J. Condensed Matter Nucl. Sci. 33 (2020) 74–80

Research Article

The Thermoneutral Potential in Electrochemical Calorimetry for the Pd/D_2O System

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Abstract

The thermoneutral potential (E_{H}) for any electrochemical reaction corresponds to the enthalpy change (ΔH) for that reaction. The D_2O electrolysis reaction produces an enthalpy change of $\Delta H = 294.600$ J/mol of D_2O which yields a thermoneutral potential of$E_{\mathrm{H}} = -1.5267$ V ($-\Delta H/2F$). This thermoneutral potential will apply throughout a Pd/D_2O calorimetric experiment except for the first day or two where the loading of deuterium into the palladium cathode occurs. The changes in ΔH and E_{H} during loading and their effect on measurements of excess power will be presented. It is concluded that the changes in E_{H} during deuterium loading do not explain the very early excess power measurements for Pd–B cathodes. Furthermore, boron may be a critical component for the excess power effect in the palladium – D_2O system.
 ISSN 2227-3123

Keywords: Boron, Deuterium, Electrochemistry, Enthalpy, Excess power, Loading, Palladium, Palladium–Boron alloys, Thermoneutral potential

1. Introduction

The loading of deuterium into palladium is an exothermic reaction that occurs readily up to a value of $x = 0.6$ (mol D/mol Pd) as represented by the reaction

$$\mathrm{Pd} + 0.3\mathrm{D_2} \rightarrow \mathrm{PdD_{0.6}}(\Delta H = -35.10\ \mathrm{kJ/mol\ D_2}), \tag{1}$$

which forms the beta phase of palladium deuteride. This value of $\Delta H = -35.10$ kJ/mol D_2 for $PdD_{0.6}$ was reported by Balej and Divisek in 1990 [1] and confirmed by China Lake experiments [2]. Similar values of $\Delta H = -34.6$ kJ/mol D_2 were reported by Flanagan [3] and $\Delta H = -34.2$ kJ/mol D_2 by Sakamoto [4]. The value of $\Delta H = -35.10$ kJ/mol D_2 will be used in this study.

It is confusing that this ΔH value is often expressed in various ways such as kJ/mol D and kJ/mol Pd. From Eq. (1), $\Delta H = -35.10$ kJ/mol $D_2 = -17.55$ kJ/mol $D = -10.53$ kJ/mol Pd at $x = 0.6$. This follows from 1 mol $D_2 = 2$ mol D and 1 mol Pd $= 0.3$ mol D_2 for $PdD_{0.6}$ formation. More generally, 1 mol Pd $= 0.5x$ mol D_2 for PdD_X

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 ISSN 2227-3123

formation. The use of either kJ/mol D_2 or kJ/mol D is convenient because ΔH is then constant over a range of D/Pd from 0 to 0.6 [3,4]. At higher loadings, the magnitude of these exothermic enthalpies decline markedly with increasing deuterium content [3,4].

Sakamoto [4] reports the equation for bulk Pd

$$\Delta H(\text{kJ/mol D}) = 49.69\ [\text{D/Pd}] - 50.75 \tag{2}$$

for D contents in the range of $0.7 < x < 0.85$ where x = mol D/mol Pd. Mathematically, this is a straight-line equation, $y = ax - b$, where y = kJ/mol D, $a = 49.69$, $b = 50.75$ and x = mol D/mol Pd. Assuming this equation applies over a wide range of *x*-values, then $y = 0$ at $x = b/a = 1.021$ and any higher loading would be endothermic. Sakamoto reports a similar equation for studies of palladium in the form of a black powder where $a = 41.89$ and $b = 44.99$ [5]. Therefore, $y = 0$ at $x = 1.074$. Fleischmann [6] postulated a new gamma-phase for Pd–D at high loading where further loading would be endothermic (ΔH positive). Therefore, higher temperatures would favor higher loadings leading to a positive feedback effect where the anomalous excess power would increase markedly with the cell temperature. For the calculation of E_{H} at the beginning of a Pd/D_2O calorimetric experiment, the value for ΔH is needed for small *x*-values.

