LOADING OF H(D) IN A Pd LATTICE

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The aim of the present contribution is to summarize what we have learnt in the last years about the ways and the means through which we are able to reach high loadings (x=D/Pd >1) in Pd-D systems.

We list in the following the main features of the above systems at high x.

1 G. Preparata [1] has stressed that when x becomes larger than a critical threshold, deuterons enter in a coherent oscillatory state. Deuterons while in the β-phase (x<0.7 at room temperature), are confined in deep and narrow wells at definite lattice sites; this occurs since the d-shell electrons of Pd through their coherent oscillations produce stationary potential wells at these sites [2]. It has been discovered however, a long time ago [3], that at x ≈ 0.8 the number of conduction electrons per Pd atom as a function of x exhibits a sharp discontinuity of its slope (see fig. 1); in other words, when for x < 0.8 each Hydrogen or Deuterium entering in the Pd lattice contributes about 0.75 electrons to the conduction band, when x crosses 0.8 each new H (D) contributes more than five electrons to the conduction band ! This means that each new guest of the lattice donates its own electron and persuades four Pd electrons to shift to the conduction band, so the whole electron structure of the Pd-H(D) system gets rearranged; the d-shell electrons which help to keep H(D) nuclei confined become less numerous and then the potential wells become shallower and wider which allows to H(D) nuclei to perform oscillations that, according to their dynamics, described in the Chap. 5 of Ref. 1, are able to tune their phase and become coherent. The raising of some electrons from the d-band to the conduction band accounts for the endothermic character of the loading at high x and for the simultaneous increase of the electric conductivity induced by the larger number of carriers. We refer to this new phase of the Pd-H(D) system as the γ-phase.
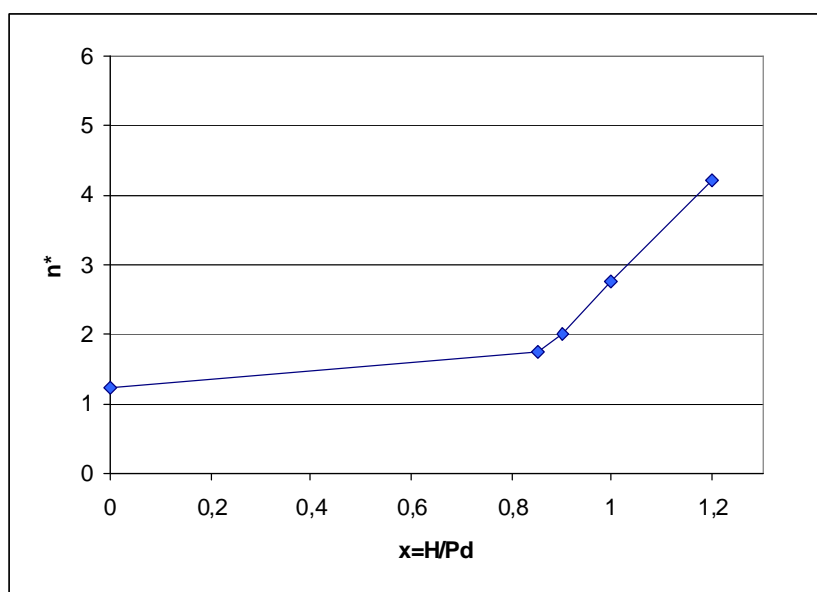

Fig.1 Effective number n* of free electron carriers per Palladium atom

2. The transition from the β to the $\tilde{\gamma}$ phase changes the quantum state of the H(D) nuclei in Pd; whereas in the β phase each H(D) has its own wave function and the full ensemble is described by a statistical mixture, where the relative phases of the hydrogens (deuterons) are uncorrelated, in the γ-phase they oscillate in unison so that the whole ensemble has a defined unique phase and is described by a unique wave function. It is well known [4] that an externally applied potential enters into the phase of the wave function of the quantum system and thus adds up to its chemical potential μ:

$$\mu(V) = \mu(0) + Z^*eV \qquad [1]$$

where Z^*e is the screened charge of the nucleus oscillating in the Pd-lattice. We stress that Eq. [1] is valid only if the system of hydrogen (deuterium) nuclei is coherent; should Eq. [1] be found valid in the real Pd-H(D) systems, this should be considered as a proof of the coherence of the H(D)'s .

