Palladium Hydride as a Reference Electrode in Aprotic Solutions

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The results of a variety of electrochemical tests indicate palladium hydride (∇dH) functions as a thermodynamic reference electrode in three aprotic solutions containing H2(g) and solvents of dichloromethane, dimethylsulfoxide, and acetonitrile. For enhanced electrical conductivity all solutions contained 0.2 M of an ionic liquid, 1-methyl-3-butyldiazolium tetrafluoroborate. As is required of all thermodynamic reference electrodes (i) the potential of β-∇dH was stable, (ii) its small amplitude anodic and cathodic polarization were reversible, and (iii) it exhibited Nernstian behavior assuming that the hydrogen cation activity is controlled by the concentration of adsorbed hydrogen, which is set by the partial pressure of H2(g).

The present study investigates the ability of ∇dH to serve as a reference electrode in several aprotic, high resistivity solutions. ∇dH has been the subject of a number of earlier investigations that have demonstrated that it serves as a hydrogen reference electrode in aqueous solutions, and also exhibits Nernstian behavior with respect to changes in the partial pressure of H2 and of pH. In fact, palladium has such a high solubility for hydrogen, that ∇dH serves as a hydrogen reference electrode even in solutions that are free of H2. The good performance of ∇dH in H2-free aqueous solutions is understandable in that H+ are made available by the aqueous solution and H is provided by the H dissolved in the ∇dH. The combination of H+ from the aqueous solution and H from ∇dH make it possible for H+ to come into equilibrium on the surface of ∇dH and thereby establish the reversible hydrogen electrode.

In order for ∇dH to serve as a hydrogen electrode in aprotic solutions it is necessary that ∇dH provide hydrogen cations just as ∇dH provided H in aqueous solutions that were free of H2(g). Tests were conducted that demonstrate that ∇dH does provide hydrogen cations when immersed in aprotic solutions and that ∇dH functions as a thermodynamic hydrogen reference electrode. A ∇dH reference electrode opens up the possibility of conducting electrochemical tests in crude oils as well as other aprotic, high electrical resistivity solutions.

Experimental

0.003 in. (76 μm) thick 99.99% palladium foil and 0.003 in. (76 μm) diameter 99.999% palladium wire were obtained from SPI Metals, USA. The foil was cut into a 2.54 × 2.54 cm square (12.9 cm2 surface area) and mechanically polished by using 6 μm, 3 μm, 1 μm, and 0.3 μm diamond suspensions sequentially. Mechanical polishing was repeated periodically during experimentation to refresh the electrode’s surface. A 5 cm length of the palladium wire was tack welded to the foil in order to electrically connect the foil to electronic instrumentation. Prior to each set of experiments, the electrode was cleaned by dipping it in concentrated sulfuric acid, followed by rinsing it in doubly deionized water, then acetone, and finally hexane. Square platinum counter electrodes measuring 2.54 × 2.54 cm were prepared from 0.002” thick platinum foil and 0.003 in. (76 μm) diameter 99.999% platinum wire, which was tack welded to the foil. The platinum counter electrodes were prepared following the same procedure as used for the large palladium electrode.

Palladium hydride (∇dH) electrodes were prepared by immersing Pt electrodes in solutions saturated with forming gas (4% H2 – bal. N2). Foils of ∇dH served as combination counter electrodes and reference electrodes (CE/RE) in electrochemical tests in which the working electrode (WE) was an ultramicroelectrode (UME) of either platinum (10 μm diameter disk) or PdH (76 μm diameter disk). The PdH isotherms measured as a function of temperature indicate that the PdH electrodes, which were formed by immersion of Pt in solutions saturated with forming gas, consist of an outer layer of β-∇dH. As the absorption of hydrogen is a kinetically limited process, thickness
of the β-PdH layer depends on the time of immersion in the solution. In most cases the electrodes were prepared by immersion for 15 minutes. Assuming that hydride formation is controlled by the diffusion of hydrogen in β-PdH, the thickness of the β-PdH layer is approximately 60 µm.\(^\text{10}\)

Selected electrochemical tests were conducted with PdH CE/RE created from palladized palladium foil. The results were similar to tests with palladium foil. Deposition of palladium black was accomplished in an aqueous solution of dilute palladium chloride in 0.1 M hydrochloric acid and a cathodic current density of 50 mA/dm\(^2\).\(^\text{12}\)

A 10 µm diameter platinum UME was obtained from C-H Instruments. Palladium ultramicroelectrodes were produced by first sealing 0.003 in (76 µm) diameter palladium wire into a soft glass capillary. The end of the tube in which the Pd wire was sealed was then mechanically ground and then polished using 6 µm, 3 µm, 1 µm, and 0.3 µm diamond suspensions. The polished, circular, 0.003 in (76 µm) diameter end-face of the wire served as a palladium UME. Prior to each test, the UME was polished using a 0.3 micron diamond suspension.

**Solutions.**—Anhydrous dichloromethane (DCM), ferrocene (Fc), decamethylferrocene (dmFc), anthraquinone (AQ), and 1-methyl-3-butyl imidazolium tetrafluoroborate [bmim][TFB], anhydrous acetone, and n-hexane were obtained from Sigma-Aldrich and used without further purification. All solvents were stored over 4A molecular sieves in a glove box filled with forming gas. All experiments, unless noted, were performed in a VAC glove box under an atmosphere of forming gas. The glove box atmosphere was periodically refreshed to ensure a dry, oxygen free environment. Test solutions were saturated by vigorous bubbling for 30 minutes with forming gas inside the glove box prior to each experiment. Experiments in dichloromethane were conducted using 0.2 M [bmim][TFB] as a supporting electrolyte, and the solution resistivity was approximately 7.8 × 10\(^{-3}\)Ω·cm.\(^\text{13}\) The electrochemical window for stability of [bmim][TFB] is approximately 4 V wide, and was stable at the potentials used in the present investigation. For experiments on AQ with water added, a very small amount of water was introduced to the dried dichloromethane outside of the glove box. The addition of water did not introduce any anomalous peaks in the voltammograms.

