

THE MECHANISM OF DEUTERIUM EVOLUTION ON PALLADIUM:
RELATION TO HEAT BURSTS PROVOKED BY FLUXING DEUTERIUM ACROSS THE INTERFACE

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INTRODUCTION

In spite of the electrochemical approach taken by Fleischmann and Pons, most of the research hitherto has concentrated upon manifesting nuclear effects (neutron emission, tritium formation) and there has been little [1,2] investigation of the situation of the surface chemistry of the palladium electrode, the mechanism by which molecular deuterium is formed or that by which adsorbed D diffuses inside the palladium, - and what its fugacity there would be. These factors may have a determinative influence on the triggering of the fusional effects, influencing not only the D/Pd ratio, but also internal cracking. Information on the relation between the surface characteristics and the fugacity may point to us conditions for the initiation of fusion.

In the present paper an interim report is given on the results of about one and one-half year's work of one sub-group at Texas A&M.

FUGACITY, MECHANISM OF DEUTERIUM EVOLUTION ON Pd

At extremely high density the properties of matter show that when the volume per atom becomes less than the usual size of the atom, the atoms lose their individuality and so the substance is transformed into highly compressed plasma of electrons and nuclei. It has been shown that at fugacities greater

than 10^{17} bar the increase in density leads to states where nuclear reactions consisting in the capture of electrons by nuclei (with emission of neutrinos) become thermodynamically favoured [3]. It is of fundamental importance to find out overpotentials for different mechanisms of deuterium evolution at which the fugacity exceeds above mentioned value. A given potential can give rise to fugacities differing by many orders of magnitude, depending on the path and rate-determining step in hydrogen evolution [see Table 3 of Ref 4]. For fast discharge-slow electrochemical desorption and for coupled discharge-combination mechanism a critical overpotentials are -0.5 V and -1.9 V, respectively.

The importance of the electrode kinetics programs reported here is to obtain independent evidence for the mechanism of deuterium evolution i.e., the sequence of reaction steps and the rate-determining step of the discharge of the deuterons on the surface, that the overpotential-dependent fugacity can be calculated [4].

The transient behavior at constant current is shown in Fig. 1.

It is usually possible from the study of such transients to obtain indications of the mechanism [5,6]. If a proton discharge mechanism is rate determining the rise time is expected to be: $\tau = 4 C_{DL}R_{DL}$, where C_{DL} is the double layer capacitance and R_{DL} is the resistance of the interface. Taking the latter as RT/iF , (with $i = 10^{-3}$ A cm^{-2} and $C_{DL} = 50 \mu$ F cm^{-2} , the calculated rise time is about 10^{-3} sec, whereas it is obvious from the diagram that it is about 100 sec.

So, this first test does not fit the mechanism derived earlier but it seems that the likely solution is that the reason for the delay in coming to a steady state is because the θ_D is coming to a slow equilibrium owing to the diffusion of the hydrogen inside or the deuterium inside.

