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## **Electrochemical Loading of Hydrogen and Deuterium Into Palladium and Palladium-Boron Alloys**

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### Abstract

Excess power production and other anomalous effects have been observed during the electrolysis of heavy water using palladium and palladium-boron alloys as the cathode materials. This study focused on hydrogen and deuterium loading into palladium and palladium-boron alloys. Improved calorimetry provided for the detection of the exothermic heat of absorption of deuterium into palladium and palladium-alloy cathodes. The addition of boron to palladium does not significantly affect the initial loading rate but slows further loading to higher levels. The presence of boron in the palladium significantly slows the rate of the deloading process. Cracks or other surface defects prevent high loading levels of hydrogen or deuterium into palladium or palladium-boron alloys.

### 1. Introduction

We have observed anomalous excess power and helium production for both the palladium-deuterium system and the palladium-boron alloy-deuterium system.<sup>1,2</sup> The anomalous excess power effect apparently requires a loading ratio of D/Pd exceeding 0.85.<sup>3</sup> This research investigates the extent of loading and the rate of the loading and deloading processes using palladium and palladium-boron alloys as cathodes in electrochemical electrolysis experiments.

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## 2. Experimental

The hydrogen or deuterium loading of palladium or palladium alloys was investigated by the weight gain of the electrode during constant current electrolysis in  $H_2O + LiOH$  or  $D_2O + LiOD$  solutions. The weight gain of the metal (M) due to deuterium loading can be represented by



The rate of deloading was also investigated by the loss of weight represented by



The weighing method involved interrupting the electrolysis and removing the electrode from the solution. In addition, the use of a sensitive calorimeter determined the rate of the loading process by measuring the power produced during the initial exothermic loading process.<sup>1,4</sup> For example,  $\Delta H = -35,100$  J per mole of  $D_2$  for the formation of  $PdD_x$  for  $x < 0.6$ .<sup>5</sup>

## 3. Results

Initial studies were conducted on palladium rods (1-mm diameter) and palladium sheet electrodes in  $H_2O + 0.1$  M  $LiOH$  solutions to test the reliability of the weighing method. Upon interrupting the constant current electrolysis and removing the palladium electrode from the cell, it was found that the loss of weight could be readily measured and that the weight change was linear with time. For five or more weighings over a 10-minute period, the plot of the H/Pd ratios versus time was extrapolated back to zero minutes to yield the initial H/Pd loading when the electrolysis was interrupted.

Loading levels of  $H/Pd > 0.7$  were readily obtained in all experiments. Both a 1-mm diameter palladium rod (Johnson-Matthey) cathode and a palladium sheet cathode (Tanaka Metals, Japan) were used in these investigations. The highest loading level for the palladium rod was  $H/Pd = 0.923$  while the highest value for the palladium sheet was  $H/Pd = 0.821$ . No obvious correlation between the loading level and the current density could be established. The type of anode used in the cell apparently affected the loading level. Higher loading levels were obtained using a platinum anode than when a nickel anode was employed. The  $H_2O + LiOH$  solution eventually became dark due to corrosion products when the nickel anode was used.

Although a loading level of  $H/Pd = 0.7$  was readily obtained in all experiments using palladium cathodes, only a few experiments yielded  $H/Pd$  ratios approaching 0.9. The highest loading occurred following the heating of the loaded palladium rod with a heat gun that caused it to glow red due to a run-away exothermic reaction of the hydrogen exiting the surface with oxygen from the air.

The study of the  $H/Pd$  ratio over a 21 day period for a palladium rod cathode showed several peaks and valleys in the loading ratio versus time. The  $H/Pd$  ratio varied from 0.79 after 3 days to a low of 0.72 at 6 days and a maximum of 0.92 at 16 days. There was no obvious correlation between  $I$  the loading ratio and any experimental variable. For most experiments, the change in  $H/Pd$  after interrupting the electrolysis was generally about -0.01 per minute.

A new calorimeter designed and built at China Lake<sup>1,4</sup> was used to measure the heat of absorption of deuterium into the palladium rod cathode. This result is shown in Figure 1. A power output of

approximately 6.5 mW is observed for 2 hours. This yields 47 Joules that compares very favorably to the expected 44 Joules based on the cathode size (1 mm x 4.3 cm), a loading level of PdD<sub>0.6</sub>, and using the reported value of  $\Delta H = -35,100$  J per mole of D<sub>2</sub>.<sup>5</sup> Figure 1 shows that most of the loading up to D/Pd = 0.6 is completed within 2 hours of the start of the electrolysis. Further loading beyond the D/Pd = 0.6 ratio yields a discontinuity in the enthalpy value.<sup>5</sup>

Energy storage due to endothermic processes early in the experiments has been proposed as an explanation for the excess heat effect.<sup>6</sup> Figure 1 shows that there is no endothermic or energy storage behavior during D<sub>2</sub>O electrolysis, hence this argument by S. E. Jones et al.<sup>6</sup> is invalid. Excess power was observed for this electrode later in the experiment.<sup>4</sup>

Loading studies for two palladium-boron alloys, both containing 0.75 weight % boron, are shown in Table 1. The loading process is much slower with the boron present than observed with pure palladium. While loading levels of D/Pd = 0.6 could be attained within a few hours for palladium cathodes, nearly 12 days of electrolysis is required to reach this loading level for the palladium-boron alloy (Table 1). Judging from Table 1, the Pd-B alloy in cell C slowly loaded to higher levels. After 100 days, the D/Pd ratio was 0.85 for the alloy in cell C but only 0.63 for the alloy in cell D. A surface flaw caused this difference. The Pd-B alloy used in cell D had a long folded-over metal region produced by the swaging of this very hard material. This acted as a long crack in the surface. Cracks or similar surface defects are a major factor in preventing high hydrogen or deuterium loading levels. Significant levels of excess power were observed for the Pd-B alloy used in cell C.<sup>2</sup> No excess power was measured for the flawed Pd-B alloy used in cell D.<sup>1,2</sup>

