

Operating characteristics and comparison of photopyroelectric and piezoelectric sensors for trace hydrogen gas detection. II. Piezoelectric quartz-crystal microbalance sensor

Constantinos Christofides and Andreas Mandelis

Photoacoustic and Photothermal Sciences Laboratory, Department of Mechanical Engineering, and Center for Hydrogen and Electrochemical Studies (CHES), University of Toronto, Toronto, Ontario M5S 1A4, Canada

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A 6-MHz piezoelectric quartz-crystal microbalance coated with palladium electrodes has been used under STP gas flow-through conditions to detect hydrogen adsorption at low concentrations ($< 5\%$ in nitrogen) where anomalous behavior has been observed due to interferences from other ambient or impurity gases (mainly O_2). A systematic study showed that a concentration of 0.4% hydrogen produced no frequency shift in the sensor due to counterbalancing effects from other gases. Thus sensor sensitivity limits were established at 0.5% hydrogen, which is ~ 200 times lower than the photopyroelectric (P^2E) sensor (part I). The hydrogen selectivity of the piezoelectric sensor was found to be inferior to that of the P^2E device.

I. INTRODUCTION

One gas-detection device, which has proved to be very useful, is the piezoelectric quartz-crystal microbalance (PQCM). King¹⁻⁴ showed experimentally that a coated quartz piezoelectric crystal could be used as a sorption detector. The detector principle is well known and was described by Sauerbrey as early as 1959.^{5,6} The oscillation frequency of a quartz crystal depends on the total mass of the crystal, and that of any coating layers (or electrodes) on the crystal surfaces. When adsorbed gas molecules are absorbed in the thin coating layer, the resonance frequency decreases in proportion to the mole number of dissolved molecules. Thus the concentration of a pollutant gas is measured by detecting a change in the crystal vibration frequency.

In recent years, coated piezoelectric crystals have demonstrated good efficiency as detectors of various pollutants. Several workers⁷⁻¹¹ have used coated crystals as sensors for sulfur dioxide (SO_2) pollution. The piezoelectric sensor has also been used by Karmarkar and Guilbault for the detection of ammonia (NH_3) and nitrogen dioxide (NO_2),¹² by Hlavay and Guilbault¹³ for the detection of hydrogen chloride (HCl), and for hydrocarbon compound detection.^{14,15} The ability of coated piezoelectric crystals to detect organophosphorous compounds has also been demonstrated.^{16,17} Piezoelectric crystal detectors for explosives and mercury (Hg) have been described by several authors.^{18,19} Recently, Deakin and Byrd have used a coated quartz crystal for the detection of electroinactive cations in aqueous solution.²⁰

The high heat capacity of H_2 makes this gas an important fuel for several industries. Furthermore, critical mixtures of H_2 and O_2 are readily combustible at ambient conditions. These are two main reasons, among others, for which during recent years there has been an increased demand for continuous monitoring of hydrogen at low concentrations. As a result, a considerable research effort has been directed toward the development of hydrogen gas sensors.²¹⁻³² It is well known that palladium (Pd) has high hydrogen solubil-

ity.³³ The absorption of hydrogen by Pd during electrolysis was observed in 1868 by Thomas Graham. Since then, the palladium-hydrogen system has been studied extensively. Because of its selectivity to hydrogen absorption, Pd has been employed as a filter for hydrogen purification, and it has also been used to provide hydrogen selectivity for various hydrogen detectors.³³ Palladium is very popular as a catalyst especially because of its hydrogenation property. The absorption of hydrogen in Pd depends on temperature and hydrogen concentration. For example, at room temperature hydrogen is more than 1000 times more soluble in Pd than in Ni .³³ From 1937 until recently, several statistical models of hydrogen absorption in Pd have been developed.³⁴⁻³⁷ All these models are based on proton occupation of interstitial sites and electronic filling of the partially empty d -band states of the Pd metal, through a postulated attractive interaction between absorbed protons. Even so, the science and technology of the detection of H_2 by the piezoelectric quartz crystal coated with Pd electrodes has not progressed quite as rapidly as the other above-mentioned applications. It is likely that the complex mechanisms of the hydrogen-palladium system³³ and the strong interference of oxygen- Pd reactions³⁸⁻⁴¹ have made quantitative aspects of this investigation very problematic. Frazier and Glosser⁴² have used a quartz crystal in order to determine the quantity of hydrogen absorbed by an evaporated palladium film. Bucur and Mecea have used a PQCM at 80 °C to study the kinetics of hydrogen sorption by thin Pd layers.⁴³ The mechanism of hydrogen sorption by thin palladium layers has also been studied at a temperature of 61.1 °C.⁴⁴ Frazier and Glosser have used the piezoelectric device in order to study the pressure-concentration (P - C) isotherms for various palladium thicknesses (in the range of 60–1200 Å at 27 °C) and showed that the phase transition of the Pd depends strongly on its thickness.⁴⁵ Under ultrahigh-vacuum (UHV) conditions, Bucur has also used a PQCM in order to study the effect of CS_2 molecules on the desorption kinetics of hydrogen from a thin Pd layer at 59.6 °C.⁴⁶ Measurements for

