

D/PD LOADING RATIO UP TO 1.2:1 BY HIGH POWER μ S PULSED ELECTROLYSIS IN PD PLATES.

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ABSTRACT

We tested metallurgically different Pd plates made with cold working procedures. We focused on the Deuterium absorption for these plates during pulsed electrolysis. We used high peak current intensity (up to 100 A) with very short (1 μ s) pulse duration, up to 20 KHz of repetition rate. The peak power of each pulse can be as large as 50 KW. The LiOD 0.3 M/I D₂O solution has at Pt net as anode.

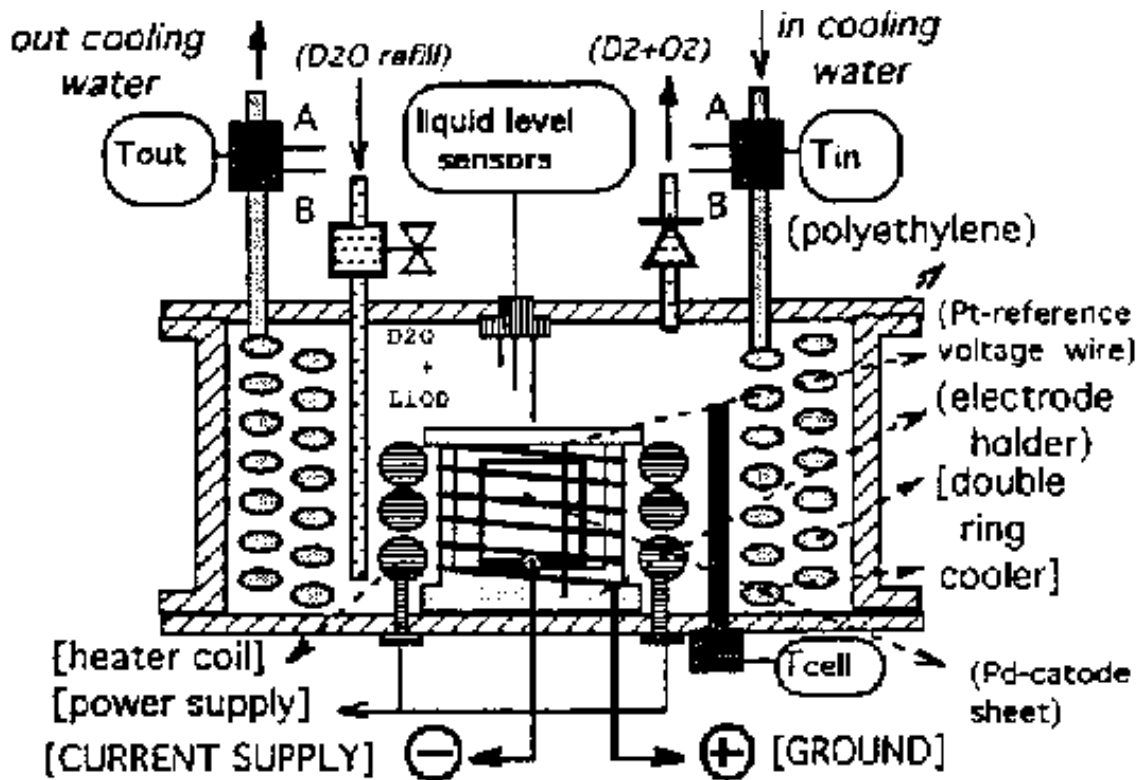
Very high D/Pd ratio (up to about 1.2:1) have been reached and the Deuterium absorption behavior versus time is strongly dependent on the metallurgy of the plates. Even surface preparation of the plates seems to play a role in the absorption phenomena.

Metallurgical and electrical parameters like hardness, over-voltage and absorption rate can give useful indications about the absorption of the Deuterium into the plate: they behave like cross-correlated parameters.

1. The Experimental Set-Up

The adopted electrolytical system was already described in the previous ICCF3 Conference at Nagoya (Japan)^[1] and, very recently, at ICCF4 Conference (Maui, USA)^[2] about the latest, significative, experimental improvements performed.