2. Determination of ΔH at Different Loadings

Publications by Balej, Flanagan and Sakamoto [1–3] all report that ΔH in mol/D or mol/D_2 remains constant from $x = 0$ to about $x = 0.6$. This seems logical because each increment of D involves the same reaction with the palladium. One can use either -35.10 kJ/mol D_2 or -17.55 kJ/mol D over this x range. However, the value for kJ/mol Pd will depend on the extent of loading. For deuterium loadings greater than about 0.6 mol D/mol Pd, then Sakamoto's equation (2) can be used. The results for ΔH at various values of *x* are given in Table 1. The results for kJ/mol D_2 are displayed in graphical form in Fig. 1.

Note that Sakamoto's equation (2) is in the form of a straight line as shown in Fig. 1, where the *y*-intercept is at $x = 1.021$ and further loading would be an endothermic process. This straight line equation gives $y = -35.10$ kJ/mol D_2 at $x = 0.6681$. Further loading then becomes more difficult and less exothermic in a linear fashion. Figure 1 appears to be an accurate display of how ΔH (kJ/mol D_2) changes during deuterium loading and gives a reasonable merging of the Sakamoto's results for high loadings with results for lower *x*-values.

Table 1. The values for ΔH at various deuterium loadings.

x (mol D/mol Pd)	kJ/mol D (*y*)	kJ/mol D_2 (2*y*)	kJ/mol Pd (*xy*)
0.01	–17.55	–35.10	–0.1755
0.10	–17.55	–35.10	–1.7550
0.20	–17.55	–35.10	–3.5100
0.30	–17.55	–35.10	–5.2650
0.40	–17.55	–35.10	–7.0200
0.50	–17.55	–35.10	–8.7750
0.60	–17.55	–35.10	–10.5300
Sakomoto, Eq. (2)			
0.60	–20.94	–41.88	–12.56
0.70	–15.97	–31.94	–11.18
0.80	–11.00	–22.00	–8.80
0.90	–6.03	–12.06	–5.43
1.00	–1.06	– 2.12	–1.06
1.10	+3.91	+7.82	+4.30

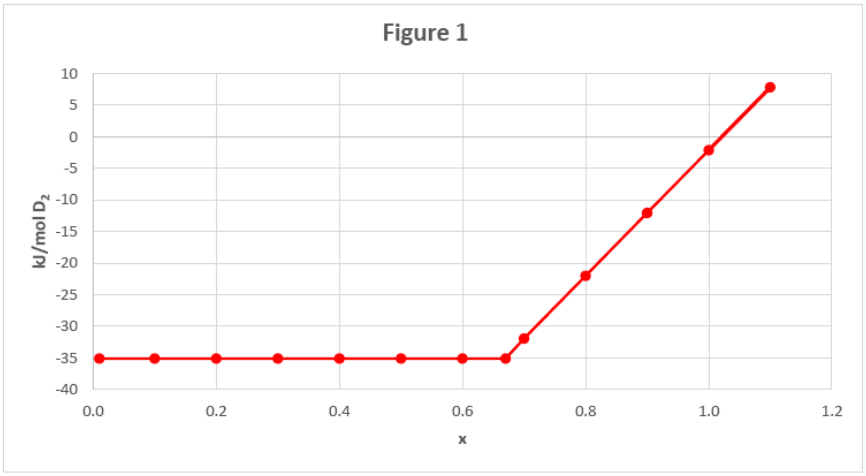

Figure 1. The enthalpy change (kJ/mol D_2) versus x (mol D/mol Pd) for the formation of PdD_X.

Table 1 results for kJ/mol Pd are shown in Fig. 2 for various x-values. The magnitude of ΔH per mole of palladium increases linearly with the loading between $x = 0$ and $x = 0.6681$ and then decreases at higher loadings.

At lower x-values, ΔH (kJ/mol Pd) $= x(-17.55$ kJ/mol D) and at high loadings, Sakamoto's equation yields ΔH (kJ/mol Pd) $= x$ (kJ/mol D) $= ax^2 - bx$. Mathematically, this is the equation for a parabola ($z = xy = ax^2 - bx$) where $z = 0$ at $x = 0$ and at $x = b/a = 1.021$. The largest magnitude for ΔH is given by $dz/dx = 2ax - b = 0$ where $x = b/2a = 0.5107$ and $\Delta H = -12.96$ kJ/mol Pd. Based on Table 1 and Figs. 1 and 2, the thermoneutral potential can be calculated at any value of x for the Pd – D_2O system. Figure 2 shows that kJ/mol Pd $= 0$ at $x = 0$

