"Quasi-Plasma" Transport Model in Deuterium Overloaded Palladium Cathodes

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ABSTRACT

The Pd-D system has been described assuming a two-population model. A "quasi-plasma" delocalized boson gas picture has been used for the deuterons exceeding the stoichiometric ratio in Pd-D compounds.

A mathematical model supported by a numerical computer code with distributed parameters has been developed in order to describe the evolution of the deuteron concentration profile inside a Pd cathode under pulsed electrolysis. Several boundary conditions have been taken into account.

A strong correlation has been found between the model system evolution and the experimental data[1].

1. Introduction

It is well established from experiments that (hydrogen or) deuterium can be loaded in the Pd lattice even above the so-called stoichiometric ratio, $X = D/Pd = 0.7$ (atoms of D per atom of Pd). Up to this value (hydrogen or) deuterium atoms are arranged in the lattice in the octahedral sites. A further increase in concentration (or loading ratio) can be described by assuming "guest" atoms delocalized arranged in shallow holes[2] corresponding to tetrahedal sites. The relative low energy barrier between two tetrahedral sites brings out to describe this population as almost free to move from a side to an other. We will refer only to D atoms.

In the following we will quote from the current literature two features of DPd compounds, showing that the D atoms exceeding the stoichiometric ratio have a very different kind of interaction with the lattice.
- It has been observed [3,4] that the diffusion coefficient of D in Pd increases steeply by almost two orders of magnitude above $X=0.7$.

This effect can be explained by assuming that the energy variation, required for an atom to move from a lattice site to another, decreases as the concentration increases. The diffusion coefficient follows the Arrenius law

$$D = D_0 exp(-E/kT)$$

where E is the energy barrier between two neighbour sites. Thus, the experimental data can be explained by assuming that the barrier is lowered when X exceeds 0.7.
- It is known [5,6] that the relative change of volume ($\Delta V/V$) of the Pd lattice cell as a function of loading ratio is a straight line, which shows a change in slope approximately at X = 0.7. This means that, for concentrations higher than this, the interaction between the D atoms and the Pd lattice changes.

These two features prompted us to propose a picture, in which the D atoms in the Pd lattice can be divided in two groups: localized atoms in the octahedral sites, and delocalized ones in the tetrahedral sites. The two groups have different kinds of interaction with the lattice. It has to be remembered that, even when X > 0.7, both groups are present: but, statistically, the delocalized fraction is negligible if octahedral sites are available, the latter's energy level being lower than for tetrahedral sites.

The model describes the behaviour of the latter population than it assumes a Pd lattice in which the octahedral sites are already filled. Since the particles are indistingushable exchanges between two population doesn't modifie the system status.

2. The model

Many experiments show that, when electrolytically charging D in Pd, the production of anomalous heat excess can be detected, if the loading ratio is in the range 0.8 - 1, or even larger. A typical feature of the first experiments was the need for a long pre-charging procedure, as long as weeks, or even months, in order for the anomalous effect to appear. More recently a pulsed technique has been used[7], consisting in either applying a sawtooth current (just at the beginning of the run), or alternating low currents to high currents with long periods ("lo-hi" technique), resulting in a much more efficient charging mechanism. This behaviour pushed us to study, from a theoretical point of view, the loading and the transport dynamics of D in Pd, for X > 0.7, in the framework of hi-lo electrolysis.

The model considers the Pd cathode as a membrane (with very high surface/thickness ratio), separating two regions. Two different instances have been considered:
A. The cathode is totally immersed in an electrolytic cell,
B. Only one of the sides of the cathode participates to electrolysis, while the other is exposed to an ambient containing D_2 gas.

It is well known that, during electrolysis, a strong electric field is present at the cathode-electrolyte interface. Furthermore, it is reasonable to assume a Thomas-Fermi like interaction between delocalized D atoms. Actually a dependence from the D concentration of the electronic shield has been assumed. We can then write an expression for the atom flow, depending both on concentration and local electric field:

$$J = -D(\nabla C + \frac{Fz^*E}{RT}C) \qquad (1)$$

where:
D diffusion coefficient, F Faraday constant, E total local electric field, C deuterium concentration , R gas constant, T temperature.

The local electric field can be considered as the algebraic sum of the applied electric field (due to electrolysis) and the reactional field due to the Thomas-Fermi like potential. The former is non-zero only at the cathode-electrolyte interface, while the latter can be calculated as a function of the loading ratio. Then. the mass transfer equation, in transient conditions, can be written as:

$$\frac{\partial C}{\partial t} = D\nabla^2 C + \frac{Fz^*}{RT}E\nabla C \qquad (2)$$

where: z^* effective deuteron charge (electrotransport)[8-9].
where C is the concentration of delocalized deuterons, R is the gas constant, F is the Faraday constant, T is the temperature, and E is the local electric field.

The interaction potential between delocalized deuterons (in the Thomas-Fermi picture) is:

$$\phi = \frac{q}{4\pi\varepsilon_o r}exp(-\frac{r}{\lambda_D}) \qquad (3)$$

where r is the distance between a delocalized deuteron and the first neighbour (proportional to $1/N^{1/3}$), λ_D is the Debye distance, and q is the electric charge.