TYPICAL GALVANOSTATIC TRANSIENT

$i = 0.001 \text{ A cm}^{-2}$, Pd foil thick 25 μm

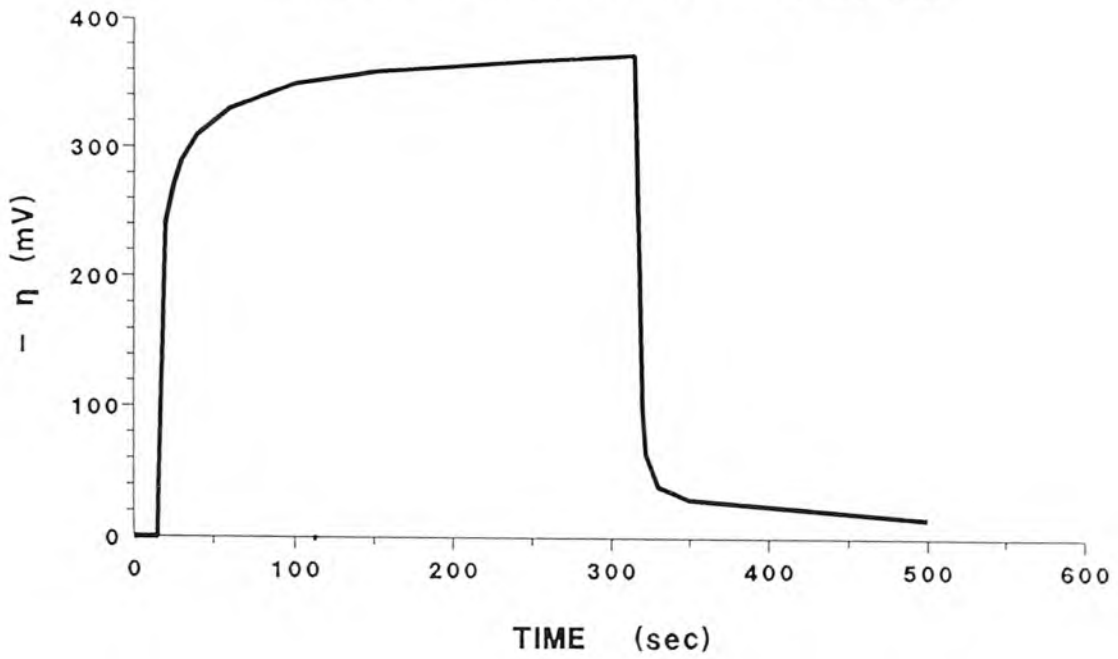


Fig. 1.

TAFEL LINES ON Pd IN 0.1 M LiOD

(after 1 hour)

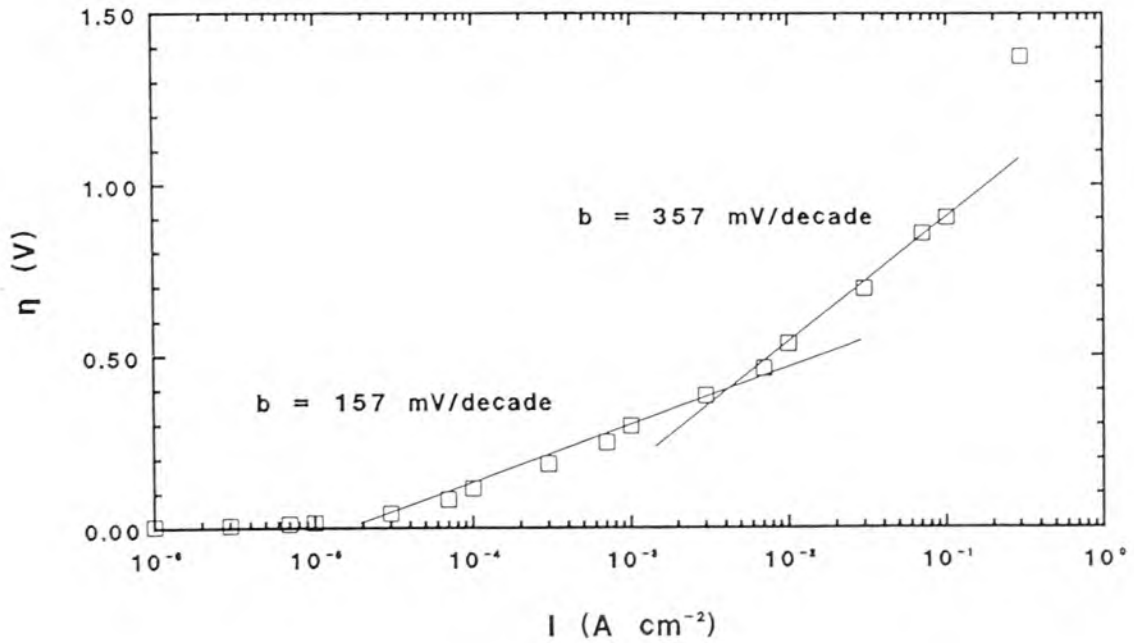


Fig. 2.

To test this let us take the thickness of the membrane which is 25 μm so that we have that from: $\Delta^2 = 2D\tau$ and with $\Delta = 25 \cdot 10^{-4}$ cm, and $D = 10^{-7}$ $\text{cm}^2 \text{sec}^{-1}$, one finds τ 60 seconds which is about the right time.

In looking at the Tafel lines (Fig. 2.) there are two separate gradients. The first one has a slope of 0.157 volts per decade which compared with the theoretical value of $2.303 \cdot 2RT/F$ which would come to 0.120 V/decade. Hence the slope is somewhat high but the formal slope of $2RT/F$ is calculated with a transfer coefficient of 0.5 and the slope we need corresponds to a transfer coefficient of about 0.34, which is quite within the bounds of acceptability [7].

