, below 70°C, relation (1) simplifies, and we use (8) to calculate K_R.

Figures 3a and 3b show a small apparent excess heat when temperature rises. This is most likely due to the heat losses by conduction, not taken into account in our formulas that assume all heat transfer is radiative. In any case, this apparent excess heat is low, at most 50 mW, or 1.25% of to the energy input. We have made attempts to change K_R with temperature, but without any significant change in the final result. Therefore, in our analysis, we have kept K_R constant with temperature.

M_0, the heavy water equivalent of the calorimeter is evaluated in runs without electrolysis by adding controlled heat pulses and measuring the rate of temperature change.
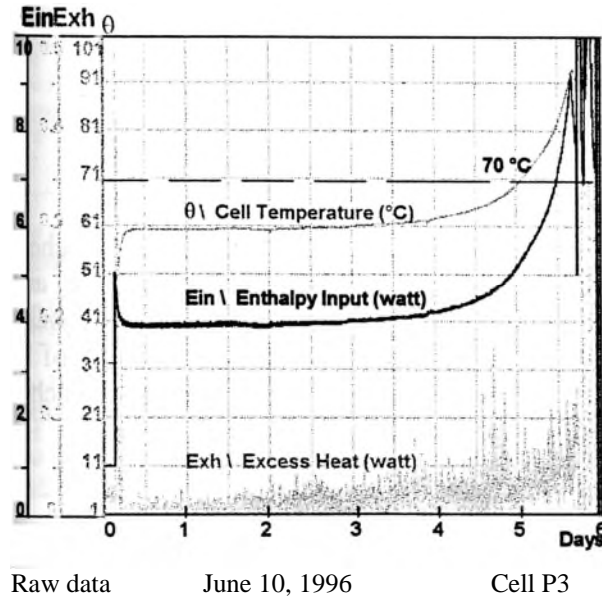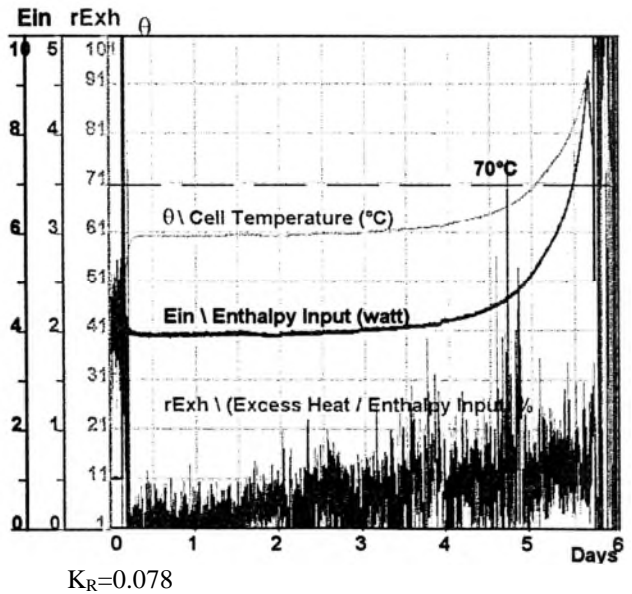