**Electrochemical tests.**—Briefly stated, the objective of the electrochemical tests was to determine the suitability of PdH as a reference electrode in aprotic solutions. Five tests were conducted. (1) Estimates of the electrode potential of PdH in DCM containing 0.2 M [bmim][TFB] were obtained by measuring the half-wave potentials of AQ, Fc and dmFc in a two-electrode cell consisting of a platinum UME and a PdH CE/RE. (2) The stability of the PdH electrode was evaluated by measuring its potential as a function of time vs. a calomel electrode in 0.2 M TBAP in acetonitrile (ACN). The reversibility of the PdH electrode in DCM with 0.2 M [bmim][TFB] was investigated by (3) small amplitude (±0.010 V) cyclic polarization experiments and (4) large amplitude (±0.5 V) square-wave polarization tests with step widths of 5s, 50s, and 500s. Both types of reversibility experiments (i.e., (3) and (4)) were carried out in a two-electrode cell in which an UME of PdH was the WE and a large PdH foil served as a CE/RE. Nernstian behavior of PdH immersed in aprotic solutions was evaluated by (5) measuring changes in the potential of PdH due to changes in partial pressure of hydrogen gas (two values of partial pressure were investigated: ≈0.04 atm and ≈1.0 atm of H\(_2\). Details are provided at the end of the present subsection). All electrochemical experiments were carried out with a Gamry PCT4-750 potentiostat.

All experiments performed in DCM with 0.2 M [bmim][TFB] were conducted with a 2 electrode cell consisting of a working electrode (WE) with very small surface area (UME) and a large counter/reference electrode (CE/RE). That is, the second electrode served as a combination counter and reference electrode (CE/RE). Because the ratio of the areas of the UME and the counter/reference electrode was so small (i.e., 7 × 10\(^{-6}\)) the current density flowing through the counter/reference electrode is insignificant, and does not polarize the reference electrode’s potential.

The stability of the potential of PdH (i.e., electrochemical test (2) listed above) was tested by measurements of the potential of a PdH UME vs. the potential of a calomel reference electrode as a function of time. The test was conducted in 0.2 M TBAP in acetonitrile (ACN), which was selected because the potential of the modified commercial calomel electrode was stable and no liquid junction potentials were introduced. The calomel electrode was formed by replacing the aqueous KCl electrolyte of a conventional SCE with lithium chloride saturated acetonitrile. In this paper we refer to the calomel electrode immersed in acetonitrile that is saturated with LiCl as a modified saturated calomel electrode (mSCE). It should be noted that while the SCE is not normally used in acetonitrile containing solutions due to disproportionation, its potential with respect to an aqueous silver chloride reference electrode was determined to be the same before and after experimentation.

Experiments to determine the Nernstian behavior of PdH in different aprotic solvents (i.e., electrochemical test (5) listed above) were conducted by measuring the change in open circuit potential of the PdH vs. a known reference associated with changing of the partial pressure of hydrogen. A custom made two-electrode cell was used, consisting of a large PdH working electrode and an aqueous SCE. The solvents chosen were acetonitrile, dimethylsulfoxide, dimethylformamide, and dichloromethane; each solvent was of reagent grade (Sigma-Aldrich) and used without further purification. The supporting electrolyte was 0.2 M [bmim][TFB] in each of the solvents. The solutions were bubbled vigorously with forming gas until a stable potential was reached, and then subsequently bubbled with 1 atm of H\(_2\) until a stable potential was reached. The half-wave potential shift of dmFc vs. PdH was also measured in DCM after saturating with forming gas and H\(_2\) to ensure the potential of the SCE remained constant throughout the experiment.

Safety regulations imposed on the Hearst Mining Building in which our laboratory is located prohibit canisters of pressurized gas with more than 4% hydrogen. A partial pressure of H\(_2\) of 1 atm was established in solutions of 0.2 M [bmim][TFB] in various solvents by on demand hydrogen generation using the ferrosilicon process.\(^\text{14}\) A 316 stainless steel vessel with emergency pressure relief was used as a reaction vessel. Silicon powder and sodium hydroxide were obtained from Fisher Scientific and were used as received. Approximately 200 mL of concentrated (20 wt%) aqueous sodium hydroxide solution was combined with a small amount of silicon powder (3 g) in the reactor at room temperature, and the vessel was purged with nitrogen and subsequently sealed. A hot plate was used to bring the reagents to 50°C. After reaching the temperature the hot plate was turned off, and the silicon reacted with the sodium hydroxide to produce hydrogen gas and sodium silicate. Large double-layered thick latex balloons were used to store the generated hydrogen, so that a constant hydrogen flow could be supplied to the dichloromethane solution. A liquid nitrogen cold trap was used to remove all humidity from the hydrogen before entering the electrochemical cell. Hydrogen gas flow was controlled with a flowmeter (Cole Parmer) to ensure a constant flow rate for forming gas as well as hydrogen.

