Repeated Heat Bursts in the Electrolysis of D_2O

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ABSTRACT

Electrolysis of D_2O with Pd rod was performed under static or dynamic charging condition. The current densities were increased in steps in a long duration of electrolysis. During static charging, the Pd electrode was removed from the cell and partially outgassed in air. Resumption of the charging produced several repeated heat bursts. In the dynamic test, cyclic torsion was applied to the Pd electrode during the charging. No abnormal reaction was found during the torsion, but sometimes repeated occurrance of heat burst was observed after the cease of torsion. Possible causes for the heat bursts are proposed.

1. Introduction

"Cold Fusion" phenomenon has received much attention since the anouncement of Fleishmann and Pons in 1989 [1]. The excess heat has been reproduced by several research groups. The characteristics of Pd and the charging condition are considered to be the key factors for the abnormal phenomenon. In this paper, the electrolysis was performed under static or dynamic charging. A cyclic torsion was employed for the latter case. Some repeated heat bursts were observed under certain conditions. The phenomenon was correlated with the possible localized enrichment of deuterium in the defective structure produced during the test.

2. Experimental

A. Static Charging

An annealed palladium rod (99.95% purity, Tanaka) in a diameter of 3 mm was used as a cathode, which was surrounded by a wire-wound platinum anode. The Pd rod was annealed at 1100 K in vacuum for 2 hr before the electrolysis. The cell with 400 ml of electrolyte (0.1M LiOD in D_2O) was immersed in a 20-liter thermally insulated water tank. The experimental setup of the cell and tank has been reported previously [2]. The charging current densities were increased in steps from less than

0.1 to 1.8 A/cm^2 in a prolonged electrolysis. The electrolyte was automatically replenished to maintain a constant volume. The parameters monitored included the cell and tank temperatures and the cell current and voltage.

B. Dynamic charging

A cylindrical tensile specimen of Pd rod was mounted in a torsion testing machine. The gage section in a diameter of 3 mm and 3 cm long was enclosed in a glass cell for charging. The center of the cell bottom where the rod went through was sealed with silicon rubber so that cyclic torsion could be applied during the charging. The torsion amplitude was controlled at $\pm 3^o$ except higher ranges were used in the last run. The frequency was set at 0.1 Hz. The charging current density varied from 5 to 50 mA/cm^2. Cyclic torsion was applied after the specimen had been saturated with deuterium at a selected current density. The duration for each torsion was about 2 hr. After that, the charging current was increased and a similar sequence followed. Sometimes the charging current was also varied during the torsion to examine the effect of concentration gradient. Two thermocouples, one in the cell, the other one just outside of the cell, were used to monitor the temperature difference during the test.

3. Results

A. Static Charging

During the prolonged electrolysis, the temperature difference between the electrolyte and the tank water depended on the magnitude of charging current. A difference of 10 ^oC was observed for 1.8 A/cm^2. The cell temperature occasionally showed some abnormal fluctuation, but the fluctuation was always insignificant, less than 0.5^{o}C. There was no any abnormal temperature burst during the electrolysis for seven weeks. The experiment was then stopped, and both Pd cathode and Pt anode were removed from the cell. The Pd electrode was left in air to allow the outgassing of deuterium, whereas the Pt electrode was immersed in HNO_3 solution to get a cleaner surface. After 40 minutes of interruption of the experiment, both electrodes were put back to the cell assembly and the electrolysis was resumed. A series of cell temperature bursts, ranged from 1.0 to 2.5^{o}C were observed in the subsequent charging, as shown in Fig. 1. The first burst occurred at about 90 minutes after the restart of the experiment and lasted for 20 min. Similar events repeated more than

20 times within 5 days.

B. Dynamic charging

Since the cell was not insulated during the test, there was always a constant temperature difference between the cell and the ambient air. The difference increased with the charging current due to higher joule heating. No temperature burst was ever observed during the cyclic torsion. However, in one case, repeated bursts were observed after the cease of torsion. The first burst occurred about one hour after the torsion had been stopped. Subsequent bursts took place in a period of 13 hr, as shown in Fig. 2. The longest burst lasted for about one hour and the increase of temperature in the cell was about 1.5°C. Further charging with or without torsion at higher current densities did not reproduce the same phenomenon. Even when the torsion amplitude was raised to ±10° and then ±30° in the final run, no abnormal burst was observed.

4. Discussion

The repeated heat bursts observed in static charging occurred only after the electrode had been partially outgassed. Since the lattice parameter of Pd increased from 3.89 Å to 4.02 Å after the formation of hydride (deuteride), the outgassing would cause some plastic strain in the surface layer, leading to a high concentration of dislocations. These dislocations could, in principle, provide an efficient trapping for deuterium atoms. Resumption of charging produced enrichment of deuterium around these dislocations. It has been frequently proposed that in order for the abnormal reaction to occur, a critical loading ratio of D/Pd has to be achieved. The localized enrichment of deuterium in the outgassed region might have contributed to the phenomenon.

Similar argument can also be applied to the dynamic charging. During the cyclic torsion, the degree of deformation in the outer layer was higher than that in the inner region. More dislocations were produced in the outer layer and more deuterium would segregate around these dislocations. Note that with a frequency of 0.1 Hz and an amplitude of ± 3°, the deformation rate was so high that dislocation sweep-in of deuterium would not occur. This explains why the bursts were observed only after the stop of torsion but not during the torsion. To examine whether transport of deuterium by dislocations can result in enrichment of deuterium at heterogeneous sites, a slower torsion rate or a slower extension rate tensile test should have been used.

Finally, it is reminded that the dynamic charging has one more advantage, i.e., the cyclic torsion could destroy the surface scale, allowing a regular flux of deuterium to diffuse into the electrode.

5. Conclusion

Repeated temperature bursts were observed in both static and dynamic electrolysis conditions. In static charging, the bursts occurred after partial outgassing of deuterium from the Pd electrode. In dynamic charging, the bursts occurred after the stop of torsion. The abnormal reaction could be correlated to the localized enrichment of deuterium at dislocations created by the test condition.

Acknowledgment

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References

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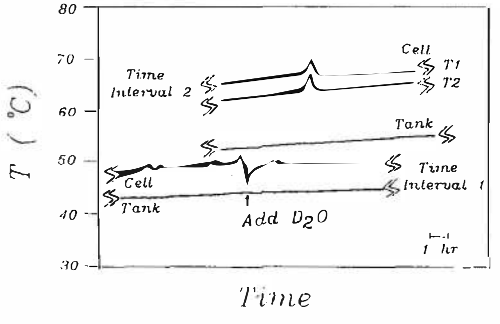

Fig. 1. Temperatures of the cell and tank in two different time intervals. In time interval 2, a higher charging current was applied and two thermocouples were used to monitor the cell temperatures at different locations.

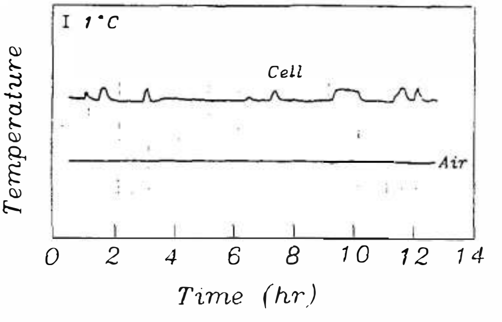

Fig. 2. Temperatures of the cell and the ambient air in one selected time interval after stop of torsion.