Research Article

Co-deposition of Palladium and other Transition Metals in H_2O and D_2O Solutions

Melvin H. Miles*

University of La Verne, La Verne, CA 91750, USA

Abstract

The co-deposition of palladium, ruthenium, rhenium, nickel, and iridium were investigated in H_2O and D_2O ammonia systems (NH_4Cl/NH_3). Significant amounts of excess power were observed only in the deuterated Pd/D_2O system. There was no anomalous excess power observed for the co-deposition of ruthenium, rhenium or nickel in any H_2O or D_2O experiment.
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1. Introduction

Anomalous effects for Pd/D co-deposition were first reported by Szpak and Mosier-Boss using the $PdCl_2 + LiCl/D_2O$ system [1]. However, commercial electroplating baths for palladium are often based on aqueous ammonia solutions (NH_4Cl/NH_3) at pH 7–10 [2]. The related $PdCl_2 + ND_4Cl + ND_3/D_2O$ deuterated ammonia system previously produced large reproducible excess power in three out of three experiments [3]. This co-deposition excess power was similar to the anomalous effects observed in other Pd–D systems [4]. Recent experiments have shown that these anomalous excess power effects were absent in Pd/H_2O controls as well as for the co-deposition of ruthenium (Ru) in both H_2O and D_2O ammonia solutions [5,6]. This study reports results for the co-deposition of rhenium (Re), nickel (Ni), and iridium (Ir) in both H_2O and D_2O ammonia systems and the use of high currents for palladium co-deposition.

The Pd/D co-deposition term implies that both palladium and deuterium are simultaneously deposited at the cathode in an electrochemical cell. Thermodynamically, palladium deposition can occur at a smaller cell voltage then D_2O electrolysis (0.5362 V vs. 1.2615 V at standard conditions). Therefore, the use of small cell currents or linear potential scan may result in the deposition of palladium without the generation of deuterium gas at the cathode, thus there would be no co-deposition. For our studies, however, the cell currents used were always sufficient for the simultaneous generation of deuterium and the deposition of palladium or other transition metals at the cathode.

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*E-mail: melmiles1@juno.com

2. Experimental

Calorimetric studies used a heat conducting isoperibolic design and electrochemical instrumentation as previously reported [7,8]. The deuterated chemicals used were Cambridge Isotope Laboratories or ACROS D_2O (99.9 at% D), ACROS ND_4Cl (98 at% D) and ACROS ND_4OD (99 at% D). The deposition of transition metals used Alfa-Aesar $PdCl_2$, $Ru(NO)(NO_3)_3$, $ReCl_3$, NiO, $NiCl_2 \cdot 6H_2O$, and $IrCl_3$. The transition metal solution concentrations were near 0.025 M except for two of the high current depositions using $PdCl_2$ where the concentration was significantly smaller (about 0.006–0.009 M). The metal deposition process generally used a constant current of 6 mA or higher where deuterium gas production can be visually observed at the cathode. However, ruthenium could not be deposited until the current was increased to 400 mA [6]. The $IrCl_3$ solution remained dark in color and could not be completely deposited even at high currents. Recent experiments have used a large current (200 or 300 mA) for palladium deposition in an effort to increase metal vacancy formation that may promote the production of large excess power effects [9].

3. Results

Previous studies of ruthenium co-deposition in H_2O and D_2O produced no measurable excess power [6]. These studies have now been extended to the co-deposition of other transition metals as well as to the high current deposition of palladium.

3.1. Co-deposition of rhenium

The use of 0.020 M $ReCl_3$ + 0.15 M NH_4Cl + 0.45 M NH_4OH + H_2O formed a very dark red solution with a pH = 9.58 at 19°C. Co-deposition at 6 mA produced a black deposit of Re at the cathode and a clear solution within 24 h. The solution became acidic (pH = 1.36), as expected, following completion of the rhenium deposition and after increasing the current to 100 mA which drives off the ammonia. Some chlorine production was also detected during this period. The ammonia and chlorine evolution events are both endothermic processes that could only produce small negative effects on excess power measurements. This cell was then placed into the calorimeter and ran for 12 days using an electrolysis current of 300 mA. As shown in Fig. 1, no excess power was detected within the experimental error of ± 5 mW.