Finally, a small number of low amplitude (±0.010 V) cyclic polarization tests of PdH were conducted in aqueous 0.1 M HCl. The polarization tests were performed in a custom glass electrochemical cell in a three-electrode configuration, using an Accumet SCE reference electrode and a large Pt foil counter electrode.

**Results and Discussion**

For a red-ox system to serve as a thermodynamic reference electrode, it must meet three criteria. Namely, the electrode must be stable and reversible, and the red-ox system must exhibit Nernstian behavior. In order to ascertain if the palladium hydride electrode functions as a thermodynamic reference electrode in an aprotic solution experiments were performed to determine if each of the three criteria were satisfied. In addition, an approximate assessment was first conducted by measuring the half-wave potentials of three organic compounds with respect to the palladium hydride electrode (PdH).
Unless stated otherwise, all experiments employed PdH electrodes that were created by immersing palladium in aprotic solutions that were saturated with forming gas (4% H2 – bal. N2). A number of studies, e.g., Wicke et al., have found that palladium absorbs hydrogen and β-PdH forms when Pd is immersed in aqueous solutions with hydrogen partial pressures greater than approximately 0.01 atm. Consequently, our PdH electrodes consist of β-PdH.

**Initial investigation of the β-PdH electrode in aprotic solutions.**—The first experiments performed were aimed at obtaining a quick, preliminary assessment of the ability of the β-PdH electrode to serve as a reference electrode in aprotic solutions.

There are no reference electrodes that function in aprotic solutions of low dielectric constant against which the potential of the β-PdH could be measured. Consequently, the β-PdH electrode was initially evaluated by using it to measure the half-wave potentials of three organic species with known red-ox potentials. In these experiments the tests were conducted with a Pt UME in a cell that contains a β-PdH CE/RE (see Appendix A) and a solution of 0.2 [bmim][TFB] in DCM with 0.1 mM either anthraquinone (AQ), ferrocene (Fc), and decamethylferrocene (dmFc) and saturated with forming gas.

A cyclic voltammogram (CV) that is representative of a series of CVs containing all three species is presented in Figure 1a. The IR-corrected version of the voltammogram presented in Figure 1a is shown in Figure 1b. A total of 11 CVs were measured using the same Pt UME and four different PdH electrodes. Each test was performed with fresh solution. The results of the 11 tests are summarized in Table I. The standard deviations of the 11 values of the half-wave potentials of AQ and dmFc were 9 mV and 5 mV, respectively. The half-wave potentials measured for Fc exhibited more scatter and the standard deviation of the 11 measurements was 23 mV.

Table II compares the difference in half-wave potentials of AQ and dmFc, AQ and Fc, and dmFc and Fc measured in the present study (column 2) with the differences reported in the studies by Aranzaes et al. and Ahmed and Khan (column 3). The studies by Aranzaes et al. and by Ahmed and Khan used DCM as a solvent but employed different supporting electrolytes than used in the current study. Both Aranzaes et al. and Ahmed and Khan employed the aqueous saturated calomel electrode (SCE) as their reference electrode. In the first two rows of Table II, the discrepancies between values obtained by the current study and those presented in Aranzaes et al. and in Ahmed and Khan are relatively large (approximately 0.050 V), which is attributed to our use of thoroughly dried DCM and to the use of DCM that was exposed to moisture by Ahmed and Khan. When comparing results obtained in this study using DCM that contained absorbed moisture (rows 3 and 4 of Table II) to those in the literature, the discrepancies (column 4) are small: approximately 0.006 V.

The small values of the discrepancies listed in column 4 of Table II suggest that β-PdH is as effective a reference electrode in an aprotic solution as is aqueous SCE, which was used by Aranzaes et al. and by Ahmed and Khan. In fact β-PdH might be superior to

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**Table I. Summary of half wave potentials for 0.1 mM of AQ, dmFc, and Fc in 0.2 M [bmim][TFB] DCM. 10 μm platinum UME working electrode, large palladium hydride CE/RE, scan rate 100 mV/s.**

| Electrode | Trial | E1/2 AQ (V) | E1/2 dmFc (V) | E1/2 Fc (V) |
|-----------|-------|-------------|---------------|-------------|
| 1         | 1     | -0.730      | 0.102         | 0.665       |
| 1         | 2     | -0.715      | 0.099         | 0.665       |
| 1         | 3     | -0.725      | 0.100         | 0.625       |
| 2         | 1     | -0.710      | 0.105         | 0.664       |
| 2         | 2     | -0.702      | 0.107         | 0.669       |
| 2         | 3     | -0.705      | 0.113         | 0.677       |
| 3         | 1     | -0.717      | 0.097         | 0.625       |
| 3         | 2     | -0.714      | 0.100         | 0.623       |
| 4         | 1     | -0.717      | 0.097         | 0.648       |
| 4         | 2     | -0.722      | 0.095         | 0.623       |
| 4         | 3     | -0.710      | 0.095         | 0.623       |
| Average   |       | -0.715      | 0.100         | 0.646       |
| Standard Deviation | | 0.009 | 0.005 | 0.023 |

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**Table II. Comparison of redox species potential differences.**

| Redox Systems | ΔE1/2 This Study (V) | ΔE1/2 Literature (V) | Deviation (V) |
|---------------|---------------------|---------------------|---------------|
| AQ - dmFc     | 0.815               | 0.765               | 0.05          |
| AQ - Fc       | 1.361               | 1.315               | 0.046         |
| AQ** - dmFc   | 0.771               | 0.765               | 0.006         |
| AQ** - Fc     | 1.313               | 1.315               | 0.002         |
| dmFc-Fc       | 0.546               | 0.541               | 0.006         |

*Under wet conditions.*
aqueous SCE because the potential measured with respect to β-PdH does not include a LJP. However, the results in Table II are not sufficient to establish β-PdH as a thermodynamic reference electrode.

