SEPARATION OF THERMAL-WAVE AND OPTICAL REFLECTANCE EFFECTS IN A PALLADIUM-PHOTOPYROELECTRIC HYDROGEN SENSOR

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The mechanisms responsible for the sensitivity of the palladium-photopyroelectric (Pd-PPE) hydrogen sensor are considered. Judging from recent experimental results, the Pd-PPE device is sensitive to hydrogen gas via two distinct effects: the difference between the thermo-physical properties of hydrogen gas and air; and the change in the optical absorptance of Pd when it is exposed to hydrogen. It will be shown that the thermal component of the detector response can be eliminated by using a suitable reference sensor. Furthermore, the utility of the Pd-PPE device will be compared with other optical hydrogen sensors which monitor the reflectance or transmittance of a palladium film exposed to hydrogen.

1. INTRODUCTION

It is widely known that palladium is capable of absorbing large amounts of hydrogen, and this makes it a promising material for the creation of sensitive hydrogen detectors.[1] Mandelis and Christofides have reviewed a wide variety of Pd-based hydrogen detectors in their recent book on solid-state gas sensors.[2] Among the large number of reported solid-state hydrogen sensors, a particularly sensitive one constructed by Butler[3] monitored the amount of light reflected from a thin Pd film at the tip of an optical fiber. For this sensor, Butler found that the reflectance of the Pd film dropped when hydrogen was absorbed into the film. The wavelength of the light propagating in the fiber was 860 nm. Butler's fiber-optic reflectivity sensor appears to be capable of detecting down to at least 0.2% hydrogen in nitrogen.

Fortunato *et al.*[4] have also measured the reflectance of Pd as a function of the H_2 partial pressure in N_2, for a number of photon energies in the range 0.6 to 2.8 eV. In this case the freely-propagating probe beam was obtained from a tungsten lamp filtered by a monochromator, and measurements were performed at a 45° angle of incidence. They found that the change (ΔR) in reflectance (R) is a strong function of the photon energy; for instance, ΔR was always negative, and its magnitude increased with both the hydrogen partial pressure and the photon energy.

Fortunato *et al.* also state that the optical absorption length of visible light in Pd is about 150 Å. Since this means that the absorptance (absorption length times the

absorption coefficient) is about two, the absorption coefficient (α_1) for visible light is about 1.3×10^8 m^{-1}; therefore, the extinction coefficient ($k = \alpha_1\lambda/4\pi$) at 850 nm is about 8.7. For such a large extinction coefficient, the reflectivity of a Pd/air interface must be greater than about 80%, and the minimum reflectivity of 80% occurs when $n^2 = k^2 + 1$ or $n \approx 8.757$, where n is the refractive index of Pd. According to Coblentz,[5] the reflectivity of Pd at 850 nm is about 72%, which is somewhat lower than the minimum value of 80% noted above. Keeping in mind this discrepancy, for the remainder of this paper it will be assumed that $R = 80\%$, $k = 8.7$, and $n = 8.757$, at 850 nm. This wavelength corresponds to that used for the photopyroelectric experiments reported here.

2. THEORETICAL

Although it is possible to measure small changes in optical reflectance using modulation techniques, it turns out that when the sample reflectance is high, it is advantageous to measure the change in optical absorptance instead. For instance, consider a single Pd/air half-space, or an opaque thin film. If A is the sample absorptance, then from energy conservation we can write that $A = 1 - R$. Furthermore:

$$\frac{\Delta A}{A} = -\left(\frac{\Delta R}{R}\right)\frac{R}{1 - R}. \tag{1}$$

Fortunato et al.[4] found that for 2% H_2 in N_2, $\Delta R/R$ was about -1.2% at 850 nm, compared to the reflectivity in pure N_2; using Equation (1), and $R = 80\%$, $\Delta A/A$ can be calculated to be 4.8%. This example illustrates that the relative change in absorptance is greater than the relative change in reflectance when the reflectance is greater than 50%. Overall, an R increases above 50%, the magnitude of $\Delta A/A$ increases relative to the magnitude of $\Delta R/R$. In conclusion, when hydrogen absorption induces a change in the optical properties of a highly-reflective, opaque film of Pd, it is advantageous to monitor the sample absorptance rather than the reflectance.