The mean excess power using thermistor 4, as shown in Fig. 1, was -1.1 ± 4.2 mW. This thermistor was placed directly in the solution within the glass cell. A second thermistor was placed in the usual position on the outside surface of the glass cell in a secondary compartment filled with Mobil-1 oil (5–30 W) as reported previously [6,7]. This second thermistor gave a mean excess power of 1.4 ± 5.7 mW. Both thermistors agree that there was no excess power within experimental error for this rhenium co-deposition study. In fact, the small departures from exactly zero excess power can be related to errors in the calculation of the electrolyte volume. Long periods between re-filling this cell were used in this rhenium co-deposition experiment to obtain the value for the effect of the electrolyte volume on the heat transfer coefficient. This study yielded the value of $\Delta k_C / \Delta V = 0.0002$ W/K mL that was used in this and following experiments [10].

3.2. Co-deposition of palladium at high currents

Recent experiments have involved the co-deposition of palladium at high currents in an effort to produce a larger number of metal vacancies and possible large excess power effects [9]. Two Pd/D_2O experiments have been completed using a high co-deposition current of 200 or 300 mA, and both produced large excess power effects. Figure 2 shows the results for one of these studies.

From Fig. 2, it is estimated that there was a total of 150 kJ of excess enthalpy in this co-deposition experiment. It appears that even larger excess enthalpy amounts could have been measured by running the experiment longer. A
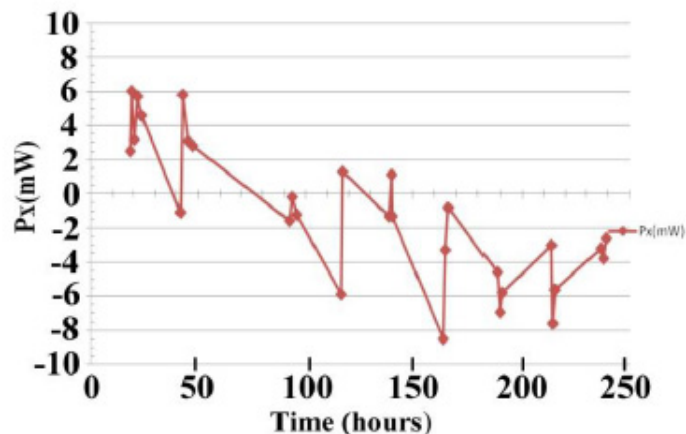
Figure 1. Calorimetric results for rhenium co-deposition in H_2O (thermistor 4).

second Pd/D_2O experiment using 200 mA for the co-deposition process produced a similar excess power effect and a total excess enthalpy of about 170 kJ. This exceeds the amount found in any other co-deposition experiment using the ammonia system. The calorimetric results for this second Pd/D_2O experiment is shown in Fig. 3. A smaller concentration of $PdCl_2$ (0.0091 versus 0.0264 M) was used in this second experiment.

The current profile for the results in Fig. 2 was 300 mA up to 118.77 h, then 400 mA until 194.00 h, then 300 mA again up to 221.50 h, and finally 500 mA to the end of the experiment. The second experiment shown in Fig. 3 used 200 mA up to 30.62 h, then 300 mA to 123.18 h, then 200 mA again until 152.32 h, 350 mA until 176.40 h, and then 300 mA to the end of this experiment. The slight dip in the excess power seems to be related to the lower current of 200 mA for this period. The cell voltage ranged from 3.898 V at 300 mA to 7.906 V at 500 mA in the first Pd/D_2O experiment (Fig. 2), and 7.092 V at 200 mA to 8.550 V at 350 mA in the second Pd/D_2O study (Fig. 3). The more
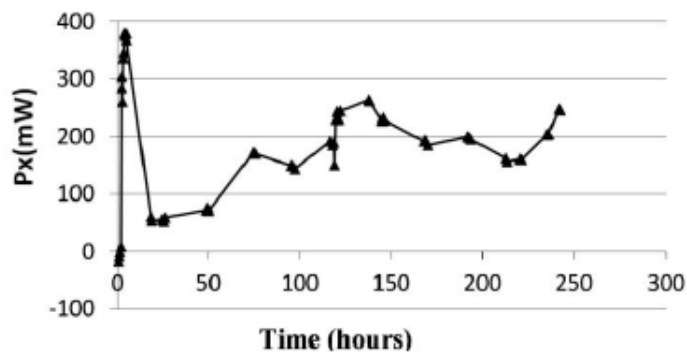

