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Numerical Simulation of Deuterium Loading Profile in Palladium and Palladium Alloy Plates from Experimental Data of Absorbed Mole Rate Obtained Using μs Pulsed Electrolysis

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Abstract

Different kinds of palladium plates have been used as cathodes in pulsed electrolysis to study the influence of metallurgy and surface treatment on deuterium loading value. We calculated local deuterium concentration by mean of the diffusion equation, using for its boundary conditions experimental data of absorption rate [1].

For the diffusion coefficient of the deuterium in metals (α , β and γ phase), depending on the local concentration ratio D/M , we have used experimental values[2].

The highest concentration gradient was found in the case of oxidized palladium sample.

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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-D₂O 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 [3] 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 [4]. The apparatus used for this experiment has already been described elsewhere [5]. It is a flow calorimeter that allows to measure in situ the deuterium absorption rate in the metallic plate (25x25x1 mm). We used these data to assign boundary conditions of the diffusion equation. The numerical integration of this equation allows us to Figure the 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:

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

where : U = D/Pd value , x = space , t = time , D = diffusion coefficient . Values for D are taken 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 the measurements we have done with pure Pd and oxidized Pd, with Pd₉₀Ag₁₀ and oxidized Pd₉₀Ag₁₀, with PdCe and oxidized PdCe, with PdY and oxidized PdY.

As concerning as the concentration profiles, we show the D/Pd ratio vs the thickness for each plate at different time steps of the loading process.

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 15·10⁴ 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.

As the absorption rate is higher than the diffusion speed, the D/Pd ratio is higher near the surface (Fig. 1b) at least until the saturation is reached. This behavior is more evident in the oxidized sample (see 88000 s). Absolute maximum value of loading ratio is the same (~1.1) for both plates.

PdAg alloy plates

As for the PdO the oxidized PdAg sample shows a higher loading efficiency respect to not treated PdAg (Fig.1c).The initial value of its absorption rate is higher than in PdO.After $7 \cdot 10^4$ 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 (~ 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 $13 \cdot 10^4$ s it becomes equal to the PdCe.

The difference between the value of the concentration profiles is quite the same during the experiment (Fig.2b).

Absolute maximum value of loading ratio is higher in oxidized palladium alloy (~ 0.9) than in not treated one (~ 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 $17 \cdot 10^4$ 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 (~ 1.1).

4. Conclusions

The oxidization surface treatment is determinative to obtain a high loading efficiency and a higher concentration gradient.Only in the case of PdAgO alloy the effect is not evident while in PdCe the difference between treated and not treated sample is very clear.In the case of PdY we obtained high value of absorption rate but for the shortest time.The best results as concerning as the concentration gradient and the final value of D/Pd rate has been obtained for the PdO sample.