Hence this first gradient which takes us from an overpotential of 0 to about -0.4 V is reasonably in agreement with a coupled discharge and recombination mechanism. As we go up to the second slope, we come into a region of the Tafel coefficient b for which there is no mechanism known and so we need a special explanation. Let it be supposed that there is a film on the surface of the electrode, - it may be a blocking film or it may be a film of adsorbed material, e.g., other atoms which form a dipole with the palladium or etc., on the surface. Suppose that the potential which is normally measured is then changed by the potential due to a dipole layer on the surface. Then it is possible to show that the new gradient should be

$$b = 2.303 \frac{RT}{T} \left(\frac{2}{3} \beta + \frac{2}{3} \frac{\Delta\mu}{\delta e_0} \right)$$

Here the δ is the thickness of the layer concerned and e_0 is the electronic charge where $\Delta\mu$ is the dipole moment of the layer. To obtain the slope concerned (357 mV/decade corresponds to a dipole of about 2.5 Debye and this is an eminently possible dipole moment, for example, were at a water layer it would be about 2.2. So that although we cannot identify what this layer is it would seem that it offers, at least for the time being, a reasonable rationalization of the results obtained.

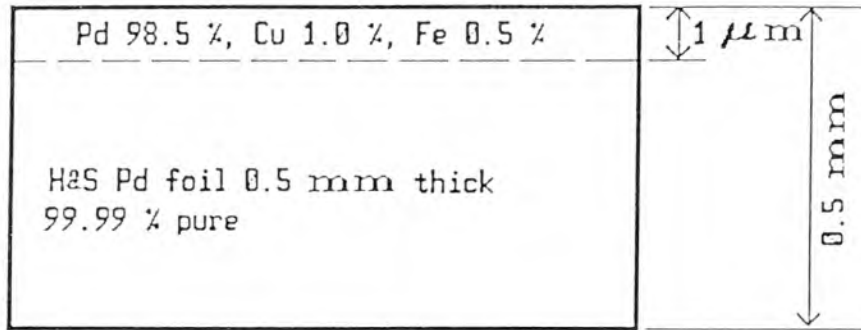
SURFACE AND SOLUTION ANALYSIS

In Fig. 3. are shown the results of an EDS analysis of an electrode (Pd, Hoover and Strong) which had had no annealing and no electrochemical treatment. The second diagram shows the situation after annealing at 800°C and cooling in an Argon atmosphere with no electrochemical treatment. The surface becomes carburized. The third diagram shows the situation after one hour electrolysis at 0.5 A cm⁻². The carburized section has broken off. This is visible in the cell and the darker looking surface is then replaced by a bright shiny surface, the composition of which at the beginning is about 96% palladium (original Pd, > 99.9). It seems probable that the carbon arises from oil in the vacuum pump used in the system for annealing.

EDS analysis showed 10% platinum in a 1 micron layer on the surface after three weeks electrolysis (Fig. 4.). It is easy to calculate that about $1 \cdot 10^{-6}$ M of platinum have deposited in three weeks (0.10 of $5 \cdot 10^{-5}$ cm³). From Faraday's Law of electrolysis follows that to deposit platinum observed would need a partial current for platinum deposition of $1 \cdot 10^{-5}$ A, and this can be regarded as the limiting current density and must be related to a certain concentration. Assuming $i_L = 0.02$ nc, where c is the concentration in M per liter it follows that the concentration of platinum in the solution is around $2 \cdot 10^{-4}$ M. Taking exchange current density of oxygen evolution on platinum around 10^{-8} A cm⁻² and from the reversible potential solution Pt of 1.2 V (NHE) one calculates the overpotential for the dissolution of Pt of approx. 0.18 V. With the assumption of Pt dissolution current of 10^{-9} A cm⁻² maximum dissolution velocity would be about 0.1 μA cm⁻² whereas the required value is about 10^{-4} A cm⁻², a discrepancy too great to be explained by the

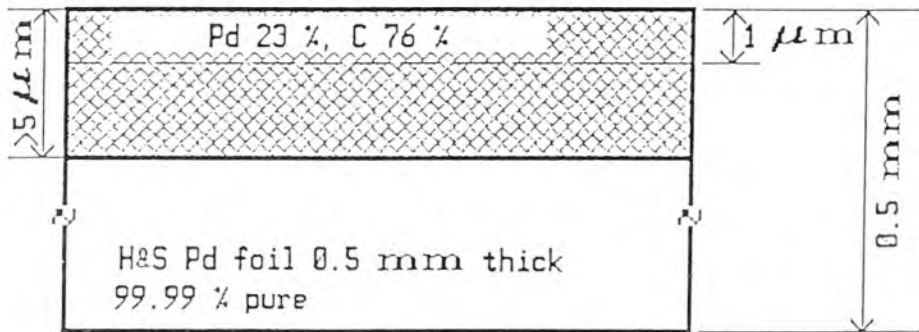
TREATMENT:

- not annealed
- no electrochemical treatment



TREATMENT:

- annealed at 800 °C, and cooled in Ar atmosphere
- no electrochemical treatment



TREATMENT:

- annealed at 800 °C, and cooled in Ar atmosphere
- after 1 hour of electrolysis at 0.5 A cm⁻²

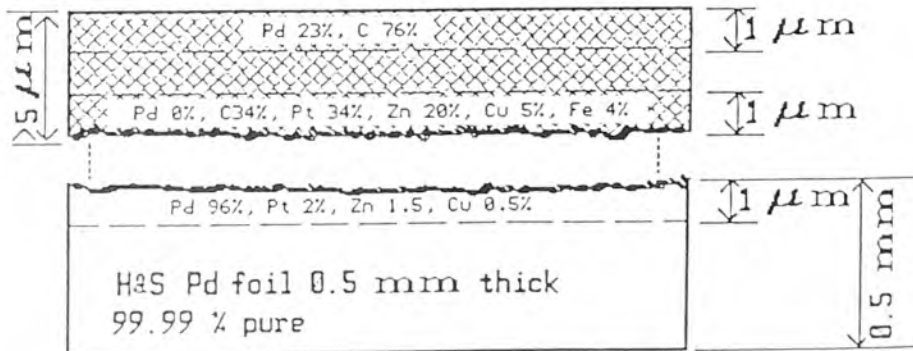
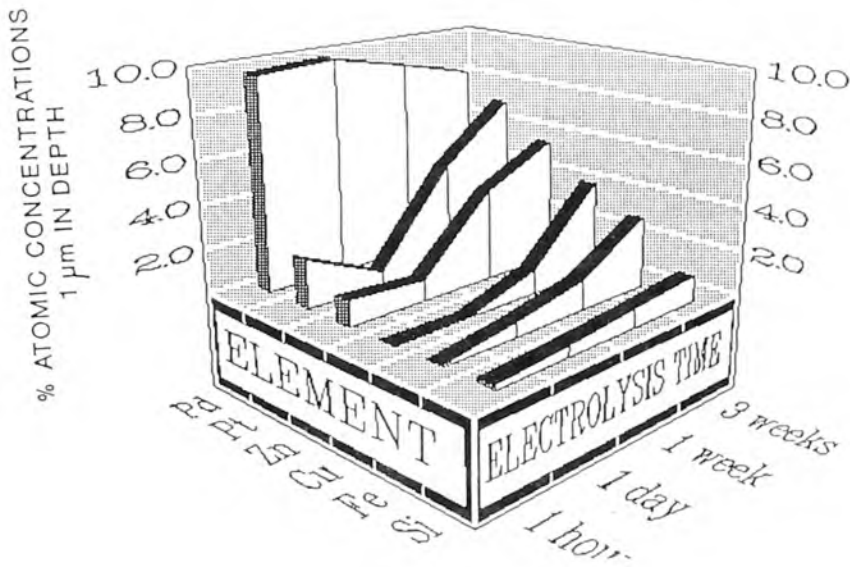


Fig.3.

EDS ANALYSIS OF Pd ELECTRODES AFTER DIFFERENT TIMES OF ELECTROLYSIS



• Pd CONCENTRATIONS ARE SHOWN 10 TIMES DIMINISHED

Fig.4.