There are two main methods for directly probing the optical absorptance of a sample. First, consider the transmittance of a thin Pd film. In order for a significant amount of light to be transmitted through the film, the film thickness must be less than the optical absorption length ($\lambda/4\pi k$), which is about 150 Å for Pd. Furthermore, for a film with two Pd/air interfaces, the transmittance of a normally-incident, incoherent beam of light is approximately:

$$T = (1 - R)^2 \exp(-4\pi kL/\lambda), \tag{2}$$

where λ is the wavelength, L is the film thickness, and R is the reflectance of a single Pd/air interface. Multiple reflections have been neglected in deriving Equation (2), which is valid for partially-opaque films ($\alpha_1 L \approx 1$).

Fortunato et al.[4] reported that when hydrogen is absorbed in Pd, it tends to

decrease the extinction coefficient. Assuming that the change in refractive index is comparatively small, we can write:

$$\frac{\Delta T}{T} \approx \frac{1}{T} \left(\frac{\partial T}{\partial k} \right) \Delta k. \tag{3}$$

Then, using Equation (2):

$$\frac{\Delta T}{T} = \frac{-1}{1 - R} \left[2 \frac{\partial R}{\partial k} + \frac{4\pi L}{\lambda} (1 - R) \right] \Delta k, \tag{4}$$

where

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}, \tag{5}$$

and

$$\frac{\partial R}{\partial k} = \frac{8nk}{[(n + 1)^2 + k^2]^2}. \tag{6}$$

If $R = 0.8$, $k = 8.7$, $n = 8.757$, $\lambda = 850$ nm, and $L = 100$ Å, then $\Delta T/T = -0.35\Delta k$.

Although the transmittance technique appears to be acceptable for monitoring absorbed hydrogen, it has certain limitations. For instance, since the Pd film must be semi-opaque, one is limited to employing thin films of thickness less than about 200 Å. On certain substrates, thin Pd films are susceptible to blistering, whereby voids are formed between the Pd film and the substrate. For example, Armgarth and Nylander[6] found that a 2000 Å Pd film on alumina (Al_2O_3) blistered in 1000 ppm hydrogen in synthetic air, while a 4000 Å Pd film did not blister after a thirty minute exposure. For optical techniques such as film transmittance, the presence of blisters may not be a significant problem, although blistering is important in the case of capacitance-sensing devices,[6] yet in both situations it is certain to lead to irreversible sensor behavior. Finally, it should be noted that very-thin (<200 Å) Pd films behave quite differently from bulk-type Pd films with respect to hydrogen absorption: Frazier and Glosser[7] found that the concentration of hydrogen [H] in a very-thin Pd film increases gradually as the H_2 pressure is increased, while bulk-type films absorb little hydrogen below a critical pressure, and then [H] increases dramatically above the critical pressure.

A second method for monitoring the optical absorptance of palladium is to use a thermal-wave technique to probe the modulated heating of the Pd due to the absorption of the modulated excitation beam. In fact, in the present case we have used a pyroelectric sensor to monitor the optical heating of a thin Pd film deposited directly onto a transparent polyvinylidene fluoride (PVDF) pyroelectric film. Our sensor typically consists of a 28 μm PVDF film with one side coated with 500 Å of Ni/Al, and the other side coated with about 285 Å of Pd. This device is inexpensive and easy to manufacture. For instance, the active Pd material is deposited directly onto the pyroelectric film, so the device is robust and compact. Also, the sensor is very durable; for Pd-film thicknesses ranging from 38 to 1000 Å, no Pd

delaminating from the PVDF film, or blistering occurred, even after repeated exposures to pure hydrogen.