3. Eq. [1], when applied to Pd cathodes in an electrolytic cell, is the "Preparata effect" , formerly termed "Cöhn-Aharonov effect "[5]. To exploit fully the impact of Eq.[1] on the loading, we need to use one-dimensional cathodes. Actually one needs V as large as possible and the ensuing electric current I as low as possible, since the heating induced in the Joule effect would spoil the coherence of H(D)'s and consequently vitiate the very existence of Eq. [1].

The solution is to use a cathode having a resistance $R=\rho l/s$ as large as possible and which implies that the length l be as large as possible and the cross section s be as small as possible; which suggests the use of a wire or a stripe, where the electrolytic current enters from the side surface and the potential is applied along the z-axis [see fig.2]. A potential V applied at the extremes of the cathode wire (or stripe) modifies the chemical potential according to Eq. [1] and induces no significant Joule heating if R is large enough. In the experiments at ENEA we have used stripes 100 cm long, 54 μm wide and 2 μm thick obtained by sputtering deposition on a non conducting surface in a bustrophedic configuration, as described in a different contribution to this Conference [6]. In the above layout $R(x=0)=R_0\approx 2500$ Ohms, so that the power released by the Joule effect is about 40 mW when V is about 10 V.

The chemical potential μ of H(D) in Pd can be decreased through the Eq. [1] by applying a negative potential and the decrease is non homogeneous along the cathode reaching a maximum where V is most negative, namely at one extreme. The application of a longitudinal negative electrical potential, decreasing the chemical potential, lowers the energy barrier that prevents the inflow of H(D)'s into Pd when x reaches the critical threshold. Consequently an additional inflow occurs abruptly and a sharp increase of x, signalled by a sharp decrease of the ratio R/R_0, is expected.

The above prediction is the phenomenological content of the "Preparata effect" and has been observed in the experiments. Notice that the Preparata effect is a purely quantum effect and has nothing to do with the electromigration. In the latter H(D)'s are pushed along the direction of the applied potential V, whereas in the Preparata effect H(D)'s are pulled into the cathode by a potential applied transversally. The Preparata effect acts quite rapidly; the electromigration could be also an effective agent for loading, although at a much slower rate (at least some days).

4. The experimental check of the Preparata effect has been performed in the experimental framework described in Ref.6 The outcome is summarized in fig.3, where the time evolution of R/R_0 , $V_{cathode}$ and of the anomalous "excess power"

$$\delta P = P_{out} - P_{input} \qquad [2]$$

are compared. It is apparent that when R/R_0 is stable at the peak value $(R/R_0)_{peak}=2$ the switch of a longitudinal potential $V_{cathode}$ along the stripe is correlated to asudden drop of R/R_0 from almost 2 to 1.3, namely a sudden increase of x from 0.7 to more than 1. It is also interesting that after about 500 seconds from this event (which is comparable with the time of response of the calorimeter) an "anomaly" appears in the output of energy.

The discussion of this topic is given in Ref. [6]; in this paper it is sufficient to stress that the onset of the phenomenon termed "cold fusion" is closely connected with the crossing of the critical value x=1, which is in turn closely connected with the application of a longitudinal potential to a cathode wire still in the γ-phase. The Preparata effect is thus verified.
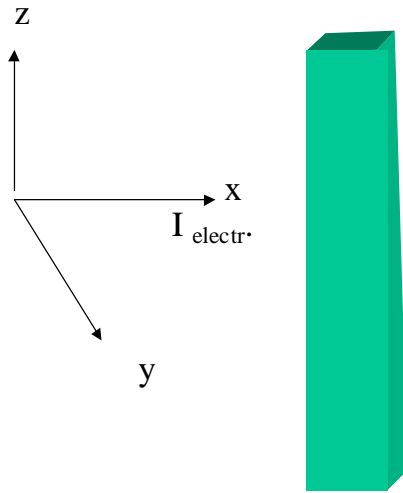