Rigorous evaluation of the β-PdH electrode as a thermodynamic reference electrode in aprotic solutions.— As previously mentioned, a thermodynamic reference electrode is stable, reversible, and Nernstian. Each of these three characteristics is now evaluated for β-PdH in aprotic solutions.

Stability.— The stability of the β-PdH electrode was investigated by measurements of its potential as a function of time in a solution containing the polar aprotic solvent acetonitrile. Figure 2 presents the variation of the potential of β-PdH measured with respect to a modified saturated calomel electrode (mSCE-described in the Experimental Procedure) in 0.2 M TBAP in ACN saturated with forming gas. The results indicate that the potential of PdH is constant at +0.064 V vs. mSCE within ±0.002 V over a period of 100 minutes. Stability measurements were made in ACN rather than DCM in order to avoid incorporation of the unknown value of the LJP developed between ACN saturated with KCl, which is the solution of the mSCE reference electrode, and DCM with 0.2 M TBAP.

Reversibility.— Reversibility of the β-PdH electrode was investigated by small amplitude anodic and cathodic polarization measurements. The small polarization (0 to ±10 mV) current (I) – voltage (V) behavior of a PdH UME in a two-electrode cell with a β-PdH CE/RE is presented in Figure 3. The curve obtained by polarization from 0 V to +0.010 V was identical to the curve obtained when the direction of polarization was reversed and the potential was decreased from +0.010 V to 0 V. The polarization was continued from 0 V to −0.010 V and the slope, \( \frac{\partial \eta}{\partial \ln F} \left| \eta \rightarrow +0 \right. \) and \( \frac{\partial \eta}{\partial \ln F} \left| \eta \rightarrow -0 \right. \) measured as \( \eta \rightarrow +0 \) and \( \eta \rightarrow -0 \), are equal as should be the case for a reference electrode. These results indicate that the β-PdH UME is reversible in aprotic 0.2 M BMIM TFB in DCM saturated with forming gas.

Nernstian behavior - Influence of hydrogen partial pressure.— To assess the Nernstian behavior of the β-PdH electrode, experiments were performed that began by investigating the effect of changing the partial pressure of hydrogen on the potential of the β-PdH electrode. Looking ahead, changes in the partial pressure of hydrogen gas had unexpected results, which necessitated additional CVs and chronon-amperometry experiments that are described later in this paper after first considering the potential of β-PdH as a function of hydrogen gas partial pressure.

The Nernst equation for the hydrogen oxidation-reduction reaction indicates the potential of a hydrogen electrode at equilibrium is dependent on the hydrogen ion activity, \( [H^+] \), and the hydrogen gas fugacity, \( P(H_2) \).

\[
\Delta \phi_e (H) = \Delta \phi_e^\circ (H) - (RT/2F) \ln[P(H_2)/[H^+]^\circ] \tag{1}
\]

Changes in \([H^+]\) and \(P(H_2)\) should change the potential of the β-PdH electrode in the manner predicted by the Nernst equation. However, as the activity of hydrogen ions in aprotic solvents is undefined, only the effect of changing the partial pressure of hydrogen was studied.

The experiments were performed using several aprotic solvents: dichloromethane, dimethylsulfoxide, dimethylformamide, and acetonitrile, and the open circuit potential between a β-PdH electrode and an aqueous SCE was measured at partial pressures of hydrogen of 0.04 atm (i.e., forming gas) and 1 atm. The results of the Nernstian experiments in the aforementioned aprotic solvents are summarized in Table III.

The results of the experiments in DMF will be discussed first. The experiments with the solvent dimethylformamide displayed approximate Nernstian type behavior. The magnitude of the potential shift as a result of changing the hydrogen partial pressure was −0.055 V, which is larger than the theoretical value of −0.041 V. Nevertheless, the direction of the potential shift is consistent with the Nernst equation. The reason why the potential shift is larger than the theoretically predicted value is not yet known. Certainly, the non-ideal behavior of H₂ in liquid hydrocarbons is a likely contributing factor.

![Figure 2](image-url) Open circuit potential of PdH electrode vs. modified SCE in 0.2 M TBAP in ACN.

![Figure 3](image-url) I vs V plots of β-PdH UME in 0.2 M BMIM TFB in DCM saturated with Forming Gas during polarization from 0 to +10 mV to −10 mV at a rate of 10 mV/s. The curve obtained by sweeping the potential in the positive direction was identical to the curve obtained by sweeping the potential in the negative direction.

| Solvent          | ΔE 0.04 atm H₂ (V) | ΔE 1 atm H₂ (V) | ΔE (V) |
|------------------|-------------------|----------------|-------|
| Dichloromethane* | −0.117            | −0.081         | +0.036|
| Dimethyl sulfoxide | −0.435           | −0.397         | +0.038|
| Acetonitrile     | −0.26             | −0.224         | +0.036|
| Dimethyl formamide| −0.265            | −0.32          | −0.055|