Figure 2. Calorimetric results for the co-deposition of palladium in D_2O at 300 mA.
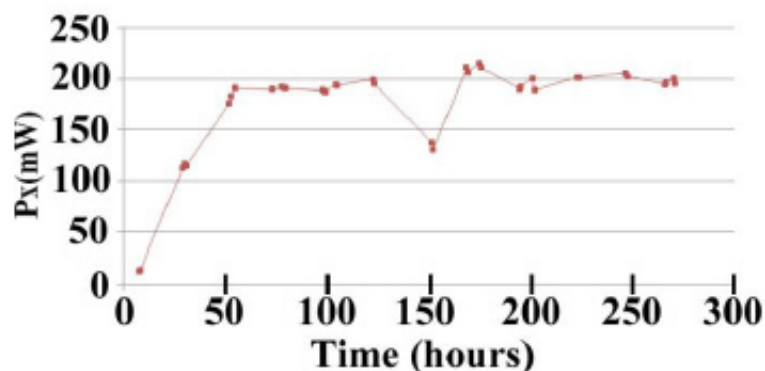
Figure 3. Calorimetric results for the second co-deposition of palladium in D_2O at 200 mA.

constant excess power effect in the second experiment (Fig. 3) may be related to the more narrow range in the cell voltage.

Control studies of Pd/H_2O using co-deposition at 300 mA unexpectedly yielded small excess power effects. The consumption of H_2O was also smaller than calculated suggesting possible recombination. It was found that not all of the palladium remains on the cathode substrate with high current deposition, and small palladium particles were visible in the solution that may cause recombination. The excess enthalpy in this Pd/H_2O experiment was about 60 kJ. In a second Pd/H_2O study, a smaller concentration of $PdCl_2$ (0.0063 M versus 0.0247 M) was used. In this experiment, the H_2O consumed slightly exceeded the theoretical amount (28.0 mL versus 27.28 mL). The excess enthalpy produced was also significantly smaller at 35 kJ. This still leaves, however, a small unexplained excess power effect for the Pd/H_2O control system. Further experiments are needed to resolve these findings. However, another laboratory has reported excess power in light water experiments using high current co-deposition [11].

Experimental cooling curves at the end of studies produced by shutting off the electrolysis current provide a tool that may distinguish between the Fleischmann–Pons excess power effects (FPE) and other types of excess power such as recombination [7]. At this zero current, the calorimetric equation simplifies to

$$C_p M \, dT/dt = -k_C(T - T_b) + P_X, \tag{1}$$

where $C_P M$ is the heat capacity of the calorimetric system (J/K), T is the cell temperature (K), T_b is the constant bath temperature (K), k_C is the conductive heat transfer coefficient (W/K), and P_X is the excess power effect (W). For FPE excess power, P_X often continues after the current is set to zero (Heat-After-Death, see [16]). In contrast, other types of excess power go to zero immediately when $I = 0$. By assuming $P_X = 0$, Eq. (1) can then be integrated to give

$$\ln(T - T_b) = -(k_C/C_p M)t + \ln(T_0 - T_b). \tag{2}$$

The rearrangement of Eq. (2) yields

$$\Delta T = \Delta T_0 \exp(-k_C t / C_p M), \tag{3}$$

where $\Delta T = T - T_b$ and $\Delta T_0 = T_0 - T_b$. This exponential decrease in ΔT is shown experimentally in Fig. 4 for the cell temperature using thermistor 2 (T_2).