The initial and boundary conditions are:

$$C(x_1, t=0) = 0$$

$$a) \quad C(x_o, t) = \begin{cases} C_1 & t_o < t < (2n+1)t_s \\ \\ C_2 & (2n+1)t_s < t < 2(n+1)t_s \end{cases} \qquad (n = 0,1,2,......)$$

$$E(x_o, t) = E_o \delta(x_o)$$

b) $\quad x = L; -D\frac{\partial C}{\partial x} = J_{ADS/DES}$

c) $\quad x = \frac{L}{2}; \frac{\partial C}{\partial x} = 0$

Where: $2t_S$ is the period of the pulsed electrolysis, C_1 e C_2 are the surface concentration, on the electrolysis side, in low and high current respectively[10].

Condition (a) describes the electrolysis side of the electrode, condition (b) describes an electrode having one side in D gas ambient, condition (c) points a symmetric electrolysis (the membrane cathode is between two equal anodic plates).

In order to evaluate the flow, in the gas ($J_{DES/ADS}$) it is necessary to write down a mass balance. Since the flow is a function of the surface concentration and of the deuterons concentration in the gas phase, we can write:

$$\frac{\partial C_{SUP}}{\partial t} = K_{ADS}C_{GAS} - K_{DES}C_{SUP} + J_{DIFF} \tag{4}$$

where

$$J_{DIFF} = -D\frac{\partial C}{\partial x}; (x = L)$$

K_{DES} and K_{ADS} are the desorption and adsorption constants respectively, C_{GAS} and C_{SUP} are the D concentration on the gas phase cathode side and in the gas bulk respectively. The desorption rate has been approximated as a lumped first order kinetic.

The gas flux from/towards the cathode produces a variation of the number of D molecules in the gas phase producing a pressure variation:

$$\frac{\partial P}{\partial t} = \frac{RT}{V}\frac{\partial N_{GAS}}{\partial t} \tag{5}$$

where P is the gas pressure, V is the gas volume and N_{GAS} is the number of D molecules within the gas (ideal behaviour is assumed).

The D concentration variation in the gas is:

$$\frac{\partial C_{GAS}}{\partial t} = \frac{1}{RT}\frac{\partial P}{\partial t} \tag{6}$$

The model just described has been solved numerically by finite-difference method. For the adsorption/desorption constants, data from the literature have been used.

3. Results and conclusions

The main features emerging from this model are the following:
1. The period ($2t_S$) of hi-lo electrolysis affects the charging efficiency and the concentration profile (see Fig.1): with a proper period, strong concentration gradients are set up.
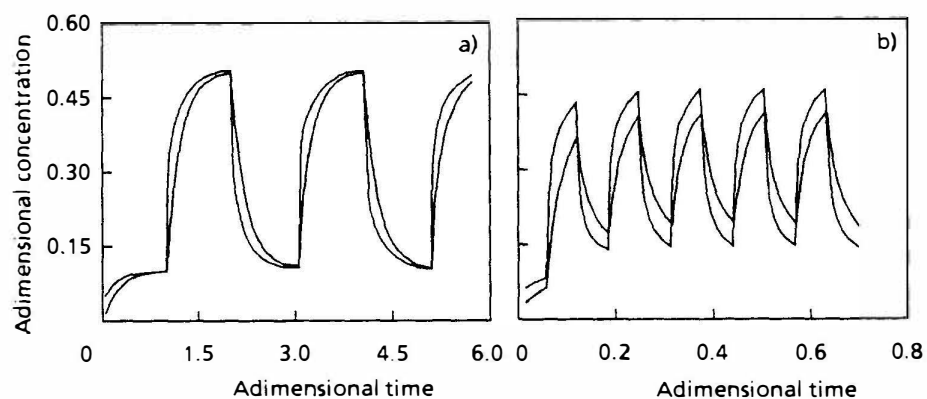
Figure 1. Concentration evolution in two contiguous slabs near the cathode surface in the electrolysis side. Profile in b) has been obtained with a period 4 times shorter than the one of a) case. Note the different time scale.
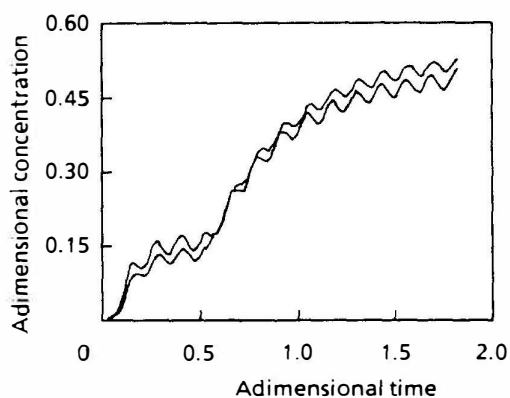

Figure 2. Concentration profiles evolution in two contiguous slabs near the cathode surface exposed to D2 gas. The perturbation simulates the inversionof the flow on the gas side.

2. A strong external electric field enhances the charging efficiency and the global loading ratio: it has been observed[6] that an increase in the potential across the cell (at constant current) announces the production of heat excess.

3. The inversion of flow on the gas side produces a compression on the delocalized deuterons (see Fig.2), and the rate of loading is increased.

The experiments performed at ENEA/Frascati[1] show that a strong D2 gas adsorption is detected when heat excess is produced. Thus, the model gives a satisfying description of the diffusion of deuterons in a Pd cathode under electrochemical loading: it was possible to establish a correlation between the deuterium dynamics within the cathode and the production of heat excess: the model analysis leads to the following consideration concerning the development of excess of heat oriented experiments. The electrode surface should be maintained active from the absorption point of view and an "ad hoc" poisoning on the surface, aimed to reduce the deuterium recombination and/or to enhance the cathodic over-potential, should be studied. In the geometry of the cell, particular care should be given to the evaluation of the currents distribution.

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