*Experiment also performed using half wave potential shift of dmFc vs. PdH reference electrode with identical results.
The potential shifts of the β-PdH electrode measured in the other three solvents (dichloromethane, dimethylsulfoxide, and acetonitrile) were surprising. The equilibrium potential for solutions with these three solvents changed by approximately +0.037 V as the partial pressure of hydrogen was increased from 0.04 atm to 1 atm. As an increase in potential is not consistent with Nernstian behavior further investigation of the influence of the partial pressure of hydrogen was conducted. In particular, an experiment was performed in DCM to determine whether the observed potential shift was reversible. To determine whether the change in potential was reversible in DCM, after equilibrating at 1 atm of H₂, the partial pressure was reduced back to 0.04 atm and the potential was recorded. After the partial pressure of hydrogen was reduced, the potential of the β-PdH electrode decreased back to its original value over a period of several hours. The sluggish response of β-PdH to changes in the partial pressure of hydrogen is well known. As the results were reversible, the reason for the apparent “anti-Nernstian” behavior was of particular interest.

It is noteworthy that the unusual response of the β-PdH’s potential to changes in partial pressure of hydrogen is not the first report of β-PdH’s apparent “anti-Nernstian” behavior. Schuldner et al. found that the potential of β-PdH was unchanged by changes in the partial pressure of hydrogen gas over the range of 0.01 atm to 1 atm in aqueous acidic solutions. They pointed out that the behavior of β-PdH was governed by hydrogen absorbed in Pd as well as H₂ and H⁺ present in the aqueous solution, which is in contrast to the behavior of the conventional hydrogen electrode, in which the potential of platinum depends only on the H₂ and H⁺ present in the aqueous solution. In the balance of this paper we propose that the unusual response of the potential of β-PdH in aprotic solutions is related to the fact that Pd, rather than the liquid solution, is the source of H⁺.

Our explanation for the behavior of β-PdH in aprotic solutions such as those in which DCM is the solvent is presented in the following section and is based on the results of cyclic voltammetry and chronoamperometry experiments. We conclude that the β-PdH electrode in an aprotic solution does act as a thermodynamic hydrogen reference electrode, albeit not like the reversible hydrogen electrode of an aqueous solution.

Nernstian behavior – β-PdH as the source of H⁺ in an aprotic solution.— The two remaining subsections of this paper are focused on determining how it is that β-PdH can serve as a thermodynamic reference electrode in an aprotic solution. In other words the question that is addressed is: what is the red-ox couple that is in thermodynamic equilibrium on the surface of β-PdH immersed in an aprotic solution that is saturated with a particular partial pressure of hydrogen gas?

In the present subsection the results of two additional sets of experiments are presented: cyclic voltammograms (CVs) conducted with multiple sweeps and voltage amplitudes of ±0.010 V in aprotic and in aqueous solutions, and chronoamperometry tests conducted in DCM based solutions and with a large voltage amplitude of ±0.500 V. The combination of the results of these tests and measurements by other researchers of changes in work function of Pd and β-PdH caused by adsorption of hydrogen confirm the presence of both H⁺ and H₂ present on the surface of β-PdH immersed in an aprotic solution saturated with forming gas (i.e., 0.04 atm of H₂).

Since our tests are conducted in solutions saturated with forming gas the presence of hydrogen on the surface of β-PdH is not surprising. However, since all the solutions investigated are aprotic, the presence of H⁺ on the surface of β-PdH needs to be confirmed. Furthermore, it is necessary to determine if β-PdH can provide a sufficient quantity of H⁺ so that the electrode is resistant to changes in potential as required of a reference electrode.

The I-V behavior of a β-PdH UME during 15 cyclic polarizations (i.e., ±0.010 V) is presented in Figure 4. The results clearly indicate the presence of a hysteresis. Although the I-V behavior is reproducible in cycle after cycle, the hysteresis precludes assessing the reversibility of the red-ox reactions. Of course, the hysteresis is a common aspect of low amplitude cyclic voltammetry (LACV) conducted at relatively high frequencies. For example, a similar hysteresis is exhibited by 15 CVs of β-PdH in aqueous 0.1 M HCl as shown in Figure 5. As summarized in Table IV, lowering the voltage sweep rate decreases the amplitude of the hysteresis.

Of more relevance to our present study of the use of β-PdH as a thermodynamic reference electrode is the fact that the cathodic portion of the CVs indicate the presence of a reducible species, namely H⁺. Of course, the hysteresis is a common aspect of low amplitude cyclic voltammetry (LACV) conducted at relatively high frequencies. For example, a similar hysteresis is exhibited by 15 CVs of β-PdH in aqueous 0.1 M HCl as shown in Figure 5. As summarized in Table IV, lowering the voltage sweep rate decreases the amplitude of the hysteresis.

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course, the presence of H⁺ in CVs that started by anodic polarization might simply be the product of the oxidation of H. However, identical CVs were generated when the initial direction of polarization was cathodic (see Figure 6), which indicates that H⁺ are present on the surface of β-PdH not subjected to anodic polarization (see Appendix B). The cyclic voltammograms presented in Figure 6 include the transient I-V response when the potentiostat was first switched on. Figure 6a presents the results for the case in which the initial polarization is anodic. Figure 6b shows the results when the initial polarization is cathodic. Aside from the initial transients associated with the switching on of the potentiostat the CVs are nearly identical regardless of whether the initial polarization is anodic or cathodic. The results indicate the reducible species is H⁺. The plot of I vs V during the initial cathodic polarization indicates that hydrogen cations are available for electrochemical reduction on the surface of β-PdH. That is, for the case in which the first polarization is cathodic, the hydrogen cations that are electrochemically reduced could not have been created by oxidation of H during anodic polarization. Apparently, H⁺ are present on the surface of PdH immersed in the solution. The presence of H⁺ on the surface of β-PdH is supported by measurements of changes in work function caused by adsorption of hydrogen on Pd and β-PdH (see Appendix C).