The time constant (τ) for the calorimetric cell can be determined directly from Fig. 4 or calculated from $\tau = C_p M / k_C$ and yields 51 min (3060 s) for this experiment.
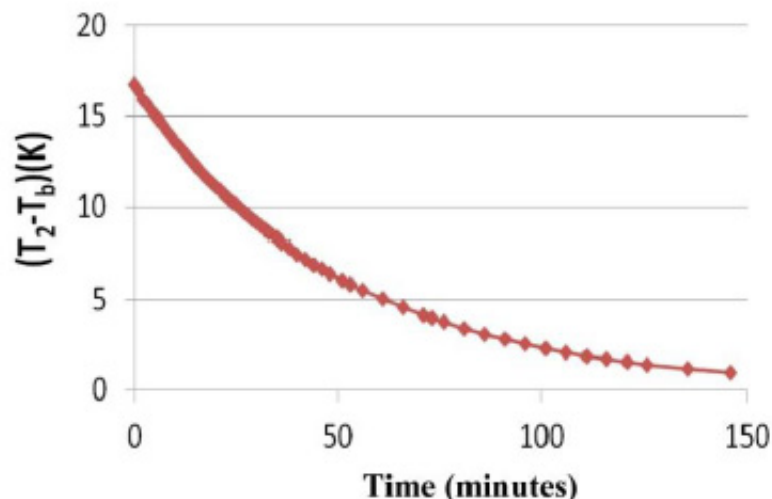
Figure 4. Experimental cooling curve for the Pd/H_2O experiment.

Figure 5 shows the application of the integrated Eq. (2) to the cooling curve for the Pd/H_2O co-deposition control that showed excess power. The experimental data fits almost perfectly with Eq. (2) ($R^2 = 0.99992$). This suggests that there was no "Heat-After-Death" and likely no FPE excess power in this Pd/H_2O control ($P_X = 0$). This is also evidence that almost all of the heat is transferred by conduction through the walls of the calorimeter to the water bath. Furthermore, the equation for this line provides for the calculation of the heat capacity of the system and yields $C_pM = 402$ J/K. A theoretical calculation of this heat capacity for this same experimental volume of H_2O in the cell (42.0 mL) yields $C_pM = 404$ J/K. Cooling curve studies for other Pd/H_2O control cells have also given near perfect agreement with the integrated Eq. (2) [7,8].

Figure 6 shows the same application of Eq. (2) to the cooling curve for the Pd/D_2O experiment involving high current co-deposition. It is readily apparent that the line fit is not as good. Furthermore, the equation for the line yields $C_pM = 476$ J/K, a value that is much too high. The presence of a lingering excess power effect distorts the fit of the data with Eq. (2) and prolongs the cooling process. This reduces the slope of the line and yields a high C_pM value. Based on these cooling curves, there was likely real FPE excess power for the Pd/D_2O experiment but not for the Pd/H_2O experiment.

3.3. Nickel and iridium co-deposition

The Rossi E-Cat [12] claims for a nickel–hydrogen system spurred interest in Ni/H_2O co-deposition experiments. Several co-deposition experiments were completed in the ammonia system using either NiO or $NiCl_2 \cdot 6H_2O$. The NiO was mostly insoluble and required increasing the current to 100 mA to obtain complete deposition and a clear solution. The $NiCl_2 \cdot 6H_2O$ was much more soluble, but there was no excess power produced in any of the nickel co-deposition experiments involving H_2O and D_2O.

The iridium co-deposition experiment proved to be a challenge. The initial 0.024 M $IrCl_3$ ammonia solution resulted in a black, insoluble suspension. Complete deposition could never be achieved even with the use of large currents up to 500 mA. Reversible Ir^{3+}/Ir^{4+} reactions are known as a "source of annoyance" for iridium chemistry that block further

reactions [13]. The calorimetry showed measurable excess power, but this may be explained by the dark color of the insoluble suspension. The dark iridium particles may partially block the transmission of visible and infrared radiative power from the cell, but more work is needed to test this assumption. There could also be iridium reactions that interfere with the electrolysis of H_2O, but this was not obvious by the measured H_2O consumption.

Iridium is one of the most resistive metals to hydrogen absorption with a very low value of H/Ir = 0.005 even at 90,000 atm hydrogen pressure at 250°C [14]. Based on this property, the small excess power in the iridium study was likely due to the dark solution color, the incomplete deposition, or some factor other than real FPE excess power.

Prior to the iridium experiment and the palladium co-deposition at high currents, the only excess power observed was for Pd/D_2O in the ammonia co-deposition system. Excess power was measured for Pd/D_2O in six out of six (6/6) experiments, while no excess power was found in 2/2 Pd/H_2O studies, 4/4 ruthenium H_2O or D_2O studies, 2/2 rhenium H_2O or D_2O studies and 4/4 nickel H_2O or D_2O experiments. Statistical calculations at this point showed only a small probability (0.0000106) that random errors could have restricted the excess power effect to only the Pd/D_2O co-deposition system. However, the Pd/H_2O co-deposition studies at high currents as well as the iridium results complicates these statistical calculations. Further experiments are needed to determine if these new small excess power effects for Pd/H_2O and Ir/H_2O are real.