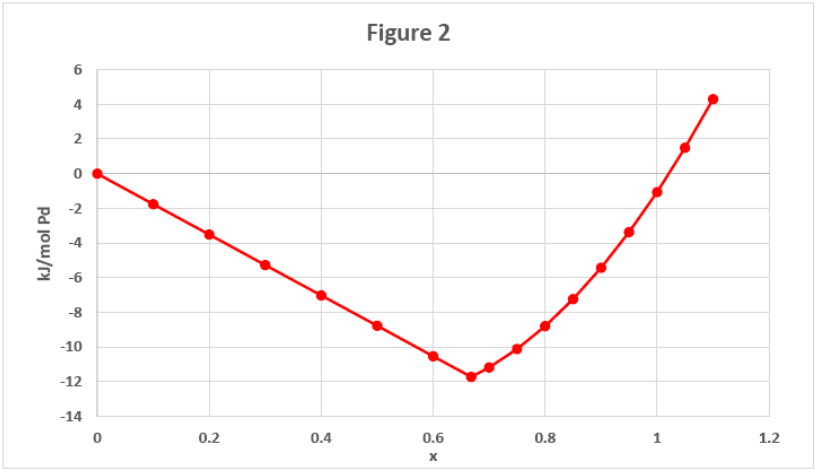

Figure 2. The enthalpy change for PdD_X formation in units of kJ/mol Pd for various x-values.

because there would be no reaction with deuterium. However, this makes both kJ/mol D_2 and kJ/mol D indeterminate (0/0) at $x = 0$. This simply means that there is zero enthalpy production for palladium when no deuterium is available.

3. The Thermoneutral Potential for Pd/D_2O Electrolysis

For the initial electrolysis of D_2O on Day 1 assuming that all of the D_2 generated is used for the palladium loading, the net reaction can be expressed as

$$\mathrm{Pd} + 0.3\mathrm{D_2O} \rightarrow \mathrm{PdD_{0.6}} + 0.15\mathrm{O_2}. \tag{3}$$

The enthalpy change is then ΔH (kJ/mol Pd) $= \Delta H_\mathrm{f}$ ($\mathrm{PdD_{0.6}}$) $- 0.3\Delta H_\mathrm{f}$ (D_2O). Therefore, ΔH (kJ/mol Pd) $= -10.530 - 0.3(-294.600) = +77.850$ kJ and $E_\mathrm{H} = -\Delta H/0.6$ F $= -1.3448$ V. A similar thermoneutral potential of $E_\mathrm{H} = -1.336$ V during the initial reaction period has been previously reported [7]. If the same calculation is carried out for the very early electrolysis period where $x = 0.01$, then the reaction is expressed by

$$\mathrm{Pd} + 0.005\mathrm{D_2O} \rightarrow \mathrm{PdD0.01} + 0.0025\mathrm{O_2}. \tag{4}$$

This gives $\Delta H = -0.1755 - 0.005(-294.600) = 1.2975$ kJ/mol Pd and $E_\mathrm{H} = -\Delta H/0.01$ F $= -1.3448$ V (the same E_H value). The thermoneutral potential is defined as the cell potential where no heat is given off and no heat is absorbed from the surroundings.

Assuming 100% of D_2 produced by electrolysis is used for palladium loading, then E_H remains equal to -1.3448 V for any *x*-value up to the formation of $\mathrm{PdD_{0.6}}$. This is because $\Delta H = -35.10$ kJ/mol D_2 remains constant for the initial formation of PdD_X (see Table 1). If $E_\mathrm{H} = -1.5267$ V is used for this initial loading, then the maximum excess power due to the deuterium loading is given by Eq. (5).

$$P_X = (1.5267 - 1.3448)I. \tag{5}$$

This equation is correct as long as 100% of the D_2 is used for loading rather than exiting the cell. This is more likely to be correct when small cell currents are used initially.