An a.c. photopyroelectric (PPE) voltage signal is created across the PVDF film when the Pd electrode is illuminated with chopped light. Since a 285 Å Pd film is thermally very thin at the employed modulation frequency ($\approx$10 Hz), the PPE signal is proportional to the optical absorptance of the Pd film.[8] For small changes of the reflectance with the extinction coefficient one can write:

$$\frac{\Delta R}{R} \approx \frac{1}{R}\left(\frac{\partial R}{\partial k}\right) \Delta k \approx 0.026\Delta k, \tag{7}$$

using the parameters listed after Equation (6). Furthermore, using Equation (1), which is valid for optically-thick Pd films, yields:

$$\frac{\Delta A}{A} \approx \frac{-1}{1 - R}\left(\frac{\partial R}{\partial k}\right) \Delta k \approx -0.1\Delta k, \tag{8}$$

using the parameters listed after Equation (6). From Equations (7) and (8) it can be seen that the fractional change of absorptance is *ca.* four times higher than that of reflectance for the same change in k.

At this point is should be noted that the fiber-optic method of Butler[3] measures the reflectance of a semi-opaque film of Pd; therefore, Equation (7) is not strictly valid. Instead, it is necessary to determine $\Delta R_L/R_L$, where R_L is the reflectance of a semi-opaque film. Ignoring multiple reflection effects, and assuming that the sample is semi-opaque ($\alpha_1 L \approx 1$), it is possible to write:

$$R_L \approx R[1 + (1 - R)^2 \exp(-8\pi kL/\lambda)], \tag{9}$$

where only the first reflection from the back interface has been considered, and R is defined in Equation (5) for normal incidence. Since, to first order,

$$\frac{\Delta R_L}{R_L} \approx \frac{1}{R_L}\left(\frac{\partial R_L}{\partial k}\right) \Delta k, \tag{10}$$

then

$$\frac{\Delta R_L}{R_L} = \left(\frac{1}{R}\frac{\partial R}{\partial k} - (1 - R)\exp(-8\pi kL/\lambda)\left[2\frac{\partial R}{\partial k} + (1 - R)\frac{8\pi L}{\lambda}\right]\right) \Delta k. \tag{11}$$

Using the parameters listed after Equation (6), $\Delta R_L/R_L \approx 0.026\Delta k$, which is the same as $\Delta R/R$. Therefore, the efficiency of semi-opaque and opaque Pd films as hydrogen sensors appears to be the same, when the reflectance mode is employed, as expected from high absorptance metal layers.

Overall, the calculations performed above indicate that the most sensitive method for probing changes in the optical absorption of a Pd thin film is to monitor the transmittance, however, there may be practical difficulties. in the experimental implementation of this method. In addition, it appears that measuring the absorptance via a thermal-wave method is also quite sensitive, and easy to implement experimentally. Finally, monitoring the optical reflectance is the least sensitive method for measuring hydrogen absorption into Pd. It should be pointed out that

although changes in the refractive index of the Pd as a result of hydrogen absorption have been neglected, even if they are included, the basic ideas presented above remain valid.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The experimental arrangement (Figure 1) was similar to the one used by Christofides and Mandelis.[9] Two separate pyroelectric elements were employed, an active sensor and a reference sensor. The active sensor consisted of a 28 μm PVDF film[10] coated on both sides with 285 Å of Pd, and the reference sensor consisted of a 28 μm PVDF film coated on both sides with 500 Å of Ni-Al. Both elements were illuminated on one face, including the Pd-coated one, with 850 nm laser light from the same GaAlAs diode laser, and both films were fully exposed to the ambient gas. Finally, both signals were pre-amplified and then fed into a lock-in analyzer. The lock-in analyzer was operated in the differential mode, monitoring the difference between the active and the reference signal. In order to maximize the sensitivity of the system electronics, when the system was immersed in pure nitrogen (or air) the pre-amplifier gains were adjusted so that the difference signal was minimized. In some cases the active signal was monitored independently, and the reference signal was ignored.