H₂O₂ reactions using the piezoelectric quartz crystal under UHV conditions have also been performed.⁴⁷ Mecea and Bucur have used the piezoelectric device for sorption studies under dynamic conditions,⁴⁸ while Abe and Hosoya⁴⁹ have used a piezoelectric quartz crystal for the detection of flowing hydrogen both in ambient air and in nitrogen (0.5% H₂ in N₂ and in air). Their limited study, however, did not lead to definite quantitative conclusions about the hydrogen-detection capabilities and operating mechanisms of the Pd-PQCMB sensor.

In this work, we report a systematic investigation of the detection of hydrogen in a flow-through system by a Pd-coated piezoelectric quartz crystal with a view to extend and elucidate previous work mainly by Abe and Hosoya.⁴⁹ The influence of system parameters that affect the physico-chemical mechanism of the sensor response is described, and a qualitative interpretation of the resonance frequency of the quartz crystal in terms of absorbed hydrogen concentration is made using a phenomenological model of the Pd-H system. A discussion of the drawbacks of the piezoelectric detector is also reported. This paper is further intended to form a basis for comparison between the photopyroelectric (P²E) hydrogen sensor described at part I³² and the piezoelectric sensor and to answer several questions concerning the anomalous behavior of this type of sensor at low hydrogen concentrations, which were left unanswered by previous workers.⁴⁹

II. THEORETICAL BACKGROUND

The resonant frequency of a quartz crystal is dependent on the geometric dimensions of the quartz plate and the thickness of its electrodes. The principle of the quartz-crystal sorption detectors is simple: When gas molecules are absorbed in a thin coating layer, which is chosen according to the desired gas selectivity on a quartz-crystal surface, the decrease in resonance frequency is in proportion to the quantity of dissolved molecules. The theory, which is outlined below, was originally developed by Sauerbrey.^{5,6} The application of an electrical field on the quartz crystal gives rise to a resonance frequency F , which can be expressed as^{50,51}

$$F = N/z, \quad (1)$$

where N is a frequency constant equal to half of the transverse wave-propagation velocity in the plane of the crystal, and z is the thickness of the crystal. The relation between the frequency change ΔF and the crystal thickness variation Δz is given by^{5,6}

$$\frac{\Delta F}{F} = -\frac{\Delta z}{z}. \quad (2)$$

Equation (2) can also be written as

$$\frac{\Delta F}{F} = -\frac{\Delta M}{\rho A z}, \quad (3)$$

where ΔM is the change of the mass of the quartz crystal due to the absorption of the gas, A is its surface area and ρ is the density of the quartz ($= 2.6 \text{ g cm}^{-3}$).⁵⁰ Using the frequency constant $N = 0.1679 \text{ MHz cm}^{-1}$ for AT-cut quartz,⁵ one finds

$$\Delta F (\text{Hz}) = -2.3 \times 10^6 F^2 \frac{\Delta M}{A}, \quad (4)$$

where now F is the resonant frequency (MHz) of the crystal in the absence of a gas absorption, ΔM is the mass of the absorbed gas molecules (g), and A is the total surface area (cm²). The minus sign conveniently indicates a decrease of F with increasing mass of the quartz crystal. Equation (4) can also be expressed as a function of concentration¹⁴:

$$\Delta F = -K_c \Delta C, \quad (5)$$

where K_c is a constant related to the resonant frequency of the coated quartz plate, and it includes a conversion factor between the mass of the absorbed gas (g) and the concentration ΔC (ppm or %), of the gas in the gas phase. Thus Eq. (3) becomes

$$\frac{\Delta F}{F} = -\frac{\Delta M}{M}, \quad (6)$$

where the total mass before any absorption of gas is⁵⁰ $M = M_{\text{PG}} + M_{\text{Pd}}$; M_{PG} is the mass of the piezoelectric crystal and M_{Pd} is the mass of the chemically sensitive layer (Pd in this case). For the experiments reported below, the minimum measurable frequency shift was on the order of 1 Hz. The mass of our Pd-coated quartz crystal was approximately 89 mg and its resonant frequency F was 6 MHz. Under these conditions, Eq. (6) shows that the minimum detectable mass of absorbed gas by the Pd layer is $\Delta M \approx 1.5 \times 10^{-8} \text{ g}$. To the best of the authors' knowledge, the theoretical detection limit for the piezoelectric quartz-crystal detector has not been calculated rigorously. Sauerbrey estimated this limit to be approximately 10^{-12} g .⁶ King's estimation was approximately 10^{-9} g .¹ It is obvious from Eq. (6) that mass sensitivity is better for detectors with high resonance frequency F .

III. EXPERIMENTAL APPARATUS

A system has been constructed which allowed us to test the response of the piezoelectric sensor to flows of H₂-N₂ mixtures, with H₂ concentrations ranging from pure nitrogen to pure hydrogen, i.e., in the 0–100-kPa hydrogen partial pressure range. The system consisted of four subsystems: gas control, temperature control, test cell, and shift frequency analysis instrumentation. The fourth subsystem was in addition to the set-up for photopyroelectric detection described in Fig. 1 of part I.³²

The temperature control system ensured that the temperature of the incoming gas flow would be the same as that of the sensor itself. A heat-exchange coil was installed on the gas mixture line, upstream from the test cell. The test cell and heat-exchange coil were suspended in a water bath to equalize their temperatures. A similar configuration was reported earlier.⁴⁹ The effect of temperature on Pd-PQCMB sensor is very important: (i) the quartz crystal shows a frequency shift with temperature change,⁵¹ and (ii) it is well known that the solubility of H₂ in Pd decreases very fast with decreasing temperature in the range of 0–100 °C.^{33,37}

The test cell was the heart of the experimental system, containing the Pd-coated piezoelectric quartz microbalance (Pd-PQCMB) detector. It consisted of a pressure vessel, which contained the piezoelectric quartz-crystal detector along with the Pd-P²E sensor of part I.³² The thickness of the

Pd coating/electrode was approximately 800 Å, deposited by a sputtering technique on both sides. The experimental setup of the reference piezoelectric quartz-crystal detector is shown schematically in the lower right-hand corner of Fig. 2, part I.³² The piezoelectric instrumentation consisted of an oscillator powered by a regulated power supply. The applied voltage was kept constant at +15 V dc. The frequency output from the oscillator was measured by a frequency counter with a resolution of 1 Hz. The response of the Pd-PQCMB sensor could be observed as a change in the resonance frequency of the crystal,^{5,6} in agreement with the simple theoretical considerations presented above.

IV. RESULTS AND DISCUSSION

Initially, the Pd-PQCMB sensor was left for several days under ambient conditions in order to observe the influence of atmospheric air on the catalyst. Afterwards, hydrogen ($[H_2] = 30\%$ in N_2) was introduced into the test cell. Figure 1 shows the variation of the resonance frequency (an increase in ΔF) as a function of time. A signal decay toward the base line was observed upon closing the inlet valve and evacuating the test cell, as expected. The phenomenon of a positive ΔF shift upon H_2 exposure is surprising in the light of the simple accepted theory presented in Sec. II above; however, it has already been observed by Abe and Hosoya⁴⁹ who used as flowing gas mixtures of hydrogen 0.5% in air and nitrogen. It has been hypothesized⁴⁹ that the ambient oxygen plays an important role in the Pd-PQCMB response: Preadsorbed O_2 on the Pd surface reacts with the introduced H_2 gas and forms H_2O which leaves the Pd surface via evaporation. Therefore, the weight of quartz crystal decreases as a result of the H_2 and O_2 reaction, which is consistent with a positive ΔF . Vannice, Benson, and Boudart⁴⁰ have studied the absorption of H_2 and O_2 on platinum black. The great similarity between Pt and Pd allows a reasonable comparison to be made between the results by Vannice and co-workers, the hypothesis put forth by Abe and Hosoya,⁴⁹ as

