ELECTROCHEMICAL INSERTION OF HYDROGEN INTO METALS AND ALLOYS

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ABSTRACT

Hydrogen in metals has possible applications in various energy storage devices. For the palladium-deuterium system, excess power production and other anomalous effects have been reported. This study focused on hydrogen and deuterium insertion into palladium and deuterium insertion into various palladium-boron alloys. The condition of the metal surface is a major factor in the insertion of hydrogen or deuterium into palladium or palladium-boron alloys. Cracks or other surface defects prevent high loading levels of hydrogen in metals. The addition of boron to palladium does not 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.

INTRODUCTION

Hydrogen in metals has possible applications in rechargeable battery systems, off-peak energy storage for electric utilities, and as the storage of hydrogen as a portable fuel for automobiles and buses. In addition, hydrogen embrittlement and hydrogen-related stress corrosion cracking are very important practical problems for metals and alloys.

Anomalous effects have been reported for the palladium-deuterium system including excess power production. This anomalous power effect apparently requires a loading ratio of D/Pd exceeding 0.85 [1].

This research will investigate the amount of hydrogen and deuterium that can be electrochemically inserted into palladium and palladium-boron alloys. Factors that affect the extent of loading and the rate of the loading and deloading processes will be investigated.

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 hydrogen loading can be represented by

$$M + x\ H_2O + xe^- \rightarrow MH_x + x\ OH^- \qquad (1)$$

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

$$MH_x \rightarrow M + x/2\ H_2 \qquad (2)$$

or by coulometry where the absorbed hydrogen is reacted electrochemically as represented by

$$MH_x \rightarrow M + xH^+ + xe^- \qquad (3)$$

The weighing method involved interrupting the electrolysis and removing the electrode from the solution whereas coulometry was performed in 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. For example, $\Delta H = -35,100$ J per mole of D_2 for the formation of PdD_x for $x \leq 0.6$ [2].

RESULTS/DISCUSSION

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 (Eq. 2) 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 $\geq$ 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 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 [3] was used to measure the heat of absorption of deuterium into the palladium rod cathode. This result is shown in Fig. 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 $PdD_{0.6}$, and using the reported value of ΔH = -35,100 J per mole of D_2 [2]. Fig. 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, and the loading process becomes endothermic [2]. No endothermic behavior, however, was detected in our experiment (Fig. 1).

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.**

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.

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).

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.

CONCLUSIONS

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.**

REFERENCES

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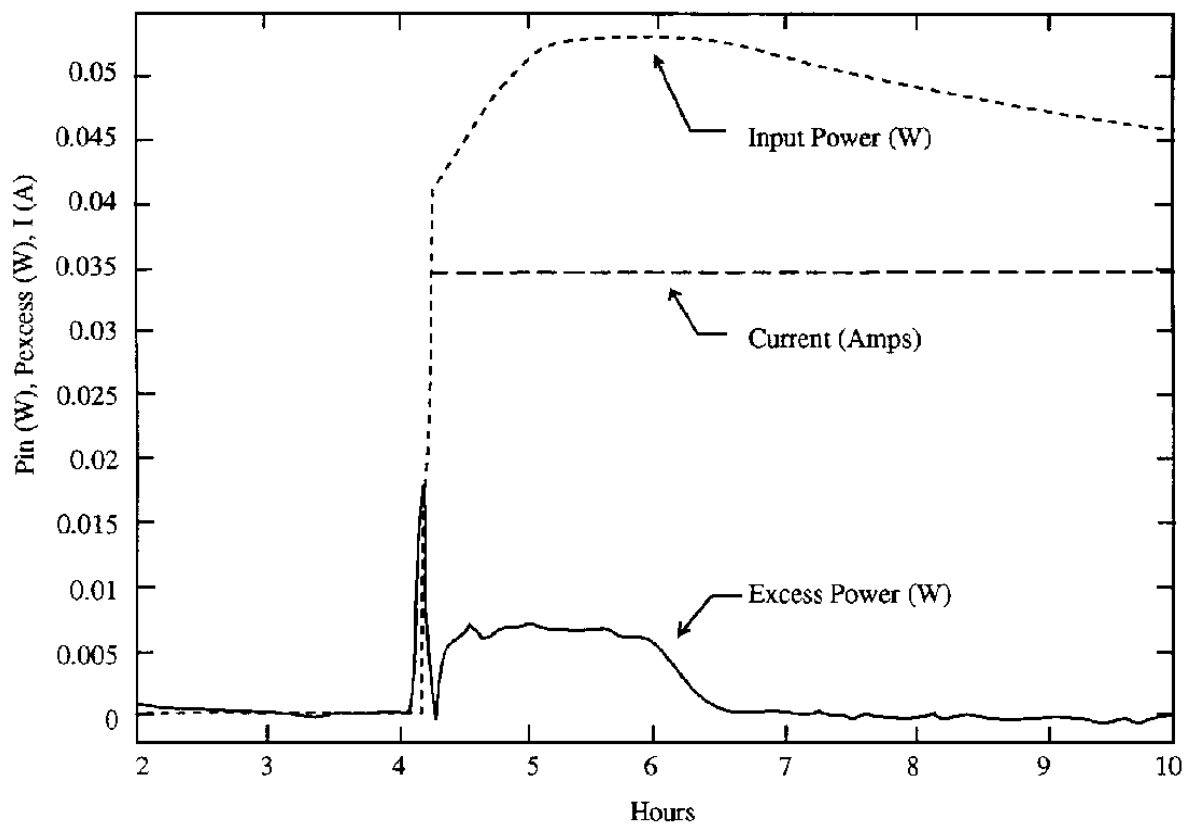
Fig. 1. Measurements of the Exothermic Heat of Absorption of Deuterium into a Palladium Wire Cathode (1 mm x 4.3 cm) using the New Calorimeter Developed at China Lake.

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

Table 2. Leading Studies by the Weighing Method Following 5
Days and 10 Days of Electrolysis.

Electrode	Xo(5Days)[a]	Xo(10Days)[b]
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

[a] I = 50 mA for 5 days.

[b] I = 100 mA for the second 5-day period.

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

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	0.67	0.687
12	0.490	0.497	0.518	0.512
36	0.350	0368	0.446	0367
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