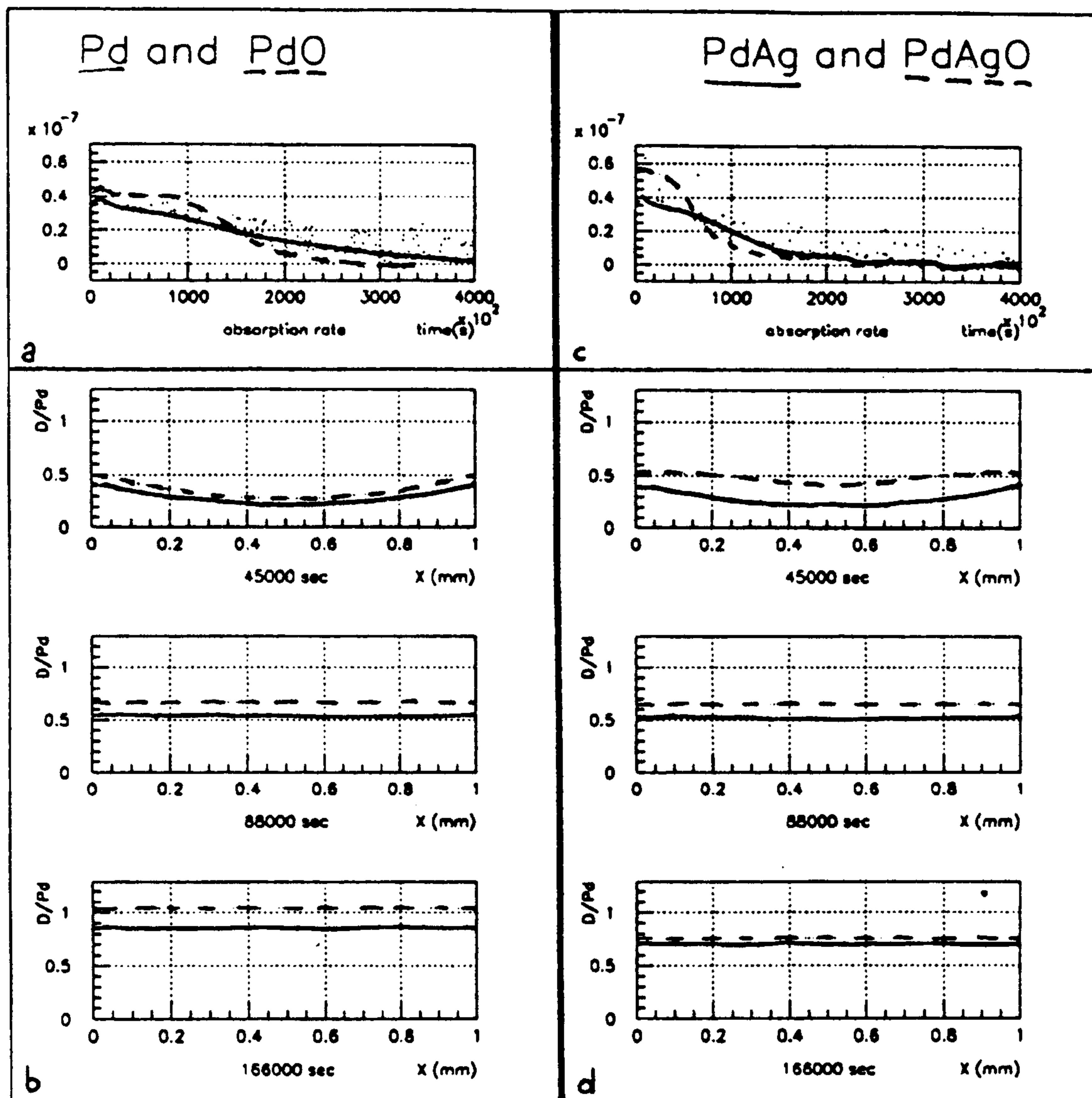


Fig.1a : Absorption rate (in moles per unit area per second) versus time for Pd (full line) and Pd oxidized plates (broken line).

Fig.1b : Concentration profiles vs the depth of Pd and PdO 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 and PdAgO plates (at 45000, 88000, 66000 s after the beginning of the experiment).

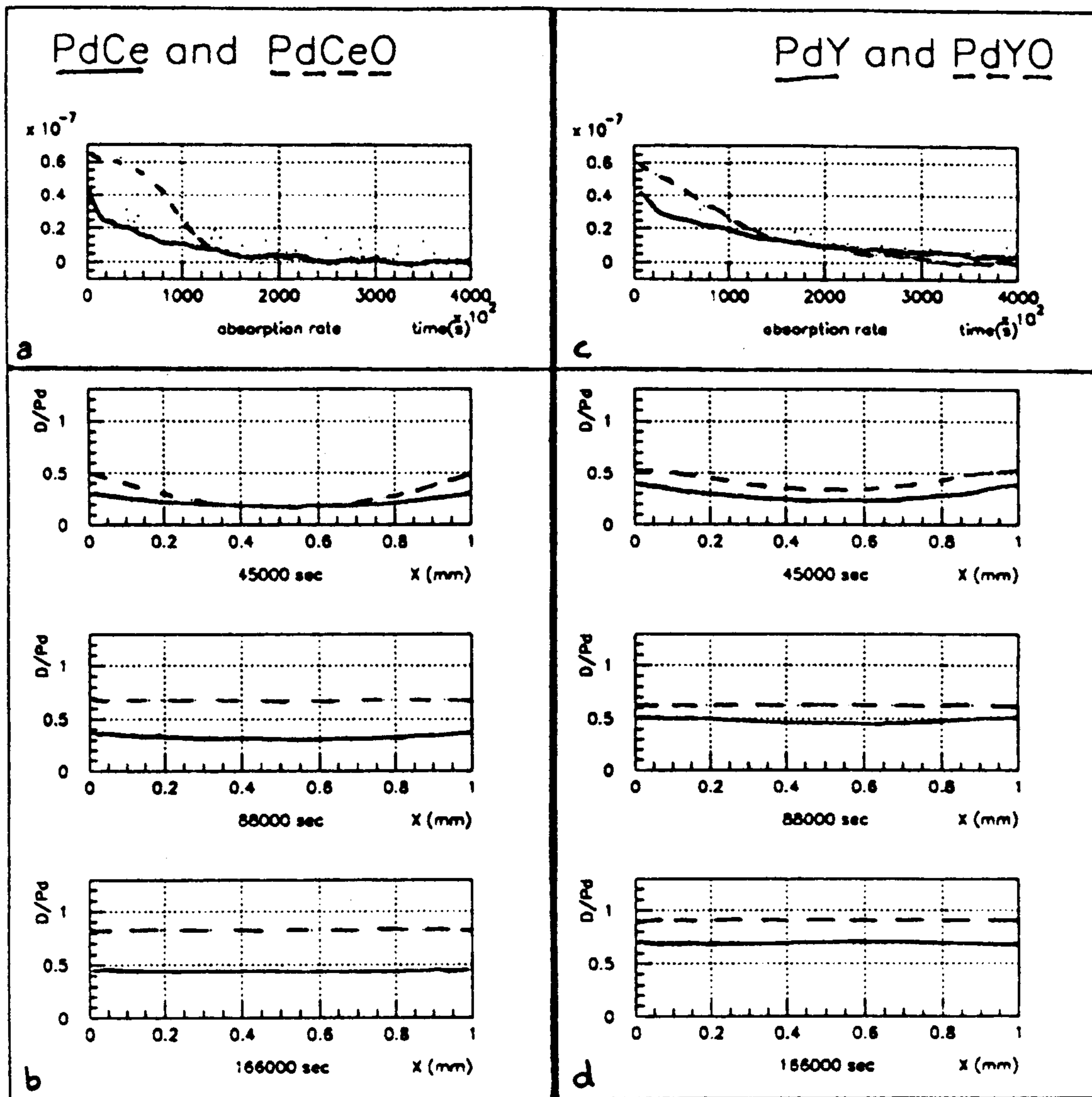


Fig.2a: Absorption rate (in moles per unit area per second) versus time for PdCe (full line) and PdCe oxidized plates (broken line).

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

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