There are two reasons for which the reference sensor was employed. First, the reference sensor helped to eliminate the signal drift which normally occurs due to temporal variations in the output of the diode laser. Second, the reference sensor helped to correct the active signal for effects related to the thermal properties of the ambient gas. It is well-known that hydrogen is a much better thermal conductor than normal air; therefore, when hydrogen is added to air, the thermal diffusivity and conductivity of the air are increased. Since the thermal-wave amplitude in the
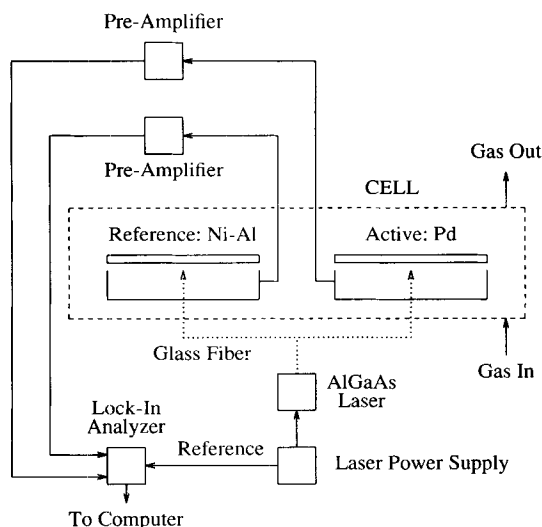

FIGURE 1 Experimental apparatus for the Pd-photopyroelectric hydrogen sensor. In the differential mode, the reference signal is subtracted from the active signal.
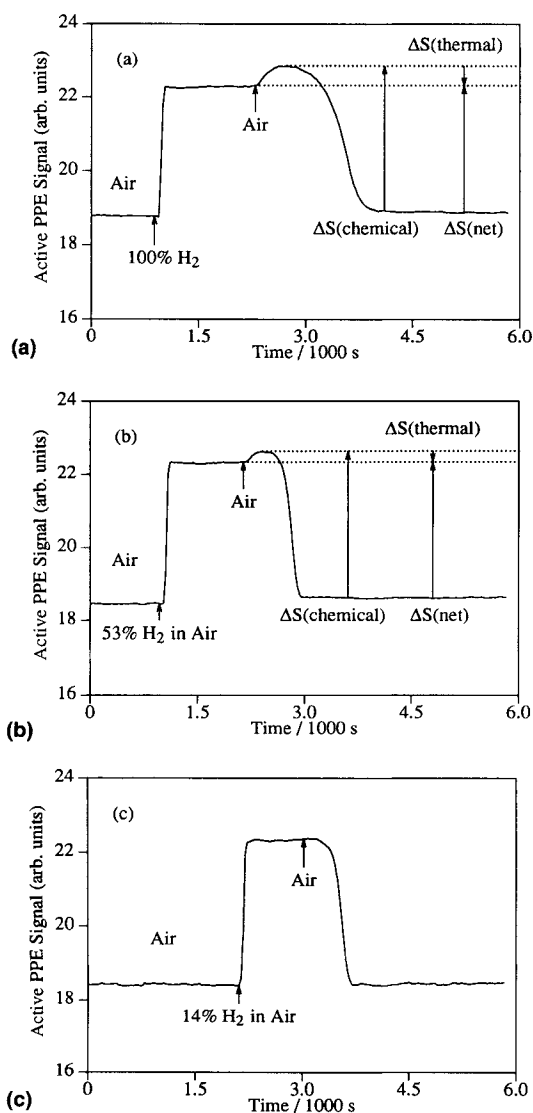
FIGURE 2   The change in active Pd-PPE signal amplitude due to the injection of various hydrogen/air mixtures into the test cell: (a) Pure hydrogen; (b) 53% hydrogen in air; and (c) 14% hydrogen in air. Refer to text for an explanation of the figure labelling. The modulation frequency was 8 Hz, and the Pd thickness was 285 Å.

pyroelectric sensor is a function of the thermal properties of the surrounding gas, it is important to account for this effect when the signal from the active sensor is being monitored.[11,12] Henceforth, variations in the active-sensor signal due to the thermal properties of the ambient gas will be called thermal effects; on the other hand, signal changes due to hydrogen chemically interacting with the Pd-coating will be termed chemical effects.

The first selection of data which will be discussed was obtained from a series of experiments in which the active signal was monitored as the ambient gas was

changed from pure air to an air/hydrogen mixture, and then back to pure air; note that the reference signal was not monitored. Figures 2a–c show the active PPE signal amplitude for various air/hydrogen mixtures, ranging from pure hydrogen down to about 14% H_2 in air.