3.4. Consumption of H_2O and D_2O

Recombination or other chemical reactions can yield false measurements of anomalous excess power for open, isoperibolic calorimeters. This can be checked by simultaneous measurements of the electrolysis gases produced and comparisons with theoretical amounts based on Faraday's law. In the Navy experiments at China Lake using palladium rod cathodes, the experimental amounts of electrolysis gases always agreed within experimental errors with Faraday's Law [15]. However, some co-deposition experiments occasionally gave evidence of recombination [15]. This was attributed to the small palladium particles formed by co-deposition floating loose in the solution and reaching the top of the electrolyte and leading to the direct recombination of a portion of the electrolysis gases.

It has been found that careful measurements of the total volume of H_2O or D_2O consumed also provides a rea-
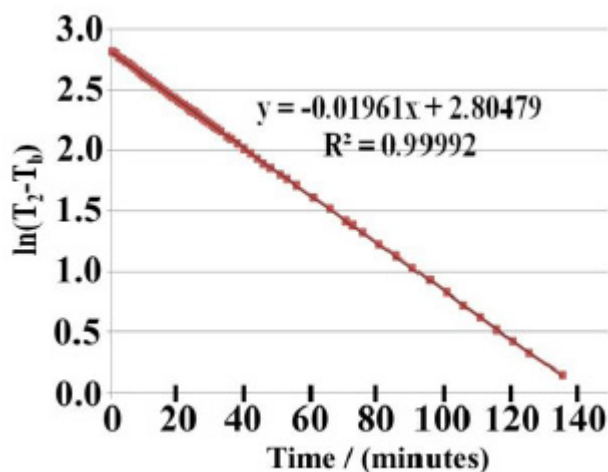
Figure 5. Integrated cooling curve results for the Pd/H_2O experiment.
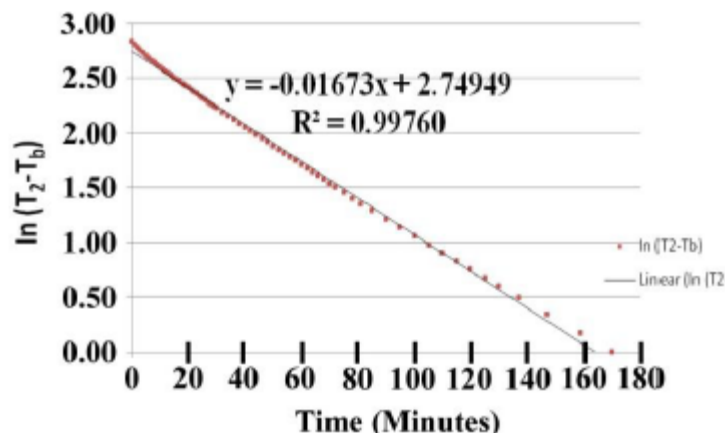
Figure 6. Integrated cooling curve results for the Pd/D_2O experiment.

sonable integrated check over the entire experiment for recombination or other chemical reactions [5,16]. Previous measurements of the volume of H_2O or D_2O consumed compared with the theoretical calculation gave a mean ratio of 1.09 ± 0.11 [5]. There are always small extra amounts of H_2O or D_2O that are evaporated and carried out of the cell by the electrolysis gases. This can vary with the geometry and the temperature at the top of the gas outlet tube, but typical measurements usually give about a 5% loss of H_2O or D_2O due to evaporation [16]. Measured and theoretical consumptions of H_2O or D_2O in recent co-deposition experiments are presented in Table 1. Several values are higher than normal due to foaming (Colorado) or due to problems with measuring the volume of electrolyte consumed.