XPS ANALYSIS OF Pd ELECTRODES AFTER DIFFERENT TIMES OF ELECTROLYSIS

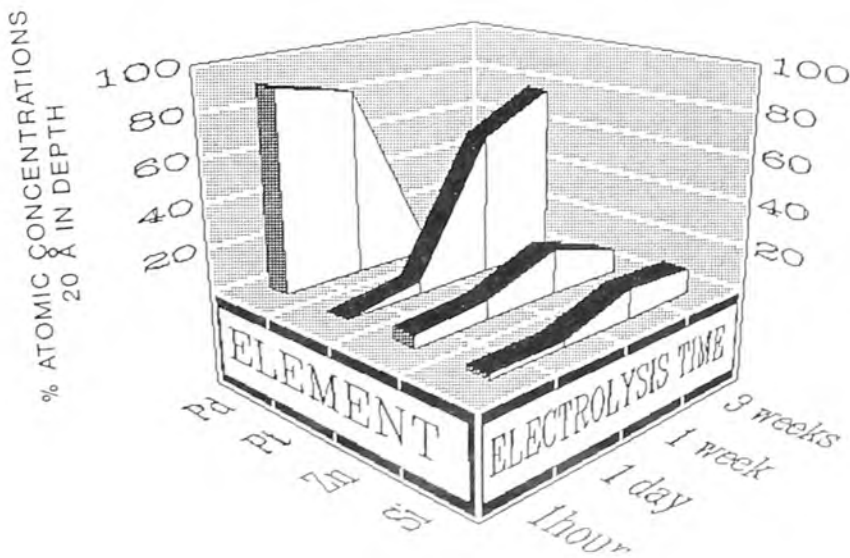


Fig.5.

approximations of the calculation. We wish to make here a suggestion that it dissolves chemically due to a breaking up of the oxide on the surface.

In Fig. 5 is shown the XPS analysis of a region near the surface over three weeks time. The platinum is the most remarkable constituent: after three weeks it covers about 80% of the surface. A conclusion from our surface analysis is that the surfaces upon which we are conducting our experiments are first of all lithium - palladium alloys and the alloy concentration is around LiPt_3 with liberal amounts of platinum covering the whole surface after three weeks and small amounts of silicon, zinc and copper and other materials. There is some evidence for dendritic growth forms.

Solution analysis

Solutions were carefully analyzed after different times of electrolysis by utilizing Inductively Coupled Plasma Spectroscopy. The results confirmed gradual increase in concentration of impurities, mainly Pt, Si and Zn, in solution during the three weeks electrolysis time.

THE HEAT BURSTS

Charging of the cells is performed typically starting with 50 mA cm^{-2} and changes in resistivity were monitored. When D/Pd ratio attained the constant value (usually after 2-4 days at these low currents charging) the current was increased to 0.5 A cm^{-2} . Almost in all cells this caused an enhancement in charging and thus increase in D/Pd ratio. After that a current was increased normally to 1 A cm^{-2} . No additional increase in D/Pd was observed by such treatment of the electrodes. The electrodes were then pulsed by applying different pulsing regims.

Pulsing regimes were carried out by the use of pulses which could take the cell cathodically up to 2 A from the open circuit condition and