well as the present results. According to these authors,⁴⁹ the water formed during the reaction leaves the surface, and in doing so, it is not replaced by additional hydrogen. The following empirical chemical reactions describe the possible mechanism on the Pd surface⁵²: Dissociation and recombination of oxygen:



dissociation and recombination of hydrogen:



and finally water formation:



According to Ponec, Knor, and Cerny,³⁸ the reaction between hydrogen and oxygen at the Pd surface at 0 °C goes to completion producing desorbable water, in agreement with the last step, reaction (7d), of the four-step mechanism (7). However, according to Lundström, Armgarth, and Petersson,⁵² the details of the water production reactions on the palladium layer are still not known. This phenomenon turned out to be a significant disadvantage of the piezoelectric quartz-crystal detector compared to its photopyroelectric counterpart. The results obtained with the 30% H_2 in N_2 (Fig. 1) indicate that gas impurities in the flowing gas mixture, notably oxygen, may play the dominant role in the response of the sensor.

At the end of the first experiment ($[H_2] = 30\%$), the cell was evacuated, then purged, and pure hydrogen was introduced immediately afterwards (Canadian Liquid Air: ultrahigh purity 99.999%). Figure 1, $[H_2] = 100\%$ curve, shows a resonance frequency decrease as a function of time. ΔF reached saturation after 2.5 min following exposure of the sensor to pure hydrogen at a flow rate of 500 mℓ/min. In the presence of pure hydrogen gas, the negative ΔF is indicative of hydrogen absorption as the dominant mechanism responsible for the resonance frequency shift. A comparison of

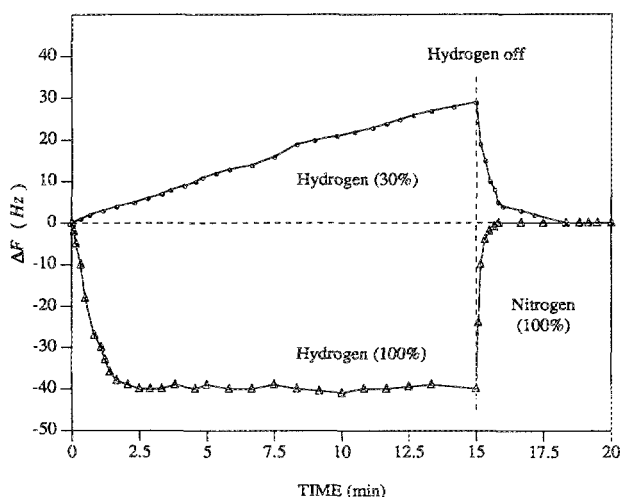


FIG. 1. Piezoelectric quartz-crystal responses as a function of time, for two different concentrations of hydrogen in nitrogen: 30% and 100%. The test cell was exposed for several days to the laboratory ambient air before the first experiment (flow rate: 500 mℓ/min; $T = 20^\circ\text{C}$).