In short, it is a flow calorimeter composed by a cylindric polyethylene vessel containing a double turned copper coil used for cooling and input-output energy computing (fig. 1). The ordinary water, passing through the coil, cools the solution. Seven temperature sensors are properly located in order to measure the produced heat and to cross-check the proper calorimeter operation. The Pt wire net was turned around a teflon sample-holder in a proper geometrical shape in order to smooth the non-uniform electric field at the edges of the plate. In this way we reduced the effect of the Deuterium discharge at the edges of the plate due to the strong electric field gradients. A reference electrode, just a Pt wire, was located in front of the two sides of Pd plate (3 mm far); the wired Pt anode (1 mm diameter) net is 1 cm far from the cathode; the electrolytic solution is LiOD 0.3 M/I D₂O. An electrovalve was inserted along the outgoing gas pipe just to define a close volume (about 150 cc) to store the gas coming from the electrolysis. We determine this volume measuring both the gas pressure developed during the electrolysis and the electric charge flowed through the electrodes: we used the gas law and the Faraday equation. In this way we are able to calculate the quantity of moles of D₂ absorbed from the Pd, measuring the missing pressure. We usually operate leaving close the electrovalve until the gas pressure reaches a definite value (50 mbar), further on we open this valve allowing the gas to flow away. A proper circuitry was made to control this cyclic operation.



A specific circuitry was made to generate very sharp high peak current pulses (rise time <300 ns at 100 A peak values). A circuit measures the flowing electric charge and the power absorbed from the cell in each single pulse. Another circuit (out-of-phase) measures both the voltage of the cathode and the voltage of the Pt wire floating electrode (RHE), which is put in the solution close to the cathode (3 mm). These voltages are properly used to determine the over-voltage parameter too. The out-of-phase voltage measurements are performed after a delay (30 μ s) from the end of the power pulse, when the Pd/Pt system is electrically decoupled from all circuitry by 2 ultra-fast power recovery diodes (40HFL80S05) properly connected in series.

2. The Deuterium Absorption Measurements

We performed some absorption blank runs using an Au plate in order to obtain reference measurements to compare with the Pd plates one. We tested three cold-worked Pd sheets (25x25x1 mm) named: T05 (TANAKA K.K.) and I65, I63C (IMRA MATERIAL). The TANAKA plate (very high hardness value: 300 Hv) was prepared with proper impurities (2780 ppm) enclosed during the melting preparation: the high hardness value reached is due to the doping (under patent). The 2 IMRA plates (140 Hv) had the same cold-worked treatments (same batch) and no impurities were added. The I63C was warmed to about 750°C for 10 minutes 2 times (after cooling to room temperature in about 20 minutes) in a oxidizing atmosphere to reduce the cold-worked hardness to the original value of pure Pd just melted (about 50 Hv). After this treatment we observed a dark-blue thin film covering the surface: this film (probably PdO) was quite hard and even resistant to 65% concentrated HNO₃ acid attack.

All the tests were performed under the following operating conditions: pulse peak current 16 A, pulse width 0.5 μ s, pulse repetition rate 5 KHz, peak current density 1.3 A/cm². These conditions are equivalent

to an electrolytical mean current of about 64 mA (i.e. only 5mA/cm²).

In figure 2 it is shown the absorption rate (in Mole/s · cm²) of the plates T05, I65 and I63C. It provides information about the quantity of Deuterium flowing through the Pd-surface per time unit and surface unit. In this figure we can put in evidence strong differences comparing the T05 and I63C (the very hard plate and hard modified surface) plates with the I65 one (softer plate): i.e. the hard plates show a relevant shoulder on the shape. This shoulder seems to indicate that, in the $\alpha+\beta$ phase, the Deuterium diffusion coefficient is higher and about constant in respect to the expected one, like the I65 plate. The I63C (modified surface) plate shows that the absorption rate, very high at the beginning of the charging up, decreases faster than the other plates and we can suppose that the modified surface is not stable enough during the whole electrolysis (Oxygen reduction at PdO surface due to D?). The absorption rate decreases during the β phase, zeroing when the D/Pd concentration reaches its maximum value equal to 1.2:1 with I63C, 1.02:1 with T05 and 0.96 with I65 (fig. 3).

The D/Pd concentration has been evaluated accumulating the absorbed Deuterium moles over time. The absorption efficiency (defined as the ratio of the quantity of absorbed Deuterium to the Deuterium developed during the electrolysis) reaches its maximum value (about 71%) in the α phase. The plate (I63C), providing the highest absorption rate and loading efficiency, reaches also the highest (1.2:1) D/Pd ratio.