As mentioned in the previous paragraph, the small amplitude cyclic polarization experiments in which the initial direction of polarization is cathodic indicate that H⁺ is present on the surface of β-PdH immersed in aprotic solutions saturated with P(H₂) = 0.04 atm. The total charge density in the first cycle of cathodic polarization is 9.1 mC/cm², which amounts to the quantity of hydrogen that is contained in approximately 15 nm of β-PdH (=PdH₁₀₆). To further determine the quantity of H⁺ that is available for electrochemical reduction during the cathodic polarization of β-PdH in aprotic solution, chronoamperometric tests were conducted in which the β-PdH UME was cathodically polarized to −500 mV vs β-PdH CE/RE for times of 5 s, 50 s, and 500 s. The plot of cathodic current density versus time is presented in Figure 7 for a test in which the potential was held at −500 mV vs PdH for 500 s. Assuming that all of the hydrogen cations that are electrochemically reduced during the 500 s of cathodic polarization are provided by diffusion of H to the surface of PdH requires a thickness of PdH equal to 0.33 μm and a hydrogen diffusivity of 5.5 × 10⁻¹³ cm²/s. The latter is well below the room temperature diffusivity of 5.5 × 10⁻⁷ cm²/s obtained by extrapolating to room temperature the diffusivity measured over the temperature ranges of 250°C – 450°C and 496°C – 946°C. Consequently, the rate of transport of hydrogen in palladium hydride required to provide hydrogen cations for electrochemical reduction at the surface of β-PdH is well below the rate at which hydrogen diffuses in β-PdH.

Nernstian behavior – Nernst equation for hydrogen electrode of β-PdH in aprotic solution. — The remaining task in establishing that PdH serves as a thermodynamic reference electrode in aprotic solutions is to explain why the direction of the change in potential of PdH with changes in P(H₂) is opposite to that of a Pt electrode in an aqueous solution. The issue is first addressed qualitatively and then quantitatively.

The Nernst equation for hydrogen, Equation 1, indicates that the potential of a hydrogen electrode depends logarithmically on the ratio P(H₂(g))/[H⁺]².[H⁺] is the concentration of H⁺ adsorbed on the electrode’s surface. [H⁺] is directly related to the concentration of H⁺ in the bulk of the solution, [H⁺]bulk, which is given by the solution’s pH. The values of P(H₂(g)) and the aqueous solution’s pH are independent and Δφ(H) decreases with increasing P(H₂(g)).

![Figure 6. (a) I vs. V plot of β-PdH UME in 0.2 M BMIM TFB in DCM saturated with forming gas during 10 mV small polarizations from open circuit at a rate of 10 mVs, anodic scan first. (b) I vs. V plot of β-PdH UME in 0.2 M BMIM TFB in DCM saturated with forming gas during 10 mV small polarizations from open circuit at a rate of 10 mVs, cathodic scan first.](image-url)

![Figure 7. Absolute current vs. time for multistep chronocoulometry of PdH microelectrode to 10 ±50 mV pulses for 500 seconds each. Only first and last pulses are shown.](image-url)
In contrast to a platinum electrode in an aqueous solution, the concentration of Hads on the surface of PdH in an aprotic solution is not determined by [Hads(ads)], which, by definition, is equal to zero. Instead, the concentration of Hads on the surface of PdH immersed in an aprotic solution is determined by the PdH’s concentration of dissolved H, which, in turn, is determined by P(H2(g)). Thus, for the case of PdH immersed in an aprotic solution both the numerator and the denominator of the ratio P(H2(g))/[H(ads)] of PdH immersed in an aprotic solution both the numerator and the concentration of Hads on the potential of platinum in an aqueous solution. Specifically, as shown below, [Hads] = P(H2(g))/[Hads] for PdH in an aprotic solution so that each of increasing with increasing P(H2(g)), which is exactly the opposite of what occurs for a platinum electrode in an aqueous solution, and is exactly as observed in our experiments.

The quantitative nature of the influence of P(H2(g)) on the concentration of Hads on the surface of PdH is estimated as follows. When palladium is immersed in a gaseous atmosphere of hydrogen or in an aprotic liquid saturated with a particular partial pressure of H2(g), H2(g) will adsorb on the palladium’s surface and dissociate into two atoms of hydrogen, as is the case for any transition metal. Some fraction of the hydrogen atoms on the surface of palladium are absorbed, diffusing into the subsurface layers and on into the bulk of the crystal and are denoted as Hads. Only that portion, x, which remains adsorbed on the surface forms the oxidized species (i.e., Hads) and the reducible specie (i.e., Hads). The reactions relevant to the Nernst equation are as follows.

\[ \text{H}_2(g) \leftrightarrow 2\text{H}_\text{ads} \leftrightarrow x\text{H}_\text{ads} + (2-x)\text{H}_\text{abs} \]

The equilibrium coefficient for partitioning of H2(g) between Hads and Habs is

\[ K_d = P(H_2(g)) / [H_{ads}][H_{abs}]^{2-x} \]

Therefore,

\[ [H_{ads}] = P(H_2(g)) / K_d[H_{abs}]^{2-x} \]