XPS DEPTH PROFILES AT DIFFERENT ELECTROLYSIS TIMES

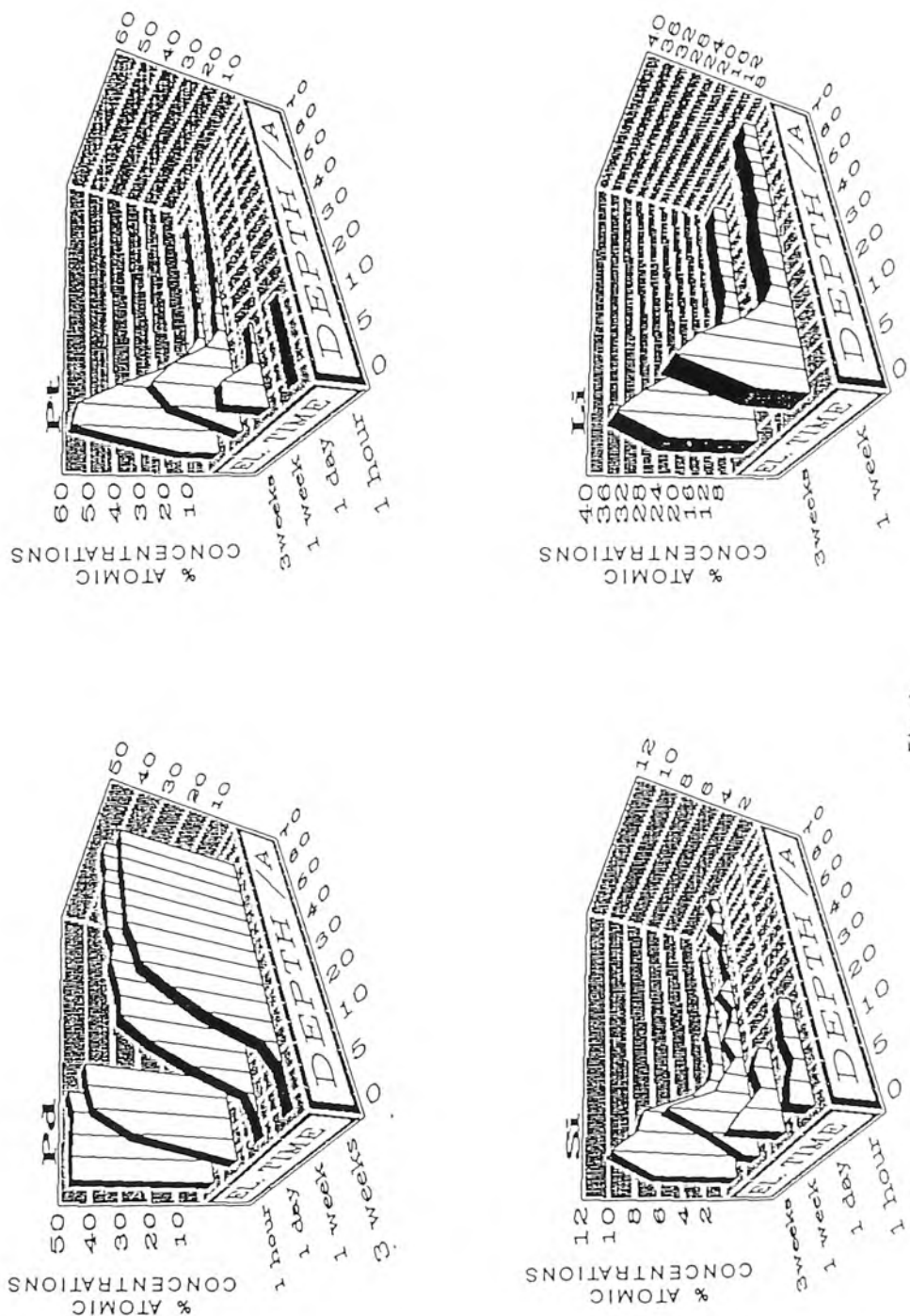


Fig. 6.