Raw data   June 10, 1996   Cell P3 K_R=0.078

Figure 3a   **Figure. 3b**

## Calibration experiment (platinum cathode)

5.2- Palladium cathodes experiments

Since the beginning of our experiments, in 1993, 18 runs have been carried out. Only five of them have produced excess heat, with high purity palladium cathodes. Figures 4a and 4b show a run with a pure palladium cathode, etched in aqua regia for five minutes. The sample has been loaded for ten days at low current (0.2 A), then the current is raised to 0.5 A. Excess heat increases from 70 mW to 170 mW at 70°C. At that point, contrary to our standard procedure, current is decreased to 0.25 A (voltage decreases simultaneously) and the input power decreases. However, the excess heat does not decrease, and has even a tendency to increase.
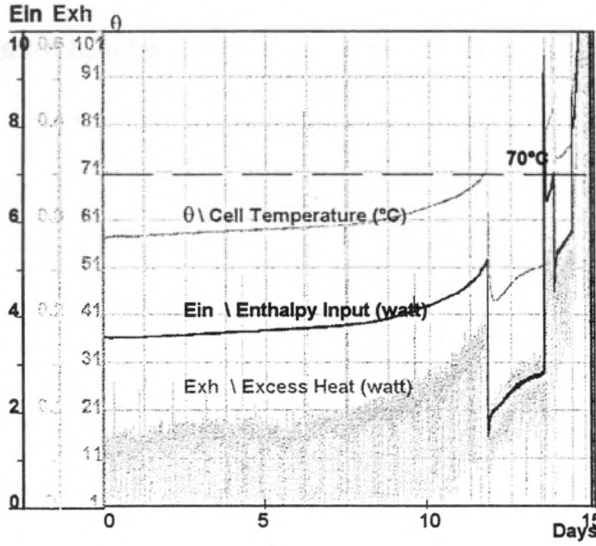
Raw data   January 30, 1996   Cell P1 K_R=0.075
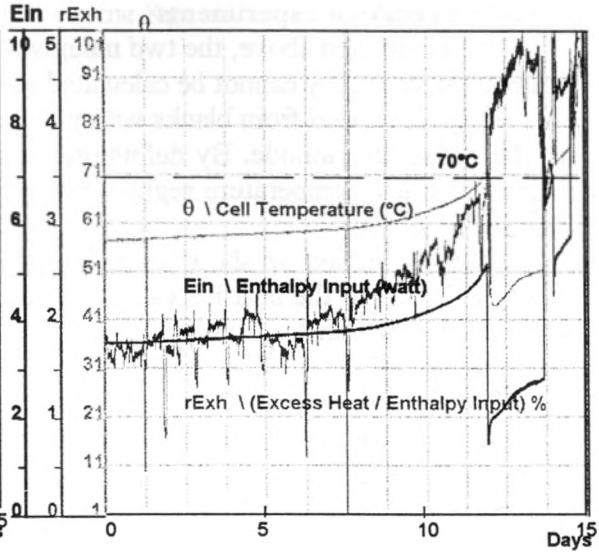
Figure 4a   **Figure. 4b**
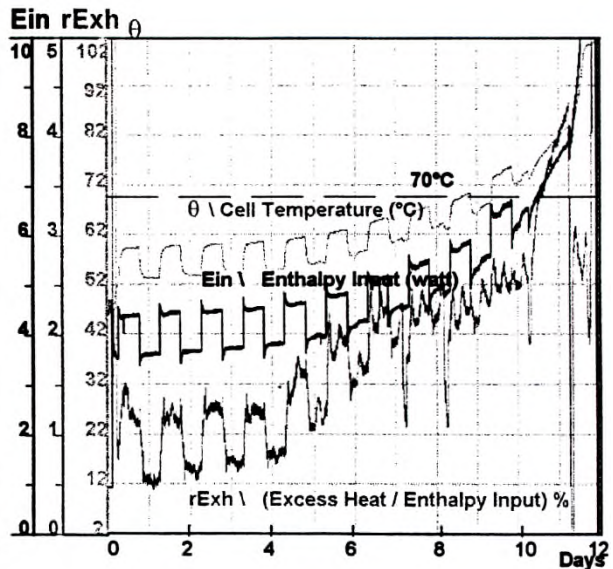
High purity palladium cathode (preliminary treatment in aqua regia)

Figures 5a and 5b show another run, where during the first three days, voltages have been switched and therefore the palladium was anodic. This has the effect of oxidizing the palladium surface, and then after making the palladium cathodic, to reduce the surface and to create a rough surface similar to palladium black. Also in this run heat pulses have been applied every 24 hours for a duration of 12 hours. At the beginning, the excess heat is 40 mW, then rises to 100 mW when temperature reaches | 60°C, and sharply rises to 300 mW above 75°C.
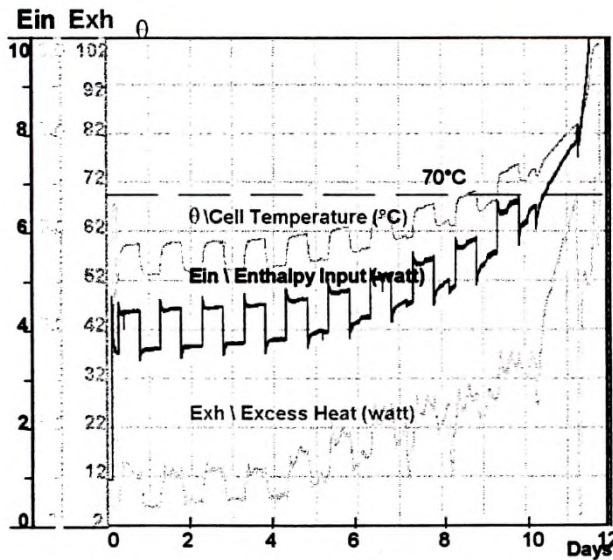
Raw data   September 39, 1996   Cell P2 K_R=0.0905

Figure 5a   **Figure. 5b**

High purity palladium cathode (initially inversed current).

