

THERMAL BEHAVIOR OF POLARIZED Pd/D ELECTRODES PREPARED BY CO-DEPOSITION

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ABSTRACT

The thermal behavior of a polarized Pd+D electrode prepared by the co-deposition technique and serving as the cathode in the Fleischmann-Pons (F/P) Dewar-type electrochemical cell/calorimeter was investigated at the NHE Laboratory in Sapporo, Japan. These measurements show that (i) excess enthalpy is generated during and after the completion of the co-deposition process, (ii) rates of excess enthalpy generation are somewhat higher than when Pd wires or other forms of Pd electrodes are used and (iii) positive feedback and heat-after-death effects were present in this system.

1. INTRODUCTION

Fleischmann et al^[1] reported in 1989 that a negatively charged palladium electrode immersed in heavy water generates excess enthalpy. Early experiments using metallic palladium cathodes exhibited poor reproducibility which was traced to the source and composition of the palladium.^[2,3] In contrast, electrodes prepared by the co-deposition technique^[4] showed good reproducibility while retaining the characteristic features observed in functional solid electrodes such as positive feedback and heat-after-death. The positive feedback refers to an increase in excess enthalpy generation with increase of the cell temperature while heat-after-death represents an extreme form of excess enthalpy generation at near zero enthalpy input. Also, of practical interest, is the fact that excess enthalpy generation occurs at low current densities when electrodes prepared by the co-deposition method are employed. These studies at the New Hydrogen Energy (NHE) Laboratory in Sapporo, Japan were the first co-deposition experiments conducted using the F/P Dewar-type calorimetric cells. A preliminary report of these experiments has been published.^[5,6]

2. EXPERIMENTAL

These experiments conducted at the NHE Laboratory in Sapporo, Japan used copper rod cathodes (2.5 cm in length and 0.4 cm in diameter) upon which palladium and deuterium were co-deposited from a solution containing 0.025 M PdCl₂ + 0.15 M ND₄Cl + 0.15 M ND₄OD in D₂O (Isotec, Inc., 99.9 at % D). This solution was lithium-free and initially buffered (pH=9-10) in contrast to the 0.050 M PdCl₂ + 0.30 M LiCl solution normally used by Szpak and Mosier-Boss.^[4] The F/P Dewar-type cell had an inner diameter of 2.5 cm and a height of 25.0 cm with the top 8.0 cm silvered.^[3,6] These cells were filled with 91 cm³ of the D₂O solution. No re-filling of the cells was necessary due to the short time period of these experiments (8 days) and the low current that were used for the first 5 days.^[5,6] The co-deposition process using a constant currents of $I=0.006$ A was essentially completed in the first 24 hours. This involves the simultaneous deposition of palladium and deuterium onto the non-absorbing copper substrate.

These experiments based on the F/P design used a Hi-Tek DT 2101 potentiostat wired as a galvanostat for each cell. A separate potentiostat/galvanostat was used to deliver constant current to a resistive heater used to calibrate each cell. The system was controlled by a 486 data acquisition computer which also controlled a Hewlett-Packard 44705A multiplexer and data acquisition system. The required data (cell current, cell voltage, cell temperature, bath temperature) were recorded every 300 seconds throughout the experiment. Two thermistors were positioned at different locations in the cell to yield two independent

measurements of the cell temperature. Nearly identical cell temperatures were measured by each thermistor, thus there were no significant temperature gradients in the cell due to inadequate stirring.

3. RESULTS

Although three co-deposition experiments were conducted simultaneously, the results here are for Cell A-2 positioned near the center of the water bath. However, previous approximate methods of analysis show that all three cells yield similar patterns of excess power production that indicates excellent reproducibility.^[5,6]

Figure 1 shows the cell temperature and cell voltage as a function of time for the entire experiment.