EXCESS HEAT ON CELL 16-P

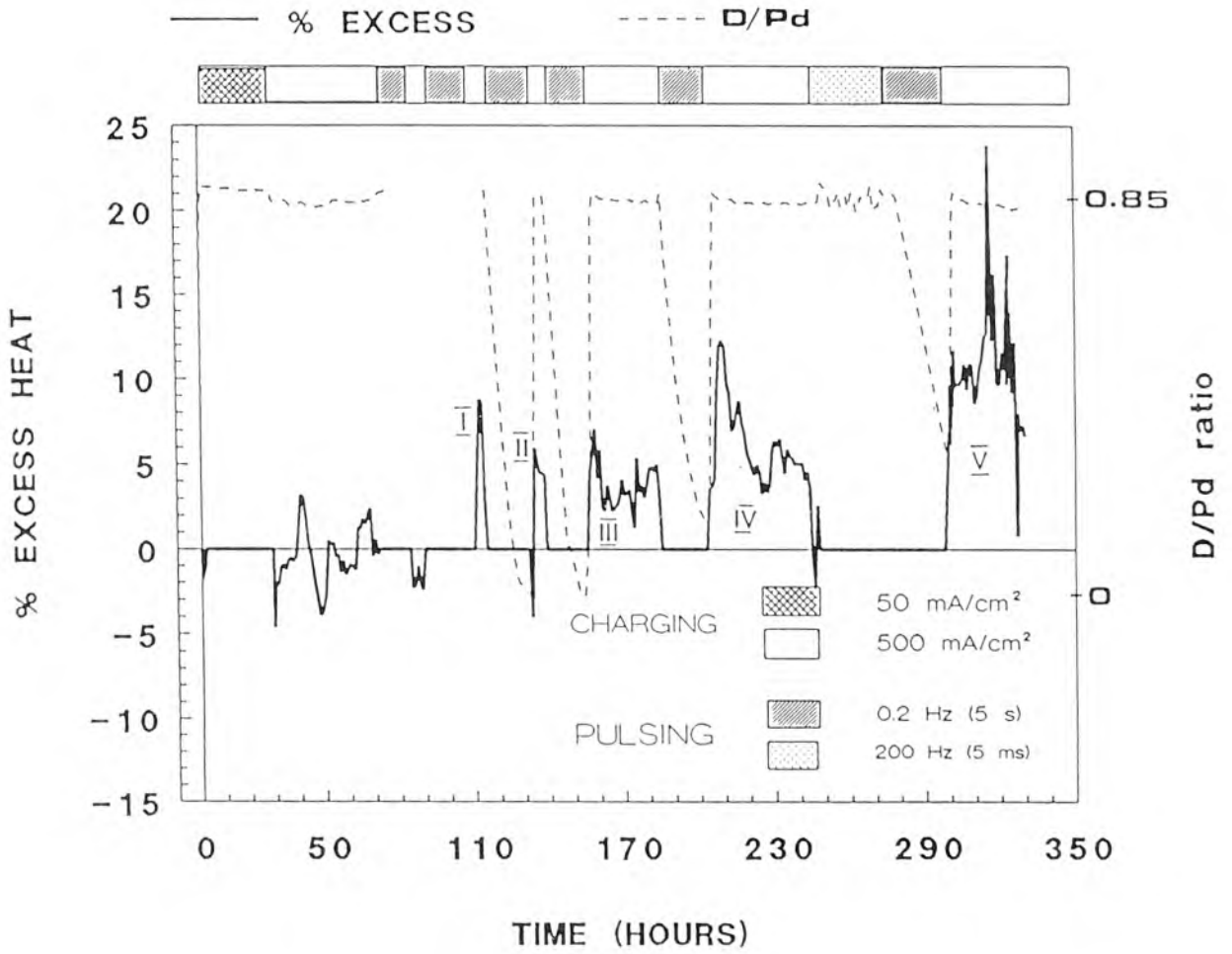


Fig.7.

anodically to 0.1 A for the discharge. The measurement of heat cycles in cells began on the 2. April, 1991 with one cell and the cells were run up to two month. Fig. 7 shows five consecutive heat bursts occurring after successive application of pulsing regime (cathodically 5s for 1 A cm⁻², and anodically 5s for 0.1 A cm⁻²). It is interesting to note that cells pulsed with 5 ms pulses did not show any excess heat. A total energy output exceeds 35 MJ/mol. A critical observation was made in respect to the effect of the pulsing upon the concentration of hydrogen in the cell. In some cases the pulsing led to a reduction of the amount of deuterium in the electrode and under these cases heat was observed (Fig. 7.). However, in most cases the pulsing did not lead to fluxing and in such cases no heat bursts were observed. In respect to charging, the incoming charge has to compete with the combination on the surface. When the surface is saturated only a small number of atoms, less than 20% at the beginning, and in the end less than 1%, actually go into the cell to diffuse in. Most recombine. On the other hand, during the anodic cycle there is no competing process and all processes lead to hydrogen dissolving anodically out of the cell. Hence, for the passage of the same number of coulombs in each direction, the anodic processes are more efficient than the cathodic: OH comes out easier than it goes in. Thus, what was found to be successful was pulsing which causes a flux inside the cell, and "cleans it out". This may apply literally to dislocation. Thus Gittus and Bockris [8] suggested that the critical point with the available of dislocation of pile ups and points of triaxial stress to be available for incoming deuterium. These materials would certainly be covered mostly with poisons, particularly with H. If, however, a flux of anodic deuterium is put in it is likely that they are cleaned out, the hydrogen dissolves away from them and when the deuterium comes in in an increasing fraction deuterium is able to get onto the dislocations and, as shown by Bockris and Supramaniam, these are the places where the internal stress is highest. Points of triaxiel

stress and other high stress areas are those where the greatest congregation of internal deuterium lies. These internal atoms must be deuterium atoms and not hydrogen. The washing out would contribute to this.

The reason some cells do not wash out may be because of films on surface. When there is too much lithium, zinc, sodium, and platinum on the surface the recombination is so high that little hydrogen goes in and when an attempt is made to bring the hydrogen out the exits are blocked.

A major conclusion of this work therefore is that a critical element is pulsing, the object of this pulsing is to flush out impurities from the inside of the electrode and that this pulsing only happens if the electrode surface is sufficiently clean.

Another observation was that the length of the heat bursts is in the region of 30 to 40 hours which corresponds to those of other workers. It is possible that, after a certain time, even the dislocations poison up again, thus, there is always some hydrogen coming in and left long enough the hydrogen will displace the deuterium on the surface. This is a point in favor of utilizing very pure D₂O.

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