CALORIMETRIC ANALYSIS OF A HEAVY WATER ELECTROLYSIS EXPERIMENT USING A Pd-B ALLOY CATHODE

M.H. Miles*
New Hydrogen Energy Laboratory,3-5 Techno-Park 2-Chome, Shimonopporo Atsubetsu-Ku, Sapporro-004, Japan
M.A. Imam
Physical Metallurgy Branch, Materials Science and Technology Division,Naval Research Laboratory,Washington, D.C. 20375-5320
M. Fleischmann
ENEA, Frascati Research Centre, 00044 Frascati, (Rome), Italy

The palladium-boron alloy was prepared at the Naval Research Laboratory (NRL) using an arc melter with a water-cooled copper hearth (1). The nominal boron concentration was 0.50 weight percent boron. Two distinct phases of the same cubic structure but with different lattice parameters were present in the alloy. The Pd-B rod was polished using diamond paste, and the final dimensions were 4.71x20.1 mm (V=0.350 cm^3, A=3.15 cm^2). The cathode rod was spot welded on the side to a platinum lead wire. Quick-setting Epoxy was used to cover the spot weld area, the top of the cathode, as well as the end of the glass tubing containing the platinum lead wire.

The Pd-B cathode along with a platinum wire spiral anode were placed in a Fleischmann-Pons Dewar glass cell. The cell also contained a resistive calibration heater (0.2500 W) and two thermistors (short and long). The cell had a special Kel-F plug cap that seals all lead wires but allows the electrolysis gases to exit the cell through a small glass tube. The Dewar cell dimensions were 25.0 cm in height with an inner diameter of about 2.5 cm. This cell was filled with 90 cm^3 of 0.1 M LiOD + D_2O and placed in a large water bath containing a glass window that allowed direct observation of the electrolysis. The cell was connected to a data acquisition system that recorded the cell voltage, two cell temperatures, the bath temperature, cell current, and time every 300 s for the duration of this experiment (69 days).

The Dewar-type Fleischmann-Pons electrochemical calorimetric cells are silvered at the top (8.0 cm), thus heat transfer is confined almost exclusively to radiation across the lower, unsilvered region (17.0 cm). The calorimetric equations, therefore, are given by

$$P_{calor} = P_{El} + P_x + P_H - P_{out} - P_{gas} \quad [1]$$

where

$$P_{El} = [E(t) - \gamma E_H] I \quad [2]$$

$$P_{out} = k_R (T^4_{cell} - T^4_{bath}) \quad [3]$$

and P_{gas} and P_{calor} are the same as defined previously (1-3). These equations are consistent with those reported by Fleischmann et al. (4). The faradaic efficiency for the water electrolysis (γ) was always unity based on the D_2O consumption.

The use of these calorimetric equations to determine any excess power (P_x) required the accurate determinations of two critical cell parameters: (1) the radiative heat transfer coefficient (k_R) and (2) the water equivalent of the cell.

* Present address: NAWCWD, Code 4T4220D, China Lake, CA 93555-6100

The accurate methods used for determining these key cell parameters are presented in the NRL Report (1).

The final results are 0.85065×10^{-9} WK^{-4} for the radiative heat transfer coefficient and 450 JK^{-1} for the water equivalent of this cell (1). This Pd-B experiment is characterized by the early onset of excess power and by the presence of positive feedback. Increasing the cell temperature by the application of the 0.2500 W resistive heater often yields an increase of the excess power (1,5). The excess enthalpy effect averaged about 10,000 J/day (0.12 W) with peaks exceeding 30,000 J/day (0.35 W). A total of 700 kJ of excess enthalpy was produced over a 68 day period. The cell boiled to dryness on Day 68, and the rate of excess enthalpy generation rose to about 9.3 W at this time, or 27 W cm^{-3} based on the volume of the cathode. Furious boiling and swirling actions were centered around the cathode during this boil-off period. Results of this experiment along with the related raw experimental data are found in the NRL Report (1). The generation of excess enthalpy by the Pd-B rod continued for several hours after the cell boiled dry and electrolysis ceased (1).

Previous experiments at China Lake using similar Pd-B alloy cathodes prepared by the Naval Research Laboratory produced excess enthalpy in seven out of eight experiments (6). This suggests that palladium materials that are relatively oxygen-free are more likely to produce this anomalous effect. The oxygen originally present in the palladium reacted with the boron during the arc melting process and was removed from the system.

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