When pure hydrogen was added to the test cell (Figure 2a), the signal began to increase quickly, and within 148 seconds a new plateau (saturation level) was reached. When air was subsequently injected into the cell, the signal increased to a maximum, and then decreased steadily down to the original, pre-H_2 level. It should be noted that when N_2 was used to purge the cell instead of air, the detector signal took much longer to achieve its pre-H_2 level. This implies a chemical reaction between H_2 and O_2 which consumes the H_2 embedded in the Pd matrix.

When the 53% H_2 mixture in air was employed, the sample behavior was similar to that seen for the pure hydrogen, except that the signal "hump" related to the air injection was of a smaller magnitude. Finally, when 14% H_2 was flowed through the cell, the signal increased by a considerable amount, but no signal increase was observed when air was injected into the cell.

The observations related to Figures 2a–c can be interpreted as follows. When the H_2/air mixtures were added to the cell, two effects transpired. First, hydrogen was adsorbed/absorbed into the Pd, and the Pd lattice was transformed from the α-phase to the β-phase; this effect is known to occur when [H_2] is about 2% in nitrogen at 100 kPa.[1] (For air/H_2 mixtures, the phase transition should occur at higher hydrogen concentrations, because oxygen tends to remove adsorbed hydrogen from the surface of the Pd.) The formation of the β-phase is, therefore, expected to have caused the sample reflectance to decrease, leading to an increase in the sample absorptance, and hence, to a larger PPE signal. Since [H_2] was much greater than 2% in Figures 2a–c, it is believed that the α-β phase transition occurred in all three cases.

In addition to the chemical effect described above, the photopyroelectric signal was altered by a second counteracting mechanism, a thermal heat-loss effect. When hydrogen was added to the cell gas, the sensor signal decreased because the higher thermal conductivity of the gas increased the thermal coupling coefficients at the PVDF-gas interface and caused more heat to be lost from the sensor, resulting in a smaller thermal-wave amplitude.[11,12] Figures 2a–c will be re-examined, taking into account the ideas presented above.

First, the magnitude of the thermal effect for pure hydrogen, ΔS(thermal), is represented by the height of the "hump" with respect to the post-H_2 plateau, as depicted in Figure 2a. The time-dependence of this effect can be understood by considering that when air was injected into the cell, the thermal properties of the ambient gas changed quite quickly, but a much longer time was required for the hydrogen atoms to leave the Pd sample than it originally took for the H atoms to be absorbed. Therefore, in this case the thermal and chemical effects can be separated because they show a much different time response. On the other hand, when hydrogen was initially added to the cell, it was not possible to isolate the two effects because they had roughly the same time response. The magnitude of the chemical effect for pure hydrogen, ΔS(chemical), is represented by the distance from the pre-H_2 level to the top of the "hump," as depicted in Figure 2a.

With respect to the data shown in Figure 2b (53% H_2), it should be apparent

that the fractional change ΔS(thermal) of the thermal effect is smaller relative to the fractional change ΔS(chemical) of the chemical effect, when compared with the data of Figure 2a. This is due to the fact that the thermal effect is a strong function of the hydrogen concentration, while the chemical effect is almost independent of [H_2] above 4%, since the α-β phase transition is complete for any [H_2] above $\approx 2\%$ in nitrogen. Finally, Figure 2c shows that the thermal effect is negligible compared to the chemical effect for [H_2] < 14%.

Figure 3 shows a plot of ΔS(chemical) versus [H_2] in air, derived from the data of Figures 2a–c. This figure indicates that the increase in optical absorptance due to the α-β phase transition causes the sensor signal to increase by about 22% when [H_2] > 14% in air. Furthermore, note that when 2% H_2 in N_2 was injected into the cell, the chemical effect caused the signal to increase by about 9%, which is a much larger change than was seen by Fortunato et al.[4] (-1.2%) during their monitoring of optical reflectance changes for a 1000 Å Pd film deposited on a quartz substrate exposed to 2% H_2 in N_2. Therefore, it appears that the thermal-wave method described in this paper is indeed a more sensitive method of monitoring
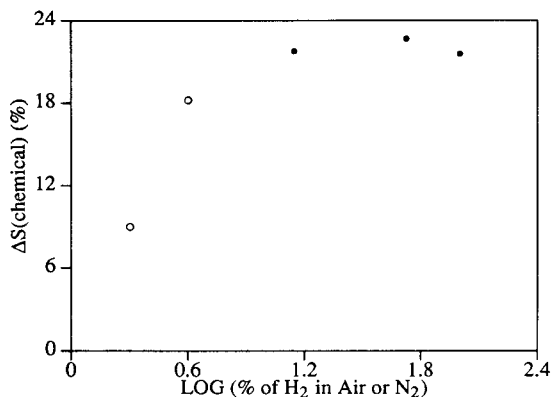