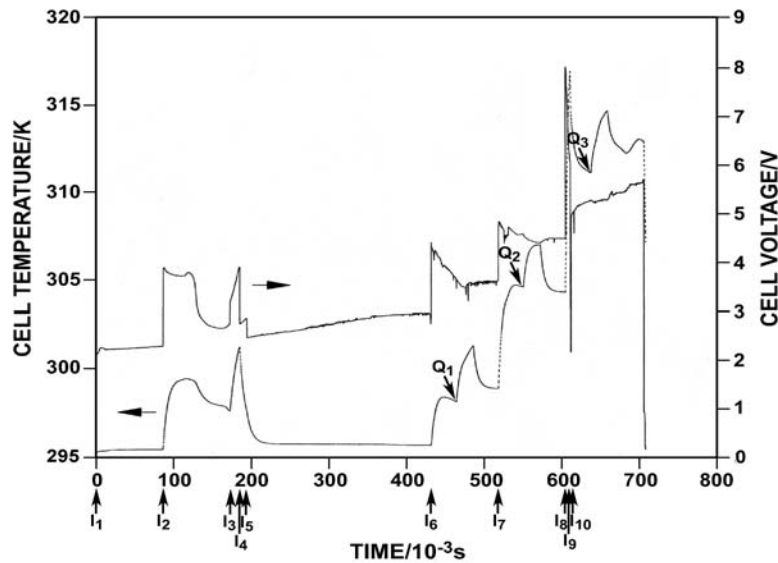


Fig. 1. Cell temperature and cell potential as a function of time for this entire co-deposition experiment. The charging currents were $I_1 = 0.006$ A, $I_2 = 0.1$ A, $I_3 = 0.2$ A, $I_4 = 0.05$ A, $I_5 = 0.02$ A, $I_6 = 0.1$ A, $I_7 = 0.2$ A, $I_8 = 0.4$ A, $I_9 = 0.02$ A, $I_{10} = 0.3$ A. The heater calibration pulses (6 hours each) were $Q_1 = Q_2 = Q_3 = 0.2500$ W

Important features are the three applications of the resistive heater (Q_1 , Q_2 , Q_3) with 0.2500 W added input power to the cell for six hours. The ten changes in the cell current are indicated by the I_1 , I_2 , etc. arrows along the time axis. Briefly, three distinctly different time periods can be identified. The first period includes the co-deposition ($I_1 = 0.006$ A), charging at 0.1 A (I_2) increased to 0.2 A (I_3) and followed by a stepwise reduction to 0.05 A (I_4) and 0.02 A (I_5). The second time interval is the period of low charging rate ($I_5 = 0.02$ A) for about 72 hours. The third time interval is characterized by operating at larger cell currents hence higher cell temperatures and by the three engagements of the calibration resistive heater.

The 11-point average of the excess power (Q_i), in this co-deposition experiment is shown in Fig. 2.