Fig.2   The electrolytic current flows along the x-axis, orthogonal to the side surface of the wire, whereas V is applied along the z-axis
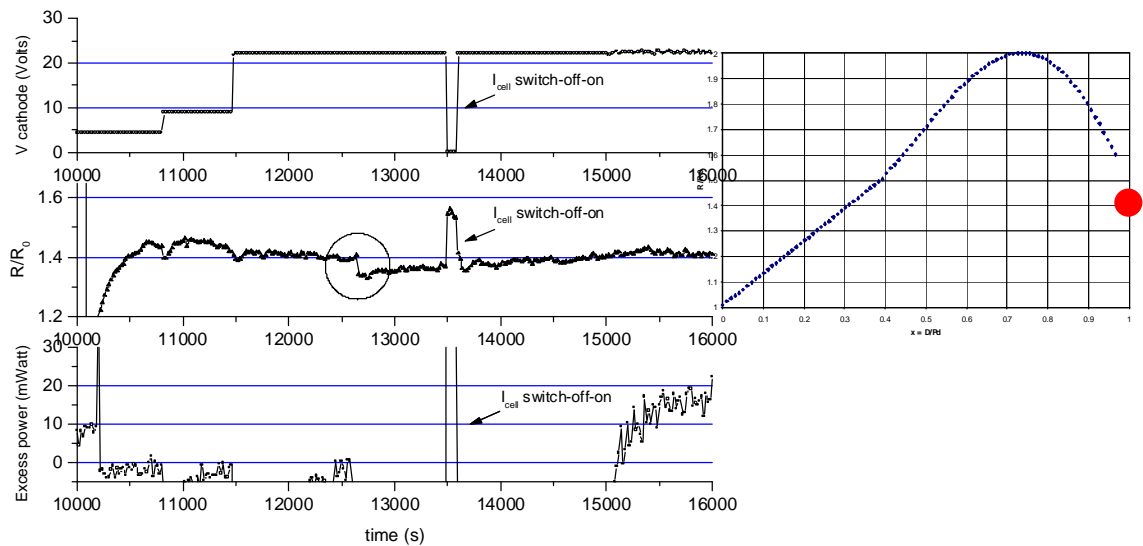

Fig.3 Time evolution of R/R_0; Vcathode and Delta P in a typical experiment. It can be seen in the circle the R/R_0 drop, corresponding, in the insert (Baranowskji curve)to $x \geq 1$. The current switch off-on allow to determine the position at left right or at right of the R/R_0 maximum (here at right). Excess heat rise is shown in the bottom line.
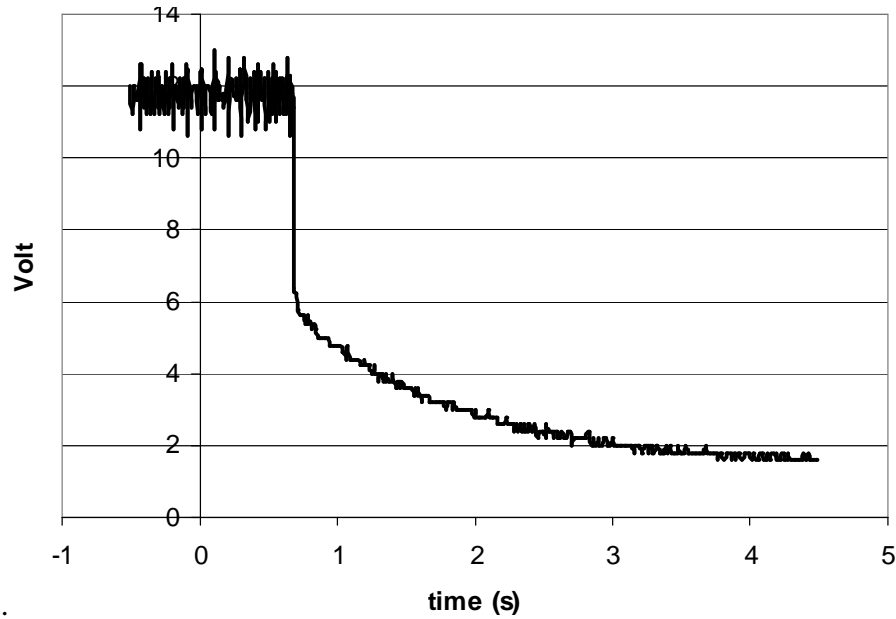
Fig. 4 Time evolution of the voltage between cathode and anode at the current shut off.
The measured time constant is $\tau = 1.5$ sec.