At boiling, the electric current is maintained constant, (0.5 A), and as the overvoltage increases, the input energy grows up to the maximum of the power supply, in our case 75 Watts (maximum voltage 150 Volts). In all of our experiments showing excess heat at boiling, we have observed a sudden jump in power input towards the end of the experiment indicating a sudden change in the overvoltage. This might be due to the formation of a water gas film at the surface of the cathode when large quantities of heat are produced, either by electrical heating or possibly by the excess enthalpy itself. As described in section 3.2, the exact evaluation of the excess heat can be made only at the end of the experiment, since it is difficult to follow accurately the water level during the experiment. However it is very likely that most of the excess heat occurs at the end of the experiment after the voltage burst. We call this last period the "grand finale."

Table 2 shows five experiments that have brought to boiling, along with a platinum experiment. The final column relative to the last phase is calculated assuming no excess heat before the voltage jump.

Experiment	Date	Electrolyte Volume (cm^3)	Enthalpy Input (electrolysis) (joules)	Enthalpy losses (to bath water) (joules)	Available Enthalpy (joules)	Enthalpy used for total vaporisation (joules)	Excess Heat (joules)	Mean relative excess heat %	Relative Excess Heat during "grand finale" %
P1 Pd 1st sample	January 30, 1996	84	419,100	254,700	156,876	181,499	24,623	16	153
P1 Pt	Calibration March 18, 1996	85.5	425,700	240,600	185,100	184,740	360	-0.2	No burst
N Pd 1st sample	September 3, 1996	80	318,700	151,000	167,700	172,856	5,156	3	18
P3 Pd 1st sample	September 14, 1996	74	221,200	72,190	149,010	159,892	10,882	7	36
n Pd 2nd sample	September 30, 1996	72	308,600	178,700	129,900	155,570	25,670	20	97
P3 Pd 2nd sample	October 2, 1996	78	290,700	132,800	157,900	168,535	10,635	7	29

Table 2. Boiling regime: enthalpy balance

6-   Discussion

Several questions raised during our work have been answered, but many more are still open. In this section we will try to give indications of what we believe is correct and what still needs more work.

One of the criticisms of the Fleischmann and Pons work has been the temperature uniformity inside the cell. If temperature varies, the radiation law is not valid, and all radiation losses calculations should be wrong. We have looked carefully at this point, and by raising the thermistor, from its standard location in the middle of the cell all the way to the surface of the water. We have seen no significant temperature variation, indicating that mixing by the gases of the electrolysis is sufficient.

On the assumption that all heat losses are due to radiation, our platinum blank experiments indicate that this is a good approximation, and that the maximum error might be in the higher temperature range, and should not exceed 1%.

Concerning condensation on the inner surface of the plug, again our platinum runs indicate that it is negligible.

The main point that needs to be addressed is the importance of the various parameters that make these

experiments irreproducible. Many known and many more unknown parameters are important and deserve discussion.

We have shown that overvoltage is very important. Probably it helps increase the deuterium loading in the near surface region of the cathode, especially in the final phase.

Many groups have emphasized deuterium loading as the important factor. In our case we have not measured it, but we are not sure that this is an important information, since all electrical or weight measurements are average values that are not valid in this type of experiments where most likely reactions occur near the surface.

It is our experience that the palladium history is of prime importance. However we have been unable to decide if a simple treatment such as aqua regia is good or bad. Impurities might play a role, but we do not know which ones are necessary. What is the role of lithium, not as the electrolyte, but as part of reaction?

Another important aspect is the quality of the heavy water. We have used D_2O with a purity of 99.5%. It is also possible that in the loading phase the electrolyte gets purified slowly by differential electrolysis of the light water that escapes first. The long loading period might then be necessary to eliminate hydrogen.

This last assumption is one of the reasons why loading might be long, up to several weeks.

We have never observed any heat after death as mentioned by Fleischmann and Pons. [2]

7-   Conclusions

Our experience during this last three years, leads us to conclude that the Fleischmann and Pons calorimeter is very accurate and well adapted to study cold fusion phenomenon. It is simple and precise. However precautionary measures must be taken:

- the Dewar must be of excellent quality, i.e. good vacuum, in order to eliminate heat
  losses by conduction, and operate with radiation losses only,
- temperature calibration of the thermistors must be done very precisely,
- all electrical feedthroughs must be sealed off in order to eliminate spilling off of electrolyte
  by capillarity.

Our results concerning the relative excess heat (percentage of excess heat to enthalpy input) can be summarized as follows:

- below 70°C, between 0 and 5%
- between 70°C and 99°C, about 10%
- at boiling, up to 150% especially in the final phase which appears as the best condition to
  get a large amount of excess heat.

As already done by S. Pons, with ICARUS 9, it is necessary to operate at boiling on a permanent basis to obtain the most significant results.

References

1. M. Fleischmann and S. Pons, J. Electroanal. Chem, 261,301(1989)

2. M. Fleischmann and S. Pons, Phys. Letters. A 176, 118 (1993) 118 -129