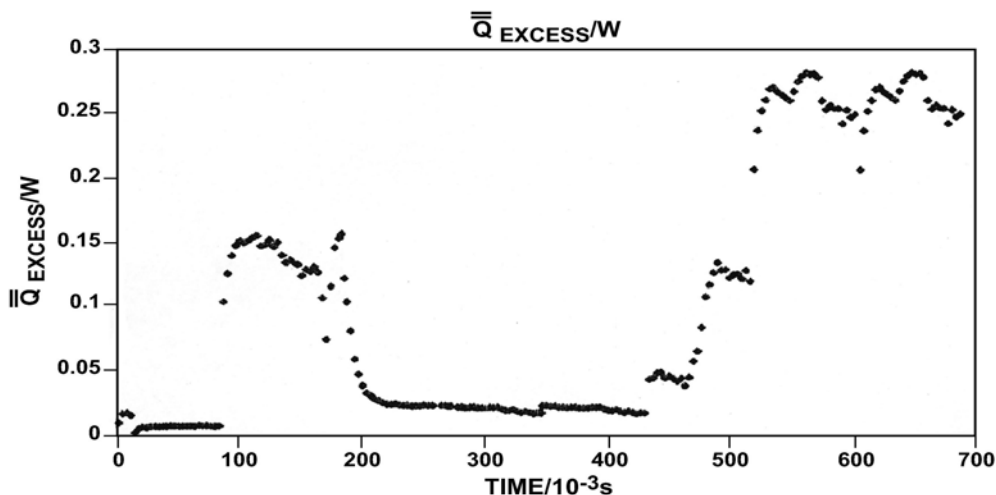


Fig 2. Rate of excess enthalpy generation as a function of time based on the cell parameters $k_R = 0.85065 \times 10^{-9} \text{ WK}^{-4}$ and $C_p M = 450 \text{ JK}^{-1}$.

The calorimetric equations and the method used in the data analysis have been explained in exact detail elsewhere.^[3,6,7] Viewing Fig. 2 in conjunction with Fig. 1, we find the following: (i) excess enthalpy is generated during the co-deposition process and (ii) the increase of the cell temperature, whether due to an increase in the cell current or due to the internal resistive heater increases the rate of excess enthalpy generation. This is a clear signal of positive feedback for this co-deposition experiment. The highest excess power levels exceed 0.25 W. This is somewhat larger than excess power effects generally observed with solid palladium electrodes of similar size. The data analysis presented in Fig. 2 for this co-deposition experiment was conducted by M. Fleischmann who is certainly the world's expert on the F/P Dewar calorimetric system.^[6,7] An approximate and independent method of data analysis developed by M.H. Miles while at NHE and using only laboratory notebook data obtained during normal working hours shows the same general features for the excess enthalpy generation in this co-deposition experiment.^[5,6]

A detailed view of the first application of the resistive heater calibration pulse (Q_i) is presented in Fig. 3 (see also Fig. 1). The cell temperature does not relax back to the original baseline upon cessation of this added thermal input. The cell potential at constant current has slightly decreased, yet the cell temperature has increased. This remains the simplest and clearest indication of excess power and can be easily comprehended without any calorimetric equations.^[8] The cell temperature simply cannot increase when the input power decreases if there is no anomalous excess power source. The excess power imposed on Fig. 3 from Fig. 2 shows that the actual increases in excess power is from 0.05 W prior to the heating pulse to 0.14 W following the heating pulse. Again, this is another example of positive feedback in this co-deposition system.

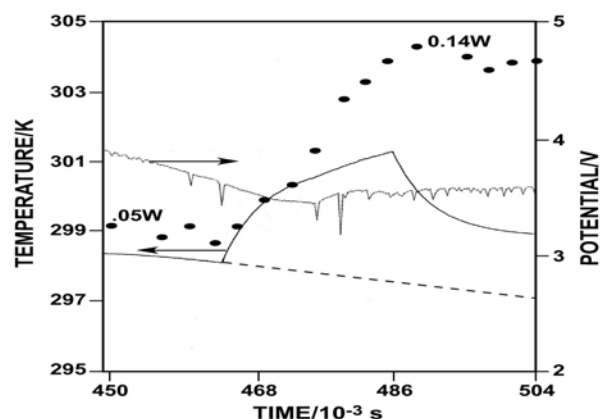


Fig. 3. The cell temperature and cell potential curves for the application of the first resistive heater calibration pulse (Q_1) for 6 hours. This illustrates the positive feedback effect.

The effect of the second heating pulse (Q_2) on the cell temperature and cell voltage is presented in Fig. 4.