In figure 4 it is shown the over-voltage* (i.e. normalized to the charge flow, V/C, see following), due to deuterium loading, versus the charge flow itself. We define the over-voltage as the difference between the cathodic potential and the reference electrode previously described. We recall that these voltages are measured during a fixed time (10 μ s) after a fixed delay (30 μ s) from the end of each power pulse (out of phase measurement). All electric potentials are measured in respect to the Pt net electrode which is connected to the electric circuit ground. During the electrolysis the Deuterium gas, developed at the cathode, surrounds the reference electrode and we can assume it as equivalent to a R.H.E. (Reversible Hydrogen Electrode). In the over-voltage calculation we take into account the fact that the peak-up electrode surrounded by the D₂ gas is not a platinized Pt, but just a pure Pt: this difference is reported by the literature to be 0.09 V for H₂ gas; we consider this value appropriate for our calculations.

We would like to note that the over-voltage* reported in figure (4) is computed subtracting, at the same experimental conditions:

- a) the Tafel component, due to the current density;
- b) the Li contribution at the total apparent overvoltage.

The last subtraction was allowed through blank experiments with the Au plate: we assume that, along the whole time of the electrolysis, there is not appreciable deuterium absorption at Au plate but only Li deposition and that the amount of Li deposited is the same in the cases of experiments with Au or Pd.

All the overvoltage considered are normalized with the charge flown and properly corrected for cell temperature variations, if any. We found that the "normalized" overvoltage* increases surface D/Pd ratio according to the metallurgy of the plates: hardest plates show largest values of overvoltage.

Conclusions

Independently from the metallurgy of the Pd electrodes, we developed a high peak current pulse technique able to load deuterium into Pd plates at values as large as, at least, 0.96:1 and 1.2:1 maximum.

The metallurgy of the plates affects the absorption rate "shape" parameter. The hardness parameter is increased by cold working from a value of 50 Hv (ordinary Pd) to about 140 Hv in two of the samples used (IMRA plates); some impurities were intentionally added to another Pd plate in order to increase this value up to 300 Hv (TANAKA plates).

A heavy warming (750°C), in an oxidizing atmosphere, at the surface of one of the two 140 Hv plates was able, along a measurable experimental time, to increase the surface hardness giving noticeable effects both on Deuterium absorption shape and absolute value stored.

It seems that high values of hardness increase the D/Pd charging ratio into the plates studied. The absorption rate shape is related to the surface metallurgy of the plates: we can hypothesize that very high D/Pd ratios (larger than the "mean" value computed) are reached at thin layers of the plate surface. We think that the short-time high-current pulses can enhance this useful effect.

The over-voltage parameter gives useful indications about the Pd plate surface status during the Deuterium absorption. An important role can play the ionic Li on the surface, in particular way when the Pd plate reaches high D/Pd values.

Some tests are in progress in order both to enhance and make steady the positive effects of "surface changing" by proper surface poisoning.