The mean value for the measured/theoretical ratios from Table 1 is a near normal 1.04 ± 0.07. However, the low values found in the first two experiments with Pd + D_2O or Pd + H_2O for depositions at 300 mA are quite unusual and suggest that some recombination occurred. The last two experiments using less $PdCl_2$ for high current depositions gave near normal ratios within the experimental error range (± 1.0 mL). It was visually observed that the use of smaller concentrations of $PdCl_2$ led to better deposits of palladium and much smaller amounts of palladium particles present in

Table 1. Experimental and theoretical consumptions of H_2O and D_2O

Experiment	Measured (mL)	Theoretical (mL)	Ratio
Ru (H_2O	45.5	40.73	1.12
Ru (D_2O)	43.0	41.83	1.03
Re (H_2O + D_2O)	34.5	31.40	1.10
Ni (H_2O)	26.0	23.62	1.10
Ni (H_2O + D_2O)	23.8	23.06	1.03
Ir (H_2O)	21.5	20.78	1.04
Pd (D_2O), Colorado	11.3	9.94	1.14
Pd (D_2O, High I)	25.7	28.46	0.90
Pd (H_2O, High I)	14.6	15.30	0.95
Pd (D_2O, High I)*	25.0	25.41	0.98
Pd (H_2O, High I)*	28.0	27.28	1.03

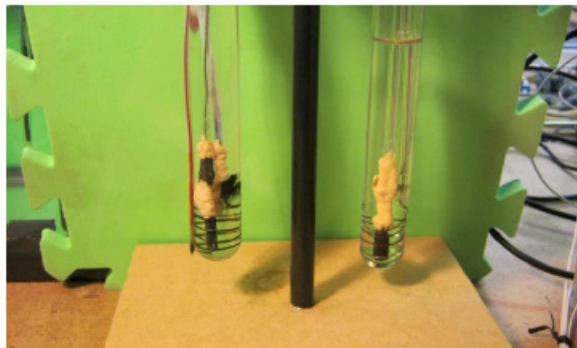*Used small concentrations of $PdCl_2$.

Figure 7. Photo of the two Colorado cells.

the solutions. Except for the high current co-deposition experiments, the measured consumption of H_2O or D_2O does not support any significant recombination in these studies.

3.5. Colorado Pd/D_2O experiment

A replication of the large excess power effect with Pd/D_2O co-deposition [3–5] was attempted by taking this calorimeter to the Coolescence Laboratory in Boulder, Colorado. The experimental protocol of low-current deposition at 6 mA followed by 100 mA and then 20 mA for three days before again increasing the current was performed exactly as previously at NHE in Japan [3,4]. The excess power results up to this point (140 h) were very similar to the experiments in Japan. However, the following increases in the current produced periods of negative excess power effects that were larger than normal experimental errors. This was never previously observed using this calorimeter and was quite confusing as well as thermodynamically impossible. This strange behavior was finally explained when bubbles of foam were observed emerging from the top of the gas outlet tube. It was later determined that this foaming problem produced an additional heat leak of about 4% for this calorimeter (k_C increased from 0.1340 W/K to about 0.1390 W/K). Because of this foaming problem, it was not possible to clearly identify any excess power production. At the end of this experiment, it was found that the epoxy used on the electrodes had not cured properly, swelled considerably in size, and likely was the source of this foaming problem. This Colorado Pd/D_2O experiment is included in Table 1 and shows a somewhat higher than normal amount of D_2O consumed that can be attributed to the foaming effects. Figure 7 shows the photo of the two cells at the end of the experiments in Colorado that used the same epoxy. The Coolescence cell using this same epoxy is on the right. The epoxy swelled by at least a factor of 10 as seen by the light colored material above the electrodes in Fig. 7. This epoxy problem was never observed in any previous experiment, but in an effort to maintain everything exactly the same as a previous excess power study, an older epoxy material was used. Later experiments using the same bottle of D_2O but no epoxy produced no foaming.

The actual calorimetric results for the Colorado Pd/D_2O experiment are given in Fig. 8. The same heat transfer coefficient (k_C) was used as in previous experiments (0.1340 W/K at 50.0 mL) because it was not possible to determine the extent of foaming and its precise effect on k_C.