For the Pd–B studies reported previously [8,9] using a current of $I = 0.1500$ A, then the maximum early excess power due to the loading would be $P_X = 0.0273$ W or 27.3 mW from Eq. (5). This is the same maximum excess power as calculated by other methods [9]. Therefore, the early excess power exceeding 27.3 mW reported for the Pd–0.5B experiment [9] cannot be explained by any change in the thermoneutral potential. The previous report of $E_\mathrm{H} = 0.9204$ V during the deuterium loading [9] was a calculation error due to the use of -35.10 kJ/mol D_2 in reaction (3) rather than the correct value of -10.53 kJ/mol Pd. These errors are frequent in the literature where incorrect units are used in ΔH calculations for the Pd–D system. For the 100% use of D_2 for loading, $E_\mathrm{H} = -1.3448$ V during this loading process. The magnitude for E_H cannot be less than this value during D_2O electrolysis. The use of Eq. (5) provides a simple method of calculating the maximum excess power expected due to the exothermic reaction of deuterium with palladium to form PdD_X at any cell current used. The Pd–B experiments produce excess power effects that significantly exceeded the maximum values expected for the deuterium loading process [8,9]. The explanation for this very early excess power for Pd–B cathodes remains unknown. Most chemical reactions of boron with deuterium would be endothermic and not a source for excess heat.

4. Applications for Electrochemical Calorimetry

After the first day or two of electrolysis in D_2O using a palladium cathode, the palladium is essentially loaded with deuterium to give PdD_X where $x = 0.6$ or higher. The electrolysis reaction then becomes

$$\mathrm{D_2O} \rightarrow \mathrm{D_2} + \frac{1}{2}\mathrm{O_2}, \tag{6}$$

where $\Delta H = 294,600$ J/mol and $E_{\rm H} = -\Delta H/2F = -1.5267$ V. There is no change expected in $E_{\rm H}$ for the rest of an experiment. Small increases or decreases in the loading may occur over time, but these are insignificant compared to Reaction (6). The thermoneutral potential ($E_{\rm H}$) provides a simple method for determining the rate of chemical enthalpy ($E_{\rm H}I$) carried outside an open calorimetric cell by the D_2 and O_2 electrolysis gases [2,7,8].

The best way to analyze the initial electrolysis period is to follow Fleischmann's method [8] and simply use $E_{\rm H} = -1.5267$ V. The excess power (P_X) due to loading cannot be larger than that expressed by Eq. (5) which assumes that 100% of the D_2 generated reacts with palladium rather than exiting the cell. Accurate measurements of excess power during the initial loading would require measurements over time of the fraction of D_2 that reacts with palladium. For the H_2O electrolysis system, Storms [10] reports that this fraction is initially near 100% but declines steadily with time to near zero after 6 or 7 h of electrolysis at $I = 0.1$ A.

The Fleischmann–Pons Dewar glass cell used in Japan [8] permitted the direct observation of D_2 gas evolution from the Pd–0.5B cathode using $I = 0.150$ A. Initially, there was only a slight gas evolution from the cathode (about 5% of expected). Even after 98 min, the gas evolution at the cathode was still very small indicating that most of D_2 generated was being used for loading. It was not until 220 min that vigorous gassing was observed at the Pd–0.5B cathode. Assuming that 100% of the cell current (0.150 A) was used for deuterium loading, it would require 254 min to load this Pd–0.5B cathode ($V = 0.350$ cm^3) to give $x = 0.6$ mol D/mol Pd.

Interest in this initial electrolysis period stems from the experiment in Japan [8] and another in the US [9] using this same Pd–0.5B alloy cathode (0.5 wt.% B) prepared by Dr. Imam at the Naval Research Laboratory (NRL). Both experiments gave significant excess power effects during the first day of electrolysis using D_2O + LiOD electrolytes [8,9]. The early excess power results for the Ridgecrest, California experiments [9] are presented in Fig. 3.

Note that the experimental excess power immediately exceeds the expected $P_X = 27.3$ mW (dash lines) due to loading and reaches a peak of 118 mW at 8 min. The excess power remains significantly higher than expected based on Eq. (5) for several hours. A discussion of the calorimetry used in this experiment has been reported elsewhere [11]. The excess power later decreased to zero for Days 2 and 3 [11] before again increasing up to 36 mW at Day 10. Much larger excess power effects near 10 W were observed during a boil-off of the D_2O in the Japan experiment [8].

