Pd/D_2O Electrochemical Cell Excess Heat Simulation Using COMSOL Multiphysics

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Abstract This report studies excess heat generation in palladium-deuterium (Pd-D_2O) electrochemical cells, building on F&P'89 experiment. Using COMSOL Multiphysics, we simulate the electrochemical processes to find out the nuclear reactions giving rise to anomalous excess heat. Observations & Experimental details of Dewar type Isoperibolic calorimeter used in F&P experiments is also mentioned.

1. Background

On 23rd March, 1989 during a press conference at University of Utah, two well known electrochemists named Martin Fleischmann and Stanley Pons announced their discovery of nuclear fusion at room temperature, also known as cold fusion or low energy nuclear reactions. They reported excess heat released during the electrolysis of heavy water at palladium electrodes. The magnitude of the excess enthalpy was so large that it was not possible to account any chemical process for this. They hypothesized that the energy came from nuclear fusion occurring at room temperature, where deuterium nuclei in the palladium lattice were fusing to form helium, releasing energy in the process.

2. Observations from *F&P'89* Experiment

- Dissolution of D in the Pd electrodes is exothermic[1].
- Most heat excess occurs when D/Pd ratio is between 0.5-0.7[2].
- Pd gives maximum excess heat among Ni, Pt & Pd with D_2[2].
- Experiments were performed using Pd cathodes of length 10 cm & diameter 0.1, 0.2, 0.4 cm. It was observed that excess specific enthalpy was maximum for electrode of diameter 0.1 cm for current density of 1024 mA cm^{-3} [1].
- Excess enthalpy output was typically 1-20 W cm^{-3} of the electrode volume maintained for periods of 100 hrs i.e. giving 0.26-7.2 MJ cm^{-3} over measurement cycles[1].
- The specific energy output was 10^2-10^3 times larger than the enthalpy of chemical processes[1].
- Low levels of tritium and neutron were detected[1].
- Enthalpy release is not due to either of well established fusion reactions i.e.[1]:
  $2D + 2D \rightleftharpoons 3T(1.01\ MeV) + 1H(3.02\ MeV)$
  $2D + 2D \rightleftharpoons 3He(0.81\ MeV) + n(2.45\ MeV)$
- They performed electrolysis galvanostatically (minimum current ~200mA) in an Isoperibolic Calorimeter[1].
- Temperature in dewar cell was measured using thermistors (resistance sensitive to temperature)[1],[2].
- Rate of excess enthalpy production increase markedly with current density. (The rate of increase is at least on the order I^2)[1].
- Time dependence of the phenomena: "bursts" in enthalpy: *Firstly*, the rate of excess enthalpy generation increases slowly with time. *Secondly*, bursts in the production of excess enthalpy are superimposed on the slowly increasing enthalpy generation. Following such burst the excess enthalpy production returns to baseline value which can be higher than just prior to initiation of the burst. *Thirdly*, cells are frequently driven to the boiling point. The rate of enthalpy production become extremely large under such conditions since the dominant mode of heat transfer is now latent heat of evaporation[1].

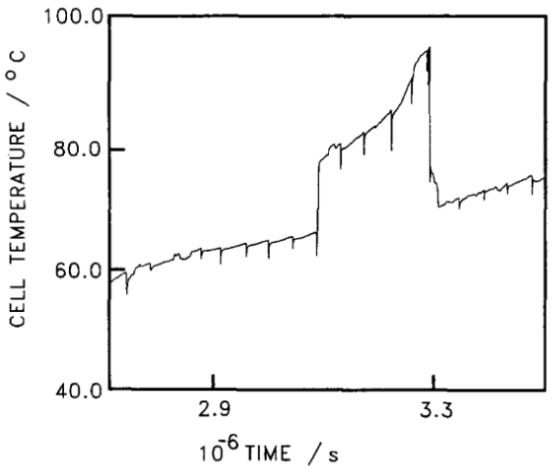

FIGURE 1. Cell temperature vs. time plot for a 0.4×1.25 cm Pd electrode in 0.1 M LiOD for a period during which the cell went to boiling.[1]