FIGURE 3   The dependence of the chemical component of the active Pd-PPE signal, ΔS(chemical), upon the concentration of hydrogen in air (●) or nitrogen (○). ΔS(chemical) is expressed as the percentage change of the active Pd-PPE amplitude following the injection of the hydrogen-containing mixture. The modulation frequency was 8 Hz, and the Pd thickness was 285 Å.
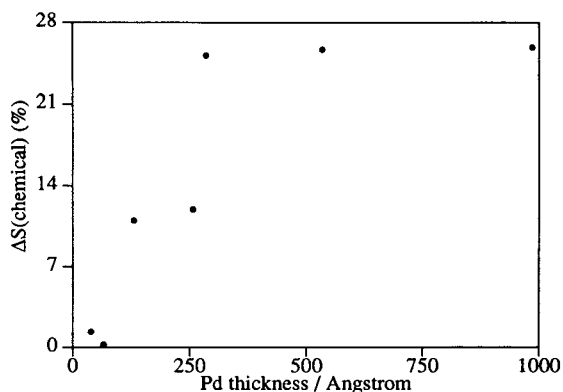

FIGURE 4   The dependence of the chemical component of the active Pd-PPE signal, ΔS(chemical), upon the thickness of the palladium layer. In all cases, pure hydrogen was used to induce ΔS.
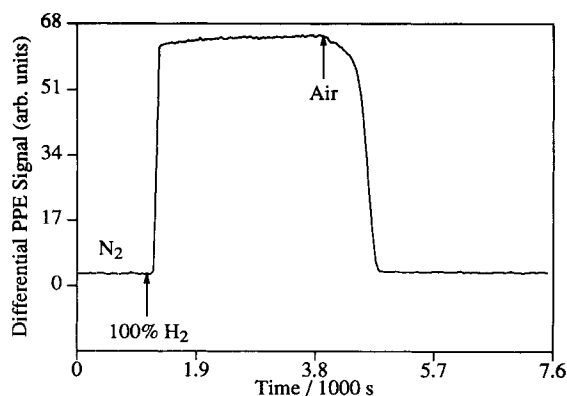
FIGURE 5 The change in the differential Pd-PPE signal amplitude due to the injection of pure hydrogen into the test cell. The modulation frequency was 8 Hz, and the Pd thickness was 285 Å.
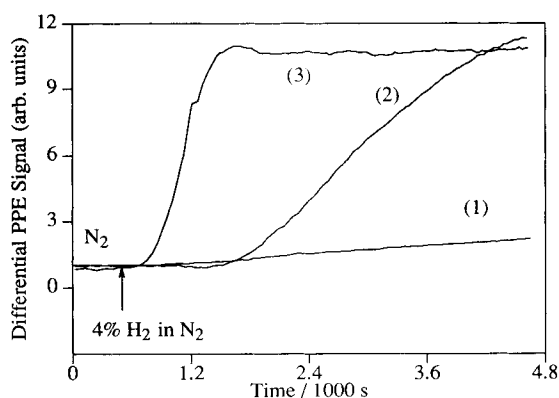

FIGURE 6 The time dependence of the differential Pd-PPE signal amplitude following the injection of 4% hydrogen in nitrogen into the test cell. For curve #1, the 285 Å Pd layer had never been exposed to pure hydrogen; for curve #2, the film had been exposed once to pure hydrogen, and for curve #3, twice to pure hydrogen. The modulation frequency was 8 Hz.

changes in optical properties than the reflectance technique, as borne out by the theoretical considerations of the previous section.