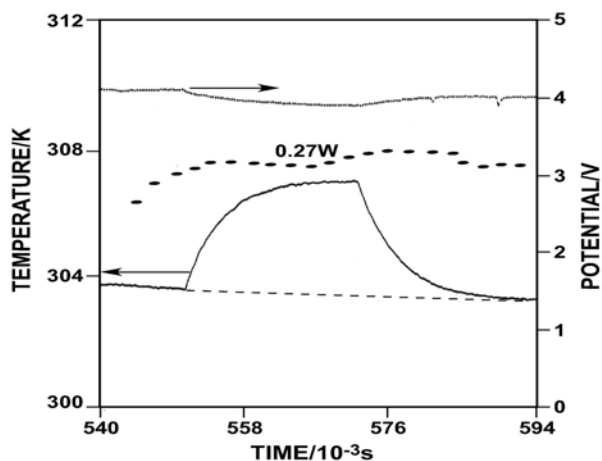


Fig. 4. The cell temperature and cell potential curves for the application of the second resistive heater calibration pulse (Q_2) for 6 hours. This illustrates the expected behavior when the rate of excess enthalpy generation remains constant.

The application of the calibration heating pulse again causes the expected increase in cell temperature. Unlike Fig. 3, however, the cell temperature relaxes back to the expected baseline upon termination of the heating pulse. This is the normal behavior when no excess power is present on when the excess power remains constant. As shown in Fig. 4, the excess power is nearly constant at 0.27 W during this heating pulse, hence there is no positive feedback. Although NHE used a time period of 6 hours for the heating pulse rather than the recommended 12 hours,^[7] the cell temperature almost attains a steady value during this second heating pulse shown in Fig. 4. In contrast, the cell temperature continues to rise during the first heating pulse

(Fig. 3) due to the increasing excess power. This presence of positive feedback makes it impossible to accurately determine the radiative heat transfer coefficient from this first heating pulse alone. Nevertheless, the NHE method for F/P cells always used solely the first heating pulse to calibrate the cell.^[6,7]

It can be seen from Fig. 1 that the cell temperature does not relax back to the expected baseline during the third heating pulse (Q_3). Fig. 2 indicates an increase in the excess power during this heating pulse, thus there is again positive feedback for the co-deposition system. The simple test of increasing the cell temperature for a period of time and observing whether or not this cell temperature relaxes to the original baseline should be investigated periodically in every cold fusion calorimetric experiment. This provides a simple test for a system producing excess power that involves positive feedback.

4. DISCUSSION

The two most important parameters to be determined for the F/P Dewar-cell calorimetry are the radiative heat transfer coefficient, k_R , and the water equivalent, C_pM , for the cell.^[6,7] These parameters are inherently connected with the cell construction and experimental protocol, hence once determined for a given cell, they can be used for subsequent experiments using the same cell. This co-deposition experiment used the same cell (Cell A-2) as a previous Pd-B study^[3,6,7] that yielded the values of $k_R = 0.85065 \times 10^{-9} \text{ WK}^{-4}$ and $C_pM = 450 \text{ JK}^{-1}$. The experimental data for the co-deposition experiment in Cell A-2 yielded good agreement with these values.

The Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8} \text{ Wm}^{-2} \text{ K}^{-4}$, and the radiation area of the F/P cell, $A = 1.33 \times 10^{-2} \text{ m}^2$, yields a minimum value of $k_R = 0.754 \times 10^{-9} \text{ WK}^{-4}$ for the radiative heat transfer coefficient for this F/P Dewar-type calorimetric cell. The softening of the Dewar vacuum with time plus heat transfer by conduction through the top of cell can readily account for the higher value obtained experimentally. The NHE analysis using the first heating pulse (Fig. 3) where there is positive feedback yields $k_R = 0.68 \times 10^{-9} \text{ WK}^{-4}$ for this F/P Dewar cell. Although a k_R value this small is not even theoretically possible, the NHE analysis still showed the presence of excess power for this co-deposition experiment.