Substituting the above expression for [Hads] into the Nernst equation gives

\[ \Delta \phi_e = \Delta \phi_e^\circ + (0.0592/2) \log[P(H_2(g))K_d^{1/2}[H_{ads}]^{2-x}/(P(H_2))]^{1/2} \]

\[ \Delta \phi_e = \Delta \phi_e^\circ + (0.0592/2)(2-x)/x \log[P(H_2(g))] \]

\[ -(0.0592/x) \log[K_d[H_{abs}]^{2-x}] \]

According to Figure 8 of Wicke et al. [Hads] is approximately independent of P(H2(g)) for 0.01 atm < P(H2) < 1 atm. Thus, changing the partial pressure of hydrogen from 0.04 atm to 1 atm changes the potential of β-PdH by

\[ \delta(\Delta \phi_e(H_{PdH})) = (0.0592/V)((2-x)/x) \log(1 - \log 0.04) \]

Setting the above expression for \(\delta(\Delta \phi_e(H_{PdH}))\) equal to the experimentally measured value of +0.037 V and solving for y yields x = 0.95. Equation 2 and the definition of x indicate that a value of x = 0.95 is approximately equivalent to the equipartitioning of H2(g) between Hads and Habs.

In summary, in an aprotic solution the concentration of Hads on PdH is a function of the partial pressure of H2(g) in the bulk solution. As a result, the influence of the partial pressure of H2(g) on the equilibrium potential of the hydrogen red-ox reaction in an aprotic solution is fundamentally different from the influence of P(H3(g)) on the equilibrium potential of hydrogen in a protic solution. Specifically, increasing the partial pressure of hydrogen results in a decrease in the hydrogen equilibrium potential in a protic solution but causes an increase in the hydrogen equilibrium potential in a protic solution.

The quantitative nature of the influence of P(H2(g)) on the potential of palladium is estimated as follows. When palladium is immersed in a gaseous atmosphere of hydrogen or in an aprotic liquid saturated with a particular partial pressure of H2(g), H2(g) will adsorb on the palladium’s surface and dissociate into two atoms of hydrogen, as is the case for any transition metal. Some fraction of the hydrogen atoms on the surface of palladium are absorbed, diffusing into the subsurface layers and on into the bulk of the crystal and are denoted as Hads. Only that portion, x, which remains adsorbed on the surface forms the oxidized species (i.e., Hads) and the reducible specie (i.e., Hads). The reactions relevant to the Nernst equation are as follows.

\[ \text{H}_2(g) \leftrightarrow 2\text{H}_\text{ads} \leftrightarrow x\text{H}_\text{ads} + (2-x)\text{H}_\text{abs} \]

The equilibrium coefficient for partitioning of H2(g) between Hads and Habs is

\[ K_d = P(H_2(g)) / [H_{ads}][H_{abs}]^{2-x} \]

Therefore,

\[ [H_{ads}] = P(H_2(g)) / K_d[H_{abs}]^{2-x} \]

Substituting the above expression for [Hads] into the Nernst equation gives

\[ \Delta \phi_e = \Delta \phi_e^\circ + (0.0592/2) \log[P(H_2(g))K_d^{1/2}[H_{ads}]^{2-x}/(P(H_2))]^{1/2} \]

\[ \Delta \phi_e = \Delta \phi_e^\circ + (0.0592/2)(2-x)/x \log[P(H_2(g))] \]

\[ -(0.0592/x) \log[K_d[H_{abs}]^{2-x}] \]

According to Figure 8 of Wicke et al. [Hads] is approximately independent of P(H2(g)) for 0.01 atm < P(H2) < 1 atm. Thus, changing the partial pressure of hydrogen from 0.04 atm to 1 atm changes the potential of β-PdH by

\[ \delta(\Delta \phi_e(H_{PdH})) = (0.0592/V)((2-x)/x) \log(1 - \log 0.04) \]

Lastly, our analysis explains the results obtained in aprotic solutions consisting of solvents of DCM, DMSO and ACN and we propose that β-PdH can serve as a thermodynamic hydrogen reference electrode in these three aprotic solutions (see caveat in Appendix D). Why PdH immersed in the aprotic solution composed of the solvent DMF behaves differently and in a manner similar to its behavior in an aqueous solution is not yet understood.

Conclusions

1. Our results suggest β-PdH serves as a reference electrode in the aprotic solution consisting of 0.2 M [bmim][TFB] in DCM. The β-PdH is stable and reversible and the half-wave potentials of dmFc, Fc, and AQ in DCM measured with respect to β-PdH differ between each other by the same amounts as measured by Aranzaes et al.16 and by Ahmed and Khan17 using aqueous SCE as a reference electrode.

2. The potential of β-PdH in aprotic solutions with solvents of DCM, DMSO, and ACN is a function of the partial pressure of hydrogen gas but the potential increases with increasing partial pressure, which is opposite to the influence of hydrogen pressure on the potential of the conventional, reversible hydrogen electrode in aqueous solutions.

3. The influence of the partial pressure of hydrogen on the potential of β-PdH in aprotic solutions is a consequence of the fact that the source of both Hads and Hads, i.e., Hads, which is established by the partial pressure of hydrogen dissolved in the liquid solution. Thus, both terms in the argument of the log expression of the equilibrium potential are dependent on the partial pressure of hydrogen, which is in contrast to the behavior of the conventional, reversible hydrogen electrode, for which the equilibrium potential depends on both the partial pressure of hydrogen and the hydrogen ion concentration of the aqueous solution.