The calorimetric results looked similar to the previous NHE results [3,4] up to 140 h when the current was increased from 20 to 100 mA. This suggests that there was no significant foaming early in this experiment. The effect at 100 mA produced the first significant negative excess power ever measured with this calorimeter. Although the calorimeter recovered to near zero excess power, it was not possible to evaluate how this foaming effect could mask any real excess
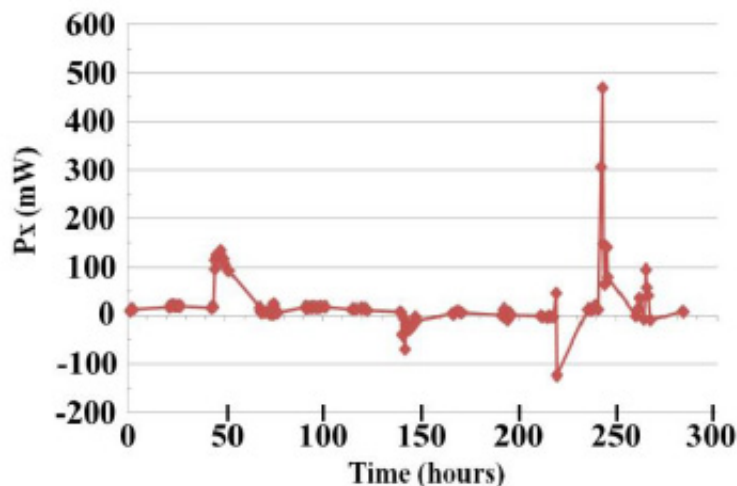
Figure 8.   Calorimetric results for the Colorado Pd/D$_2$O co-deposition experiment.

power. Increasing the current to 400 mA at 217 h produced an even larger negative excess power effect due to the visible foaming carrying heat out of the vent tube at the top of the cell. At times the cell voltages became very large and approached the limit of the electrochemical instrumentation (30 V), thus the cell current had to be scaled back. Due to the unusually high cell voltage, encountered, additional ND$_4$Cl + D$_2$O was injected into the cell at 241 h. This significantly lowered the cell voltage. At least part of the following excess power peak up to 470 mW at I = 400 mA could be due to a new episode of chlorine evolution that was detected and possible NCl$_3$ formation. Normally, there is no need to add additional ND$_4$Cl, and there is no measurable chlorine production at this stage of the experiment. However, large increases in the cell voltages have been observed in other excess power producing experiments for Pd/D$_2$O co-deposition in the deuterated ammonia system [3–5]. In contrast, the measured cell voltages have always been normal for the Pd/H$_2$O studies. Something unusual other than chemistry is likely implicated in these large cell voltage increases in the Pd/D$_2$O system while normal cell voltages were always observed in Pd/H$_2$O systems.

There are several possible explanations for the large cell voltages observed in the Pd/D$_2$O ammonia co-deposition systems. One explanation is the loss of most of the electrolyte by the net reaction

$$ND_4Cl \rightarrow 2\,ND_3 + D_2 + Cl_2, \tag{4}$$

where D$_2$ is formed as normal at the cathode but Cl$_2$ is produced at the anode while the electrolysis gases drive off the ND$_3$. A second more unusual explanation involves the very large electrode area up to 10^6 cm^2 formed by the palladium deposition [17]. It can be shown that an electrode surface this large could absorb all ions present in the cell into the electrode double layer and leave practically no ions in the solution. In the Colorado experiment, the addition of another 0.15 M of ND$_4$Cl created a sudden decrease in the cell voltage from 22.2 to 2.84 V for a cell current of 20 mA. This effect could be rationalized by either of these two explanations. It is not known why this large loss of electrolyte has only been observed in the Pd/D$_2$O system. The Pd/D$_2$O and Pd/H$_2$O system both show similar amounts of chlorine production and display similar chemistries. Is it possible that hot spots or some type of nuclear radiation in the Pd/D$_2$O system promotes decomposition of the ammonia electrolytes?

4. Conclusions

Large amounts of excess power and excess enthalpy have only been observed in the deuterated Pd/D$_2$O co-deposition system. There was no excess power observed for the co-deposition of ruthenium, rhenium, or nickel in any H$_2$O or D$_2$O experiment. High current deposition of Pd in D$_2$O has produced large excess power and excess enthalpy effects. In fact, the total excess enthalpy of 170 kJ exceeds that of any previous co-deposition experiment in the deuterated ammonia system. Similar high current deposition studies of palladium in H$_2$O, however, have produced smaller excess power and excess enthalpy effects. Cooling curves of both the Pd/D$_2$O and Pd/H$_2$O systems indicate that the smaller excess power effects for Pd/H$_2$O are likely due to recombination or other chemical effects. Numerous problems were encountered in the attempted co-deposition of iridium. This is the only study where complete deposition of the metal was unattainable.

Acknowledgment

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