

## Numerical simulation of deuterium loading profile in palladium and palladium alloy plates from experimental data obtained using $\mu\text{s}$ pulsed electrolysis.

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### Abstract

Various palladium cathodes have been studied to determine the influence of metallurgy and surface treatment on deuterium loading. In this paper we apply a numerical solution to the appropriate differential equation to calculate the time dependent local deuterium concentration inside the plates. We use experimentally determined deuterium coefficients for the  $\alpha$ ,  $\beta$  and  $\gamma$  phases [1].

We find the highest concentration gradient in the case of oxidized samples.

### 1. Introduction

The aim of this work is to find correlation between local deuterium concentration and bulk and surface characteristics of the cathodes used in pulsed electrolysis. A high peak current (about 15 A) and very short pulses (800 ns) generator has been used to perform electrolysis in 0.3 N LiOD-D<sub>2</sub>O solution.

We tested pure palladium, palladium-silver, palladium-cerium and palladium-yttrium alloys, to see if a higher hardness (Ag) or the addition of a rare earth (Ce, Y), that has a high capability of absorbing deuterium, could be useful for increasing D/Pd ratio.

We also tried to verify if a surface oxidization treatment [2] influences the local concentration of deuterium. In fact, during the electrolysis, the PdO reduces and the area of active surface increases because of the formation of nanocrystals of palladium[3]. The flow calorimeter used for this experiment and our method to measure in situ the deuterium absorption rate in the metallic plate (25x25x1 mm) have already been described elsewhere [4],[5]. We used absorption rate data to assign boundary conditions of the diffusion equation. The numerical integration of this equation allows us to figure the time dependent concentration profiles of deuterium in the plates.

### 2. Methods

We described the deuterium motion in metal as due to the diffusion only and we integrated [6] the parabolic partial differential equation in one space variable:

$$\frac{\partial U(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ \mathcal{D}(U(x,t)) \frac{\partial U(x,t)}{\partial x} \right]$$

where :  $U = D/Pd$  value,  $x =$  space,  $t =$  time,  $D =$  diffusion coefficient.  $D(U)$  is obtained fitting data from experimental measurements of the diffusion coefficient. For the boundary conditions we have chosen :

$$J(t) = D(U(x,t)) \frac{\partial U}{\partial x}$$

where  $J(t)$  is the deuterium current flowing through the plate surfaces. We calculated this current as the number of moles entering the plate for second for square centimeter. In the following we compare the results of these measurements for pure Pd and oxidized Pd, for Pd<sub>90</sub>Ag<sub>10</sub> and oxidized Pd<sub>90</sub>Ag<sub>10</sub>, for PdCe (Pd 99.9x %, Ce 0.0x %) and oxidized PdCe, for PdY (Pd 99.9x %, Yttrium 0.0x %) and oxidized PdY. As concerning as the concentration profiles obtained by our numerical method we show the D/Pd ratio vs the thickness for each plate at different time steps of the loading process. It has to be noticed that for Pd alloys and oxidized samples we can show just a qualitative trend because we used the same values of the diffusion coefficient we used for pure palladium.

### **3. Results**

#### ***Palladium plates***

At the beginning of the loading the absorption rate of oxidized palladium shows a plateau that is absent in the pure one (fig. 1a). Only after  $15 \times 10^4$  s the PdO absorption rate values become less than for Pd. Meaning of this trend is that the loading efficiency is higher for treated palladium.

The difference between the values of the concentration profiles in the two samples (fig 1b) is not very evident. Absolute maximum value of loading ratio is the same ( $\sim 1.1$ ) for both plates.

#### ***PdAg alloy plates***

As for the PdO, the oxidized PdAg sample shows a higher loading efficiency respect to the not treated PdAg (fig. 1c). The initial value of its absorption rate is higher than in PdO. After  $7 \times 10^4$  s the PdAgO absorption rate become less than for the PdAg. A consequence of this trend is that the concentration profiles of PdAg and PdAgO become less and less different (fig. 1d).

Absolute maximum value of loading ratio is the same ( $\sim 0.8$ ) for both plates.

#### ***PdCe alloy plates***

The deuterium loading efficiency of not treated plate is the least among all the samples. The absorption rate of the oxidized sample is very high at the beginning of the experiment (fig. 2a) and after  $13 \times 10^4$  s it becomes equal to the PdCe.

The D/Pd ratio is higher near the surface during the first hours of the experiment (fig. 2b).

Absolute maximum value of loading ratio is higher in oxidized palladium alloy ( $\sim 0.9$ ) than in not treated one ( $\sim 0.6$ ).

#### ***PdY alloy plates***

Also in this case the treated sample shows an initial high absorption rate but without any plateau (fig. 2c). After  $17 \times 10^4$  s the PdYO absorption rate becomes less than the PdY.