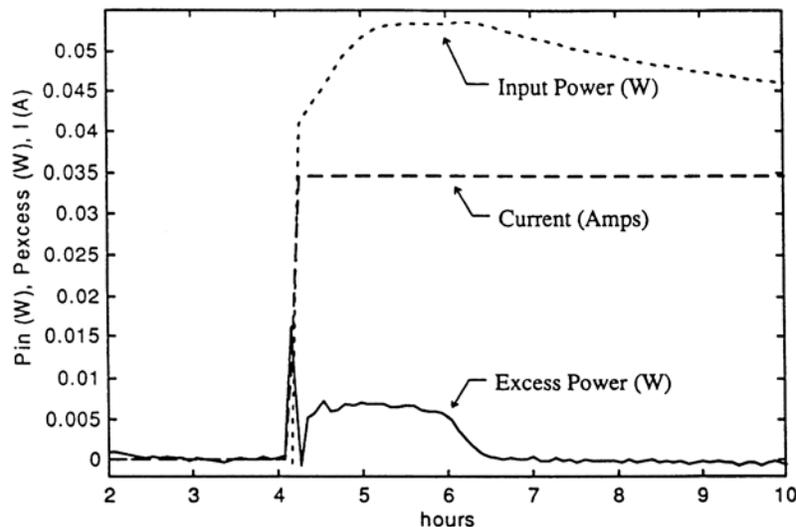


Figure 1. Measurement of the Exothermic Heat of Absorption of Deuterium Into a Palladium Wire Cathode (1 mm x 4.3 cm) Using the New Calorimeter Developed at China Lake.

TABLE 1. Loading Studies by the Weighing Method.

Time (days)	Pd-0.75% B (Cell C)	Pd-0.75% B (Cell D)
7	0.580	0.550
12	0.614	0.594
100	0.85	0.63

Further experiments investigated the effect of the boron concentration on the D/Pd loading level. Table 2 presents loading studies by the weighing method for Pd-0.50 weight % B and Pd-0.25 weight % B cathodes. Loading to the D/Pd = 0.6 level becomes considerably faster as the amount of boron is decreased as shown in Tables 1 and 2. Higher D/Pd ratios are obtained initially for the alloys containing the smaller amount of boron. Excess power was measured in all four experiments listed in Table 2.<sup>1,2</sup>

Calorimetric studies at China Lake showed that the initial exothermic loading of deuterium into the Pd-B alloys is nearly as fast as observed with pure palladium cathodes. This was a surprising result. Further loading to higher levels, however, appears to become very slow for the Pd-B alloys compared to the palladium cathodes (Tables 1 and 2).

TABLE 2. Loading Studies by the Weighing Method Following 5 Days and 10 Days of Electrolysis.

Electrode	Xo (5 days) <sup>a</sup>	Xo(10days) <sup>b</sup>
Cell A— Pd-0.5% B	0.643	0.640
Cell B— Pd-0.5% B	0.604	0.652
Cell C— Pd-0.25% B	0.692	0.716
Cell D— Pd-0.25% B	0.647	0.695

<sup>a</sup>I = 50 mA for 5 days.

<sup>b</sup>I = 100 mA for the second 5-day period.

NOTE: Microscopic examinations showed surface nicks and scratches but no major flaws on electrodes.

Coulometric measurements of the loading were attempted for the palladium-0.75 weight % B alloy. The currents obtained by potentiostatically controlling the cell voltage were only 2-4 mA, hence less than 10% of the deuterium could be reacted electrochemically (Equation 3) even after 28 hours of electrolysis. Measurements by the weighing method also showed very slow deloading rates for the Pd-0.75 weight % B alloys, i.e., the D/Pd ratio change was less than -0.001/minute. This is more than ten times slower than observed for palladium electrodes. It took 2 weeks to reach an equilibrium weight for these alloys.

Deloading studies by the weighing method for the Pd-0.50 weight % B and Pd-0.25 weight % B alloys are shown in Table 3. The deloading rate again is much slower than for palladium cathodes. About 10 days was required to reach an equilibrium weight.

Tables 1-3 show that small amounts of boron added to the palladium can produce major changes in the deuterium deloading rates. The initial rates of loading, based on calorimetry, are similar for palladium and palladium-boron alloys. Perhaps boron accumulates in the grain boundaries during the initial loading and then hinders both the further ingress and egress of hydrogen or deuterium into and out of the metal lattice.

TABLE 3. De-loading Studies by the Weighing Method.

Time (hours)	Pd-0.5% B (Cell A)	Pd-0.5% B (Cell B)	Pd-0.25% B (Cell C)	Pd-0.25% B (Cell D)
0	0.617	0.643	0.687	0.687
12	0.490	0.497	0.518	0.512
36	0.350	0.368	0.446	0.367
67	0.228	0.261	0.215	0.190
112	0.152	0.161	0.108	0.069
181	0.100	0.051	0.034	0.010
282	0.065	0.003	0.010	0.003

#### 4. Summary

Loading and deloading of hydrogen and deuterium in palladium and palladium-boron alloys can be readily studied by the weighing method. Cracks or other surface flaws affect the degree of loading that can be obtained. Small amounts of boron alloyed with palladium can slow the deloading rate by a factor of ten or more. Excess power was observed for all Pd-B alloys used in these loading experiments except for one that had a surface flaw.<sup>1,2</sup>

#### 5. Acknowledgments

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## 6. References

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