4. Since β-PdH is stable, reversible, and, Nernstian (for the equilibrium reaction: H2(g) ↔ 2Hads ↔ Hads + Hads; and Hads + e− ↔ Hads), it can serve as a thermodynamic reference electrode in aprotic solutions.

5. Compliance with the Nernst equation is based on the approximation that the concentration of Hads on PdH is independent of P(H2) between 0.01 atm and 1 atm, which is supported by Wicke et al.15

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Appendix A

The Combination Counter Electrode and Reference Electrode of Palladium Hydride

The cyclic voltammogram presented in Figures 1a, 1b was measured in a cell containing a platinum ultra-microelectrode (Pt-UME), which served as the working electrode (WE), and a relatively large β-PdH electrode, which served as a combined counter and reference electrode (CE/RE). The use of β-PdH as a combination CE/RE is justified in this appendix based on (1) the large value of the ratio of the area of the β-PdH CE/RE and the area of the Pt-UME, and (2) the sufficiently large value of the exchange current density of the red-ox reaction on the β-PdH electrode’s surface.

The area ratio of the β-PdH CE/RE to the Pt-UME was 1 in2/π0.003 in2, which equals 1.41 × 103. The anodic and cathodic polarization curve presented in Figure 3 can be used to estimate the value of the exchange current density, i0, which is used to determine the amount of polarization of β-PdH CE/RE:

\[ \Delta \phi_{H_{PdH}}(\eta) = \eta_{CE/RE} - \eta_{Pt-UME} = \frac{N_m \eta}{\eta_{Re}} - \frac{N_m}{\eta_{Pt-UME}} = i_0 \]

From Figure 3, \(\Delta \phi_{H_{PdH}}(\eta) = 0.0689\ nA/cm^2, \ i_0 = 0.0524\ nA/cm^2\) at the current density of 39.5 µA/cm2.

Returning to Figures 1a, 1b, the maximum value of the current at the Pt-UME was 6 nA. Consequently, the maximum current density that crossed the β-PdH surface was

\[ \frac{6\ nA}{1\ in^2} = 0.93\ nA/cm^2. \]
maximum polarization of the β-PdH electrode is only 0.6 μV, which indicates that the β-PdH served very well as a combination reference electrode/counter electrode in the cell.

Appendix B
Confirming Palladium Hydride is the Source of Hydrogen Cations

The CVs of β−PdH−UME measured in DCM with 0.2 M [bmin][TFB] (see Figures 4 and 6) indicate that hydrogen cations are available for electrochemical reduction despite the absence of H⁺ in the liquid phase. To rule out the possibility that contaminants such as water might be responsible for the redoxible species, similar tests were conducted in which the β−PdH UME was replaced by a Pt UME. The polarization behavior of Pt was erratic and highly nonreproducible, indicating that β−PdH was the source of hydrogen ions in the CVs of UME of β−PdH.

Appendix C
The Presence of Hα and Hα− on the Surface of PdH

This appendix is intended to provide background information on the nature of the electrical charge of H that is adsorbed on Pd. The experiments that are discussed were conducted on Pd in a vacuum and exposed to various partial pressures of H2(g).

Measurements of changes in the work function of palladium caused by adsorption of hydrogen indicate that anionic and cationic hydrogen exists on the surface of palladium.26−27. The electrical charge of hydrogen adsorbed on Pd depends on the structure of the palladium surface (i.e., the crystallographic plane and the presence of crystals), the effects such as ledges) and the concentration of hydrogen adsorbed. In Pd−H, Conrad et al. indicated that the concentration of hydrogen dissolved in bulk Pd had no effect on the alloy’s work function.25 Consequently, measured values of the work function were associated with the amount and electrical charge of adsorbed hydrogen. Conrad studied adsorption of hydrogen on 2 mm thick single crystals of Pd (110) and (111) at temperatures of 35°C to 100°C. The maximum value of the equilibrium partial pressure of hydrogen that was measured was < 10−3 torr, which is several orders of magnitude smaller than the equilibrium pressure in solution with β−PdH so that the results are of hydrogen adsorbed on Pd metal and not of H adsorbed on β−PdH. The results indicated that adsorbed hydrogen increased the work function of palladium, which indicates that the adsorbed hydrogen was negatively charged.

Dus’ et al. repeated the measurements of Conrad et al. mostly at a temperature of 78 K and extended the tests to higher values of equilibrium partial pressure of hydrogen.24 The experiments of Dus’ et al. were conducted on thin films (≈100 nm thick) of Pd. At low equilibrium partial pressures of hydrogen, which corresponded to hydrogen adsorbed on metallic Pd, the work function of palladium was increased in agreement with the higher temperature results of Conrad et al. Once the equilibrium partial pressure of hydrogen was raised above a critical value further increases in partial pressure decreased the work function, indicative of the adsorption of positively charged hydrogen.

In trying to explain the origin of the positive charge of adsorbed hydrogen it is too simplistic to claim that hydrogen adsorbed on Pd, which contains a relatively high concentration of hydrogen, donates its electron to d-band vacancies of Pd metal. Over 40 years ago Switendick demonstrated by a combination of calculations and experimental results that hydrogen induces electron states in Pd that are well below the Fermi level of Pd.28−30 Since Switendick’s seminal work a number of experimental and theoretical studies have agreed that hydrogen fundamentally changes the band structure of Pd. Since the adsorption process is irreversible and hysteretic, measurements made in vacuum/H2(g) behavior the same as Hads on PdH that is immersed in DCM.

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