Early in the third day of this experiment, the current was decreased from 0.2 A (I_3) to 0.02 A (I_5) for the weekend (Fig. 1). Although the excess power decreased due to the lower temperature of the cell (Fig. 2), it nevertheless equaled approximately 100% of the input power during this time period. Thus, there is significant excess enthalpy generation at low current densities in co-deposition experiments. This observation has practical implications – it indicates the possibility of constructing systems employing fluidized bed electrodes for high thermal efficiencies. The continued generation of excess enthalpy at low or zero enthalpy input has been observed in many cold fusion experiments and is generally called the heat-after-death effect.^[3,6,7]

The total integrated excess enthalpy for this entire co-deposition experiment (Fig. 2) is 75 kJ. The total consumption of D_2O measured after the completion of this experiment was $7.7 \pm 1.0 \text{ cm}^3$. This is within experimental error for the theoretical value of 7.2 cm^3 assuming 100% efficiency for the faradaic electrolysis reaction, $D_2O \rightarrow D_2 + \frac{1}{2} O_2$. Therefore, there was no measurable recombination of the electrolysis gases as has been proven repeatedly for cold fusion experiments.^[3,6-8] Furthermore, any recombination would not likely yield the positive feedback and heat-after-death effects that were observed in this co-deposition experiment.

The polarized electrode surface prepared by the co-deposition technique has been monitored using an infrared camera. These experiments have revealed the existence of “hot spots”.^[9] Consequently, loading of deuterium into the palladium lattice does not occur with spatial uniformity. Microscopically large yet macroscopically small regions attain a state that can function collectively in absorbing large quantities of deuterium. The net result is localized reaction volumes that manifest themselves as hot spots. No such data are available for solid palladium electrodes.

5. SUMMARY

The negatively charged Pd+D electrode prepared by the co-deposition technique and investigated in a F/P Dewar calorimetric cell showed the following characteristics:

1. Thermal behavior that is similar to that observed for solid palladium electrodes, i.e., positive feedback and heat-after-death effects.
2. Excess enthalpy generation during the co-deposition process and at substantial rates at low cell currents.

The first observation may shed light on the origin of the excess enthalpy generation while the second may be of practical interest.

ACKNOWLEDGEMENT

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REFERENCES

1. M. Fleischmann, S. Pons and M. Hawkins, *J. Electroanal. Chem.*, **261**, 301 (1989).
2. M.H. Miles, B.F. Bush and K.B. Johnson, *Anomalous Effects in Deuterated Systems*, NAWCWPNS TP 8302, 99 pp., September 1996.
3. M.H. Miles, M.A. Imam and M. Fleischmann, "Calorimetric Analysis of a Heavy Water Electrolysis Experiment Using a Pd-B Alloy Cathode", in *Energy and Electrochemical Processes for a Cleaner Environment*, C. Comninellis, M. Doyle and J. Winnick, Editors, Proceedings Volume 2001-23, The Electrochemical Society, Inc., pp. 194-205 (2001).
4. S. Szpak, P.A. Mosier-Boss and J.J. Smith, *J. Electroanal. Chem.*, **302**, 255 (1991).
5. S. Szpak, P.A. Mosier-Boss and M.H. Miles, "Calorimetry of the Pd+D Co-Deposition", *Fusion Technology*, **36**, 234 (1999).
6. M.H. Miles in *Thermal and Nuclear Aspects of the Pd/D₂O Systems, Volume 1: A Decade of Research at Navy Laboratories*, S. Szpak and P.A. Mosier-Boss, Editors, Technical Report 1862, SSC San Diego, February 2002.
7. M.H. Miles, M. Fleischmann and M.A. Imam, *Calorimetric Analysis of a Heavy Water Electrolysis Experiment Using a Pd-B Alloy Cathode*, Naval Research Laboratory Report, NRL/MR/6320-01-8526, 155 pp., March 16, 2001.
8. M.H. Miles, "Calorimetric Studies of Pd/D₂O+LiOD Electrolysis Cells", *J. Electroanal. Chem.*, **482**, 56 (2000).
9. S. Szpak and P.A. Mosier-Boss, *Il Nuovo Cimento*, **112 A**, 577 (1999).