The difference between the behavior of the concentration profiles of the two plates is less than in the case of the PdCe samples (fig. 2d).

Absolute maximum value of loading ratio is the same for both plates ( $\sim 1.1$ ).

#### 4. Conclusions

The oxidation surface treatment is determinative to obtain a high loading efficiency. In PdCe the difference between treated and not treated sample is very clear also in the concentration profiles. In the case of PdYO we obtained high value of absorption rate but for the shortest time, while in PdO the value of the absorption rate has remained high for the longest time. The oxidized palladium sample has also reached the highest final value of D/Pd rate.

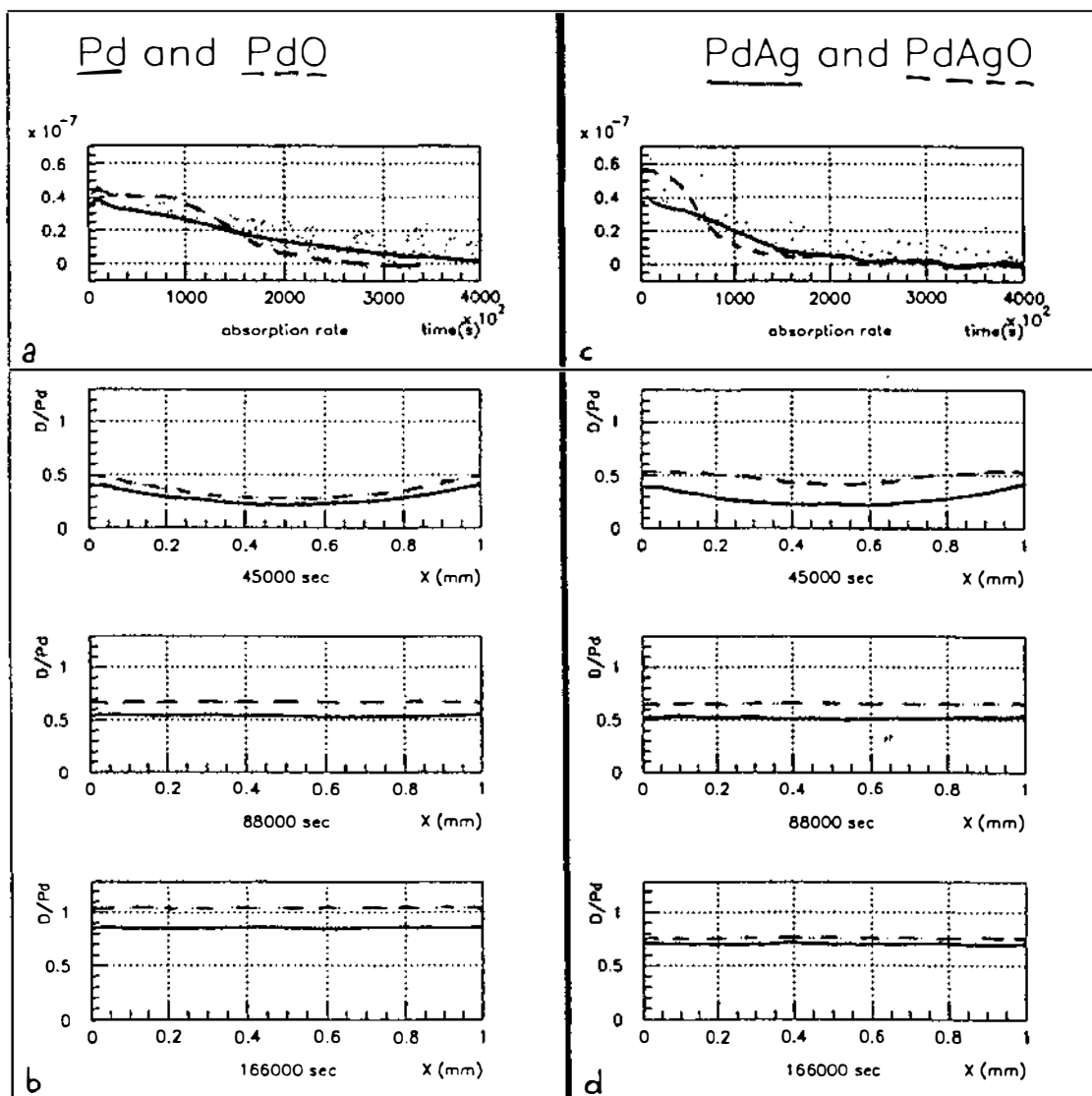
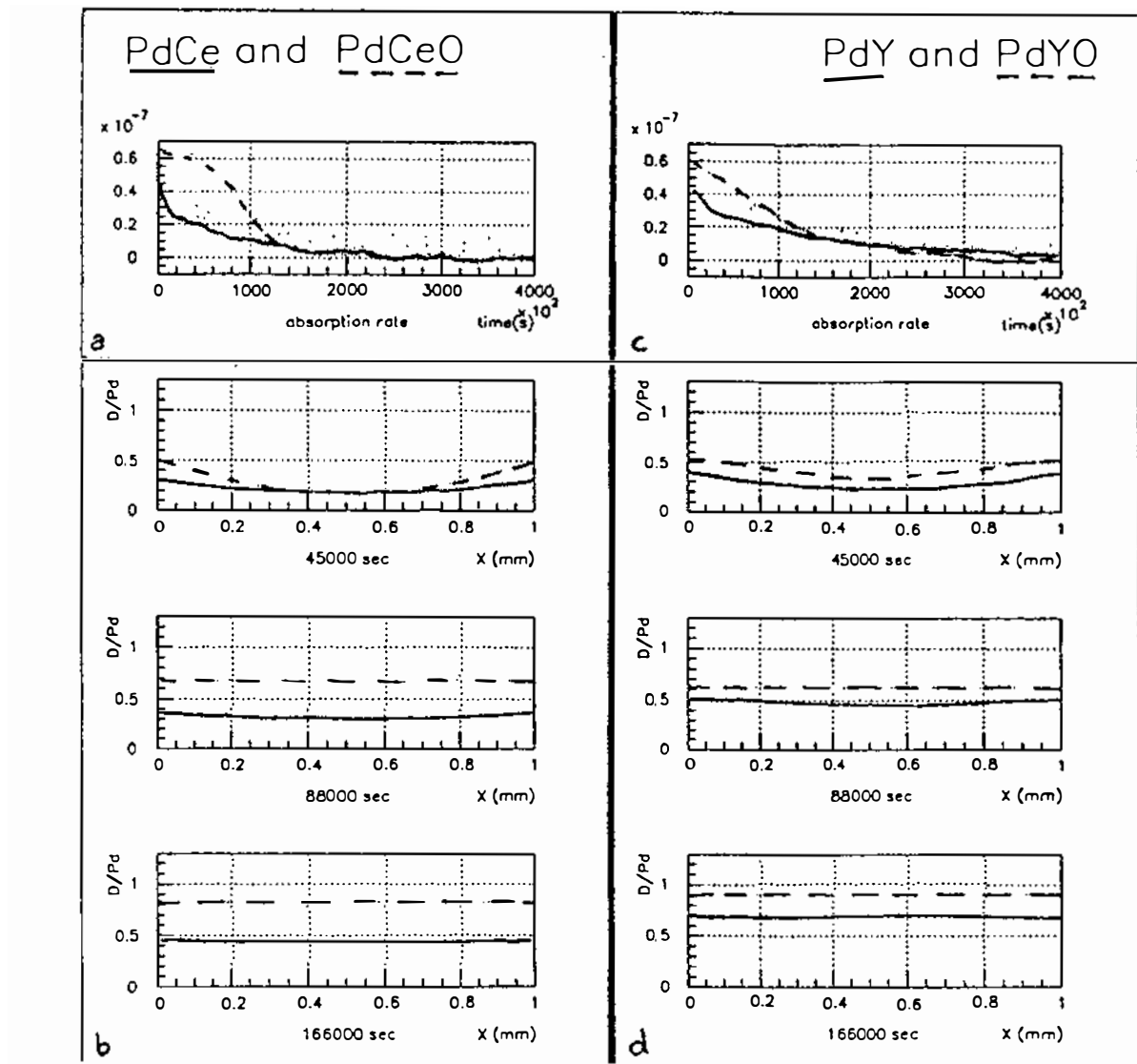


fig. 1a : Absorption rate (in moles per unit area per second) versus time for Pd (full line) and Pd oxidized plates (broken line).  
 fig. 1b : Concentration profiles vs the depth of Pd (full line) and PdO (broken line) plates (at 45000, 88000, 166000 s after the beginning of the experiment ).  
 fig. 1c : Absorption rate (in moles per unit area per second) versus time for PdAg (full line) and PdAg oxidized plates (broken line).  
 fig. 1d : Concentration profiles vs the depth of PdAg (full line) and PdAgO (broken line) plates (at 45000, 88000, 166000 s after the beginning of the experiment ).



**fig. 2a:** Absorption rate (in moles per unit area per second) versus time for PdCe (full line) and PdCe oxidized plates (broken line).

**fig. 2b:** Concentration profiles vs the depth of PdCe (full line) and PdCeO (broken line) plates (at 45000, 88000, 166000 s after the beginning of the experiment ).

**fig. 2c:** Absorption rate (in moles per unit area per second) versus time for PdCe (full line) and PdCe oxidized plates (broken line).

**fig. 2d:** Concentration profiles vs the depth of PdY (full line) and PdYO (broken line) plates (at 45000, 88000, 166000 s after the beginning of the experiment ).

### References

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