3. Dewar type Isoperibolic Calorimeter

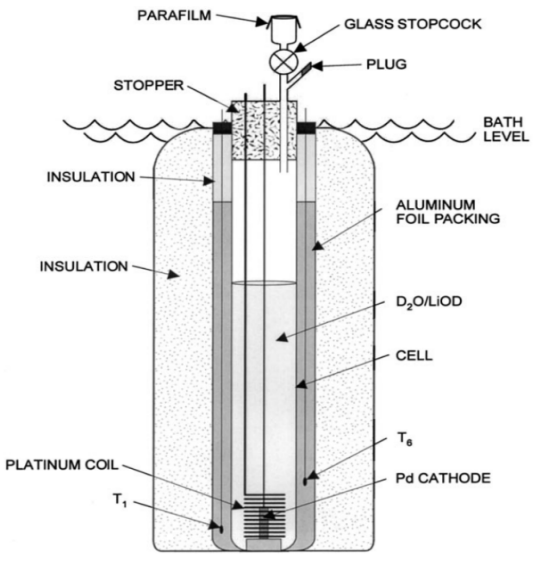

FIGURE 2. Schematic of the calorimetric design for Cell.[4]

3.1 Description

In Isoperibolic calorimeter, water bath is maintained at constant temperature. Isoperibolic calorimeter is an open thermodynamic system in which the major mode of heat transfer is by Electromagnetic Radiation (Infrared Radiation) and D_2 & O_2 escapes as soon as they are generated.[5]

3.2 Advantages

Advantages of using Dewar type isoperibolic calorimeter are:

- Wide range of cell temperature (20°C - B.P. of electrolyte).
- Wide range of cell input power (0 - 10W).
- Designed such that heat transfer is only by EM Radiation.
- Inner silvering reduce heat loss by reflecting infrared radiation back into the cell.
- Direct visual observation inside the cell.
- Can measure anomalous excess power of range 0.1mW.
- High accuracy (Power = ±1mW and error = ±0.1%)
- Provides very stable temperature readings.
- Relatively low cost (4-12 lakh).

3.3 Factors affecting excess heat

Physical Factors on which F&P excess heat effect depends:

- Cell diameter & Height (determine volume of electrolyte used).
- Rate of change of electrolyte level.
- Effectiveness of stirring by electrolytic gases (D_2, O_2).
- Dynamic range of power input.
- Magnitude of Kr (Radiative heat transfer coeff) & CpM (Water equivalent of system; Cp = heat capacity of D_2O;

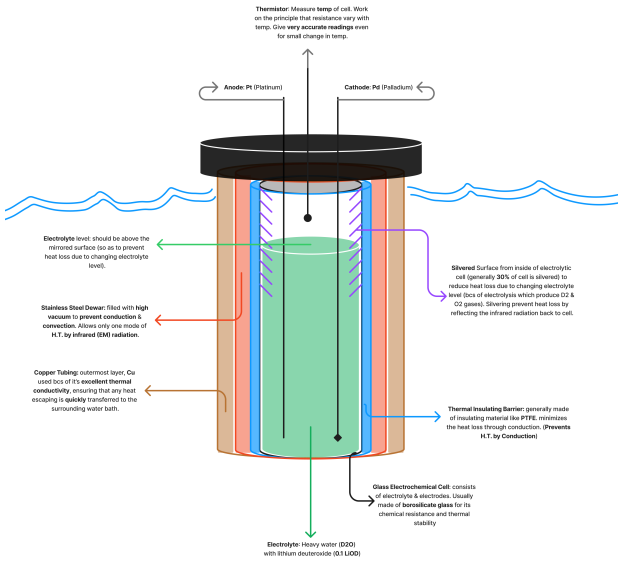

FIGURE 3. Illustration of dewar type isoperibolic calorimeter

3.4 Excess heat measurement

$$P_{calor} = P_{El} + P_H + P_X + P_{gas} + P_R + P_C + P_W$$
$$P_R = \mathrm{Kr}^* f(\mathrm{T}); \text{ where } f(\mathrm{T}) = T_{cell}{}^4 - T_{bath}{}^4$$
$$P'_R = P_R + P_C + P_W = -K'_R * f(\mathrm{T})$$
$$P_{calor} = C_P \mathrm{M}^* (\mathrm{d}T_{cell}/\mathrm{dt}) = P_{El} + P_H + P_X + P_{gas} - K'_R * f(\mathrm{T})$$
$$P_X = C_P \mathrm{M}^* (\mathrm{d}T_{cell}/\mathrm{dt}) + K'_R * f(\mathrm{T}) - P_{El} - P_H - P_{gas}$$
$$P_X \approx C_P \mathrm{M}^* (\mathrm{d}T_{cell}/\mathrm{dt}) + K'_R * f(\mathrm{T}) - P_{El}$$

where P_{calor} = Power due to temp change in calorimeter; P_{El} = Electrical Power (VI); P_H = Power applied by internal heater; P_X = Excess power; P_{gas} = Power carried away by the electrolysis gases exiting the cell; P_C = Power due to conduction; P_R = Net Electromagnetic Radiation; P_W = Pressure-volume work done by generated gases exiting the cell; $K_R = \sigma A$ = Radiative heat transfer coefficient; A = Area of unsilvered region inside cell; σ = Stefan-Boltzmann constant; K'_R = Pseudo heat transfer coefficient; P'_R = Pseudo radiative power term; C_P = Heat capacity of D_2O; M = Mass equivalent of D_2O;[1],[2],[3],[4],[5]