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References

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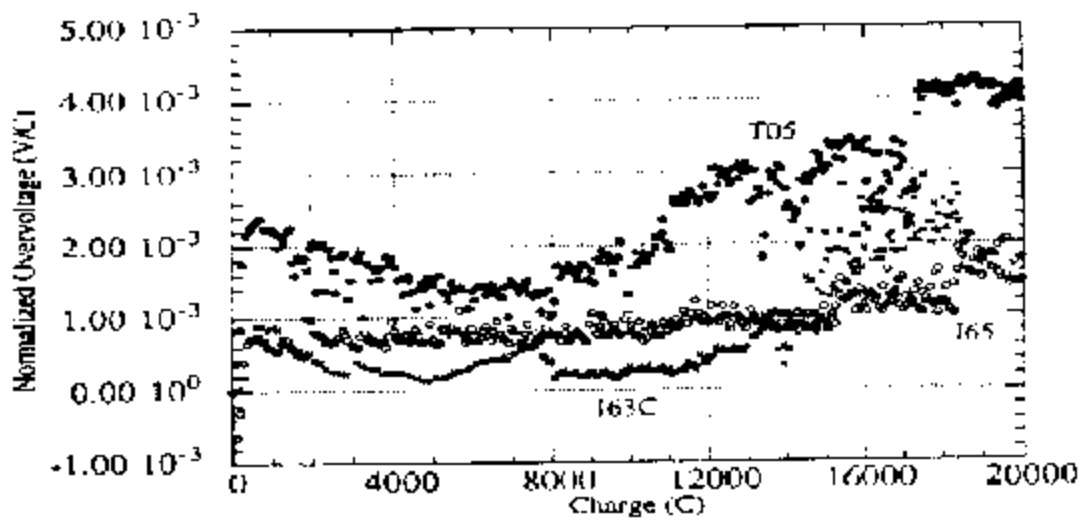
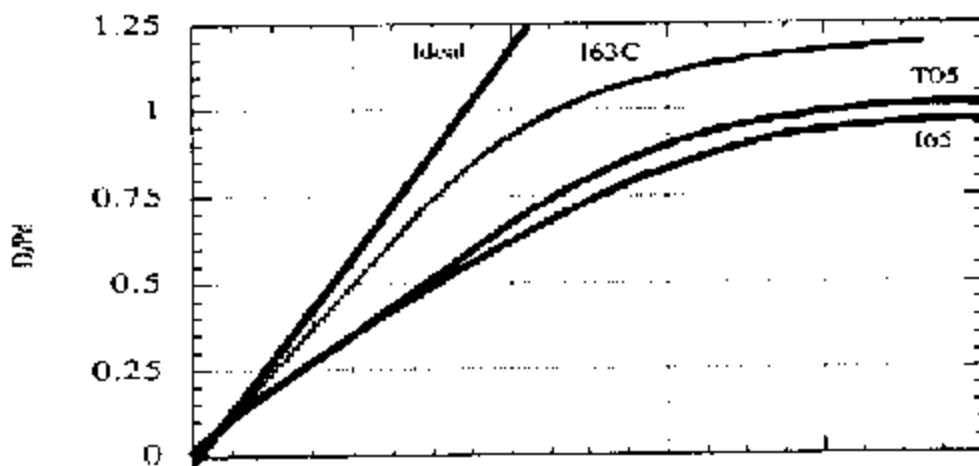
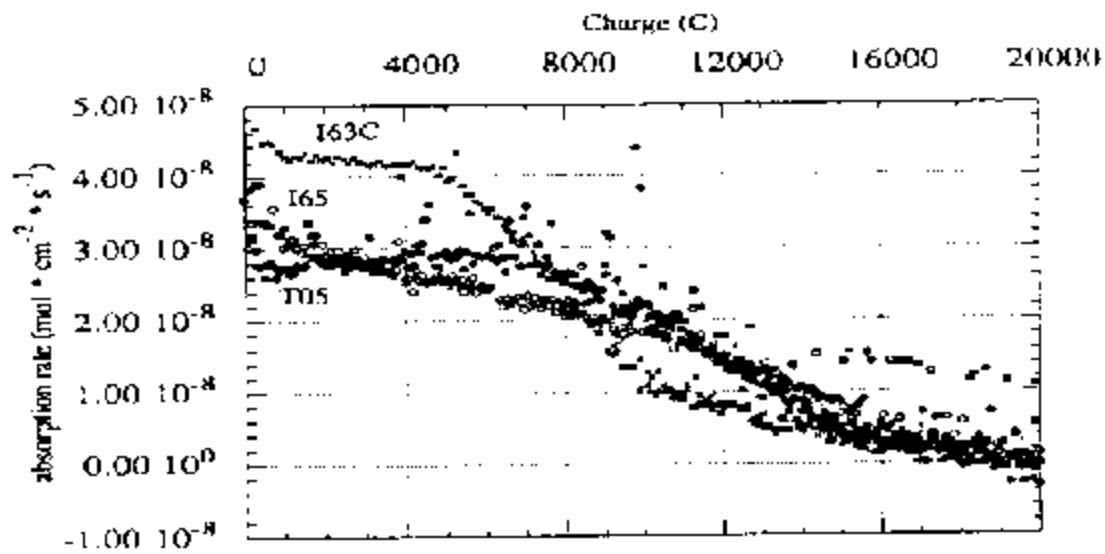


Fig. 2- The absorption rate during the first charging up.

Fig. 3- The D/Pd ratio reached by the plates.

Fig. 4- The normalized overvoltage* parameter indicates the D role.