It is interesting to note that Butler[3] observed that $\Delta R/R = -6.5\%$ for 2% H_2 in N_2, which is also a much larger change than was seen by Fortunato et al.,[4] although less than the present sensor. This may have been due to the fact that Butler used a 150 Å Pd film, while Fortunato et al. used a bulk-type material. In fact, Frazier and Glosser[7] indicate that very-thin and bulk-type Pd films show quite different hydrogen absorption isotherms. Overall, it is not clear why Butler's fiber-optic reflectance sensor showed a much larger relative response than was observed by Fortunato et al.[4] Butler further observed a $\Delta R/R$ of -8% for 10% H_2 in N_2, while our PPE sensor gave a signal increase of at least 22%.

In order to examine the effect of varying the thickness of the Pd layer upon the chemical signal, a number of experiments were carried out using PVDF electrodes with different thicknesses of Pd; like the experiments presented in Figures 2a–c, no reference sensor was employed. In summary, under 100% H_2 exposure in nitrogen it was found that the chemical signal was a strong function of the Pd

thickness. For instance, Pd layers of 38 and 65 Å showed almost no chemical effect in pure hydrogen; Pd layers of thickness 130 and 256 Å showed about a 11.5% signal increase in pure hydrogen; and Pd layers of thickness 285, 534, and 985 Å displayed about a 25% signal increase in pure H_2. These results are consistent with the data of Frazier and Glosser[7] who showed that for thin Pd films (<520 Å), the transition to the β-phase is retarded. Since our chemical signal is most likely related to the change in optical properties due to the α-β phase transition, it is not surprising that we observed no chemical effects for the thinnest Pd films which do not easily transform to the β-phase.

If ΔS(chemical) for pure hydrogen is plotted versus the Pd thickness, Figure 4, it becomes apparent that the curve is discontinuous rather than smooth. It is presently unclear why, for instance, the 256 Å Pd film showed the same response as the 130 Å Pd device, rather than a response closer to that obtained for the 285 Å Pd film. It is possible that variable conditions of Pd deposition on different PVDF films and/or different polarization profiles contributed to the non-smooth data shown in Figure 4.

In order to eliminate thermal effects from the active detector response in real-time, experiments were carried out using the aforementioned reference sensor, which was known to be chemically non-reactive. Figure 5 shows data obtained when the 285 Å Pd film sensor was cycled between nitrogen, hydrogen, and air. It can be seen that the reference sensor effectively eliminated the thermal "hump" which was prominent in Figure 2a.

The final set of results to be discussed is given in Figure 6, which shows the response of the 285 Å Pd film sensor to 4% H_2 in N_2, for three separate experiments. It should be apparent that the dynamic response of the sensor is very different in the three experiments presented, although the partial pressure of hydrogen is the same. The curve with the slowest time response (#1) corresponds to the Pd film before it had been exposed to pure hydrogen. The curve with the intermediate time response (#2) had been exposed once to pure hydrogen, and the curve with the fastest response (#3) had been exposed twice to pure hydrogen. This type of film conditioning has been reported previously.[9] It is our belief that when the sample undergoes the α-β phase transition upon exposure to pure hydrogen, microcracks are formed in the Pd which increase the surface area of the Pd film. The greater disorder of the surface increases the catalytic activity of the surface with respect to the adsorption and dissociation of H_2 molecules.[13]

4. CONCLUSIONS

In this paper we have demonstrated a photopyroelectric hydrogen sensor which is sensitive to the optical absorptance of a thin Pd layer which is deposited on PVDF pyroelectric film. This device is more sensitive to changes in the optical properties of Pd than sensors which measure the reflectance of a Pd film. An elementary optical model was developed for a thin, highly-reflective metal film to show that both the absorptance and the transmittance are more sensitive to changes in the extinction coefficient than is the optical reflectance. The present PPE sensor has been characterized to a significant extent, and the thermal and chemical components

which constitute the sensor response to hydrogen gas have been effectively separated. This device is currently being optimized with respect to the Pd-layer thickness and the probe wavelength. Although the present configuration cannot sense hydrogen in nitrogen when the H_2 concentration is less than about 1%, it is believed that a judicious choice of excitation wavelength and the Pd-film thickness will allow hydrogen concentrations down to about 0.1% to be detected.

ACKNOWLEDGEMENTS

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