5. An interesting element of the loading dynamics is connected with the existence of a capacity on the interface between the electrode and the electrolyte (see fig. 4). In the framework of the coherent picture of water[7] it is possible to derive the existence of a double layer on the boundary of the liquid, having a depth δ (at room temperature) of 40 Å which gives a capacity of 20 μF per unit area [8].

Consequently we could describe the loading process in an electrolytic cell as follows. At low values of x all the positive H^+ (D^+) ions enter into the cathode lattice since this channel is exothermic and there is no gas evolution. When the cathode is fully loaded in the β-phase, there is no longer an energy gain in the filling of the cathode lattice and the gas evolution starts simultaneously with the charging of the interface capacitor; it is possible to accumulate a maximum charge

$$Q = CV = 2 \cdot 10^{-5} \, S \, V \qquad\qquad [4]$$

where S is the electrode surface and a rough estimate of V can be given by the potential difference V_{c-r} between the cathode and a reference electrode nearby; V_{c-r} actually is quite stable with respect to small displacements of the position of the reference electrode. By superimposing an a.c. current having a frequency $\nu = \omega/2\pi$ on the stationary cell current, it is possible to discharge the capacitor towards the electrode; as a matter of fact, ions crossing the double layer would be acted upon by a field

$$E = \frac{V}{\delta} \approx 2.5 \; 10^{+6} \; \text{V/cm} \qquad\qquad [5]$$

if we assume a value of $V_{c-r} \approx 1$ V.

In fig. 5 the time evolution of V_{c-r} is shown, at a fixed value of the cell current; the cathode is a plate 4cm x 4cm x 2 μm. After a first time interval where V_{c-r} is quite stable (this should correspond to the β-phase loading), a regular oscillation starts, having a period of 22 seconds, that lasts a very long time. The shape of the oscillation corresponds to a quite fast charge and to a subsequent discharge of a capacitor.

The loading appears then as in a "bang-bang" fashion. The double layer capacity gets charged and the discharge occurs by the a.c. modulations induced by the instabilities of the electric current. We note that, this feature accounts for the empirical techniques for reaching high loadings based on electric current ramps, which we related to current instabilities [9].
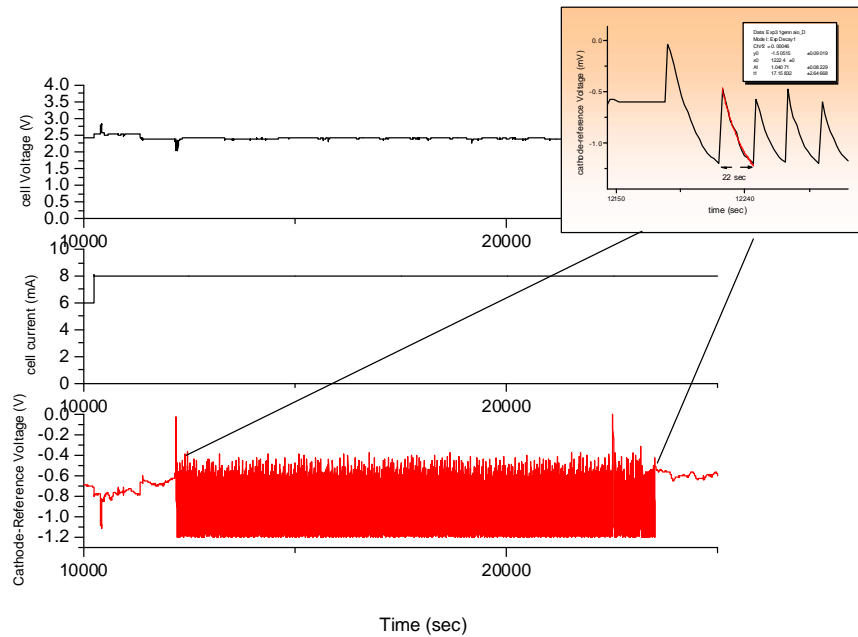
Fig. 5 Spontaneous oscillations in the Cathode-Reference voltage.

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