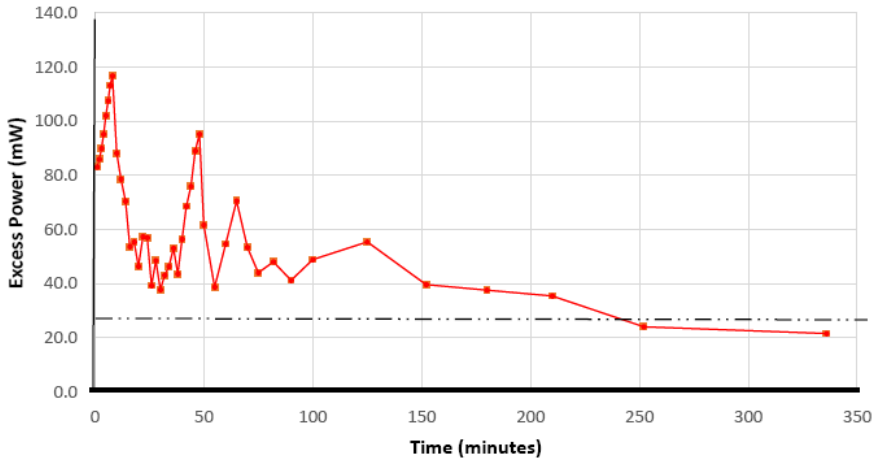

Figure 3. Early excess power for a Pd–0.5 B rod (0.47 × 2.01 cm). The peak excess power was 118 mW at 8 min. The dashed line shows the maximum excess power expected for 100% deuterium loading at the cell current of $I = 0.150$ A.

The very early excess power is quite unusual for the Pd/D_2O electrolysis system because most calorimetric experiments using palladium cathodes require weeks or even month of electrolysis before any significant excess power effects are observed [2]. The addition of small amounts of boron to the palladium must have some major unknown effect for the excess power. A previous explanation involving the thermoneutral potential does not appear to be correct [9]. The initial formation of the α-phase for PdD_X where x is less than 0.017 also fails as an explanation of the early excess power effect for this Pd–0.5 B electrode.

Is boron a critical component for the palladium in these experiments which takes a long time to be transferred from the Pyrex glass cell in an LiOD electrolyte to the palladium in most calorimetric Pd/D_2O experiments? Perhaps, most Pd/D_2O experiments fail to produce any excess power effects due to the lack of sufficient electrolysis time for the boron transfer from the glass cell or even due to the lack of a boron source in a cell not made of glass. The use of an LiOD electrolyte and its attack on the glass over time likely facilitates this boron transfer. Some results have suggested a nuclear fusion process involving boron as the source for the excess heat [12]. Seven of eight Pd–B cathodes previously investigated produced excess enthalpy [2,9]. It should be noted that a Pd–B cathode that produced excess power at the China Lake Navy laboratory was one of 18 experiments that produced both excess power and helium-4 [2,13,14]. It is an experimental fact, however, that most studies of the Pd–D_2O system do not produce any excess power effects [2,15]. This suggests that certain impurities such as boron may be essential in palladium cathodes for the electrochemical excess power effects using D_2O + LiOD electrolytes.

5. Summary

The value of the enthalpy change for D_2O electrolysis to form PdD_X remains constant at $\Delta H = -35.10$ kJ/mol D_2 (or -17.55 kJ/mol D) during the deuterium loading up to about $x = 0.6$. The value for ΔH then sharply declines in magnitude for $x > 0.7$ and even becomes endothermic near $x = 1.0$. The thermoneutral potential (E_{H}) for D_2O electrolysis is normally $E_{\mathrm{H}} = -1.5267$ V but it may decrease in magnitude somewhat during the initial deuterium loading to $E_{\mathrm{H}} = -1.3448$ V. The maximum excess power (P_X) due to the exothermic reaction of deuterium with palladium to form PdD_X is given by $P_X = (1.5267 - 1.3448)I$, where I is the cell current in amps. This effect does not explain the early excess power exceeding 100 mW using Pd–B cathodes. It is postulated that boron may be a critical component for excess power in the Pd–D_2O system. The role of boron in producing the excess power effect remains unknown.

Acknowledgements

Support for this work was received from an anonymous fund at the Denver Foundation through the Dixie Foundation at Dixie State University. An Adjunct Faculty position at the University of LaVerne in California and a Visiting Professor position at Dixie State University in Utah are also acknowledged. The author also thanks Jed Rothwell for his help with the references.

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