4. Further questions to study

- Which nuclear reaction is occurring during electrolysis of D_2O/Pd? What it's energetics?
- What is the ratio of length to diameter required for cathode to generate measurable excess heat? How is the variation of excess enthalpy with this ratio?
- What it the activation barrier of nuclear reaction happening inside the electrolytic cell? How is the energy required to cross this activation barrier achieved?
- How is the variation of cell temperature with time for different current density (with and without any reaction)?
- How is the variation of cell potential with time for different current density (with and without any reaction)?
- How is the variation of cell temperature with cell potential (with and without any reaction)?
- How do porosity of electrodes (especially Pd cathode) affect the cell temperature & excess enthalpy output?
- How do electrolyte volume (D_2O) & concentration of LiOD used affect the excess enthalpy output?
- By changing the other physical parameters, how can the excess enthalpy be maximised?

5. COMSOL Multiphysics Modeling

5.1 Modeling

To model electrolytic cell follow the steps given below:
Choose Physics: Water electrolyser (stationary & time dependent module)
Define geometry of system: Here we choose width of cathode = width of anode = 0.2 cm, width of separator = 0.1 cm & Height of electrodes = 10 cm.
Define BCs & ICs: Initial cell voltage = 1.2 V; Operating temperature = 343K; Pressure of gas = 1atm; Inlet & Outlet boundary for gases; KOH Electrolyte concentration = 6M;

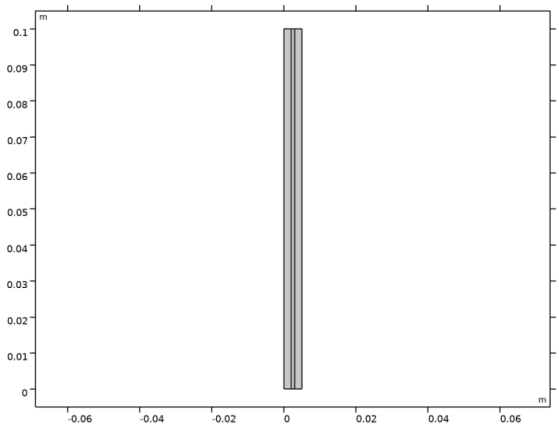

FIGURE 4. Model geometry for water electrolysis: L-R (Cathode-Separator-Anode)

5.2 Study & Results

We used the 'finer' mesh for our analysis & varied the cell voltage from [1.2V,1.9V] to obtain the following E_{cell} vs Current density plot for water electrolysis.

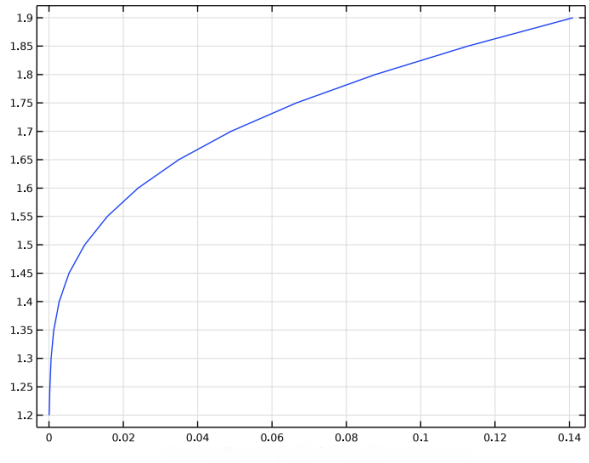

FIGURE 5. E_{cell} (y-axis) vs Current density (x-axis) curve for water electrolysis

References

[1] Fleischmann M., et al.: *Calorimetry of the palladium-deuterium-heavy water system*. Electroanalytical Chemistry, 1990.

[2] Melvin H. Miles, Martin Fleischmann: *Isoperibolic calorimetric measurements of the fleischmann-pons effect*.

[3] Miles, Melvin H.: *Fundamentals of isoperibolic calorimetric for cold fusion experiments*.

[4] Miles, Melvin H.: *Calorimetric studies of pd/d_2o+liod electrolysis cells*. Electroanalytical Chemistry, 2000.

[5] Storms, Edmund: *Science of low energy nuclear reactions*. 2007.

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