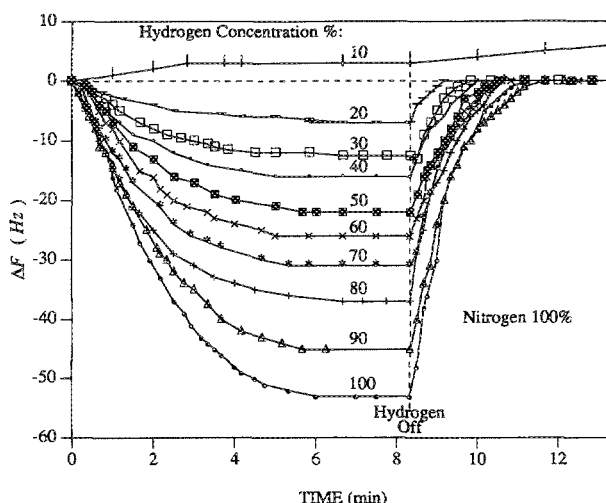


FIG. 2. Piezoelectric quartz-crystal response as a function of time, for various concentrations of hydrogen in nitrogen: 10%–100% hydrogen (flow rate: 500 mℓ/min; $T = 20^\circ\text{C}$). Data taken after the exposures indicated in Fig. 1.

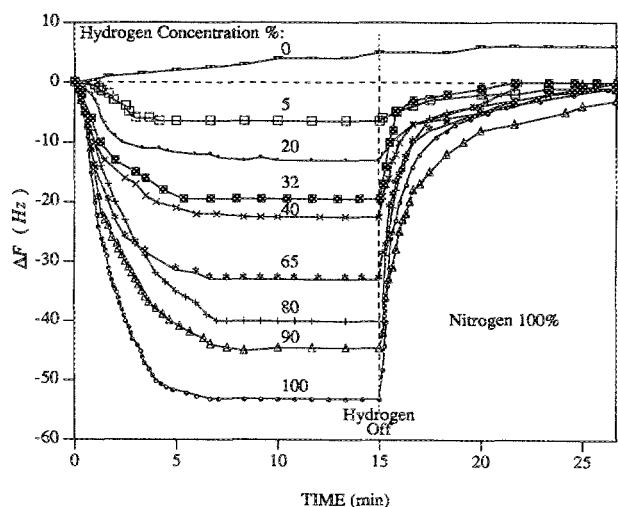


FIG. 3. Piezoelectric quartz-crystal response as a function of time, for various concentrations of hydrogen in nitrogen: pure nitrogen to pure hydrogen (flow rate: 500 m³/min; $T = 20^\circ\text{C}$). Data taken after the exposures indicated in Fig. 2.

the 30% and 100% $[\text{H}_2]$ response curves of Fig. 1 demonstrates, for the first time, the importance and extent of the interference of ambient species other than H_2 in determining the Pd-PQCMB behavior with respect to nonpure hydrogen flows.

Details of intermediate experimental Pd-PQCMB responses are shown in Figs. 2–4 for various hydrogen concentrations after the first exposure experiment of the Fig. 1. Figure 2 shows piezoelectric responses as functions of time under the same temperature and flow rate conditions. At times between 0 and 8.3 min the prescribed concentration of hydrogen was introduced into the test cell. We note that because of the introduction of a certain partial pressure of H_2 in N_2 the resonance frequency decreases to a steady-state

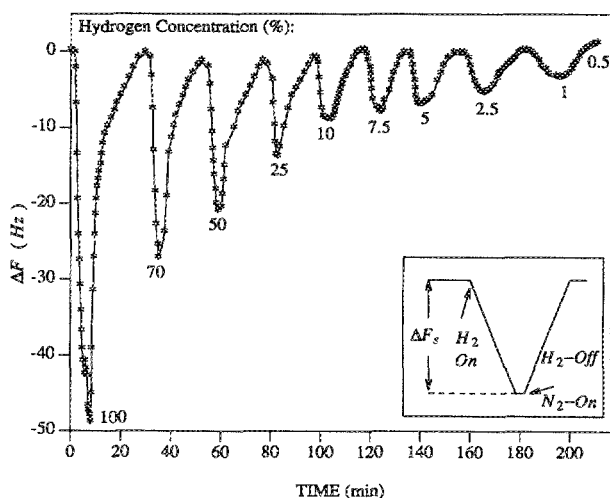


FIG. 4. Piezoelectric quartz-crystal response as a function of time, for various concentrations of hydrogen in nitrogen: 0.5%–100% hydrogen (flow rate: 500 m³/min; $T = 20^\circ\text{C}$). Data taken after the exposures indicated in Fig. 3. After those exposures the sensor exhibited reproducible response independent of exposure number. Inset: definition of ΔF_s .

value, which seems to represent the equilibration of the Pd layer with the ambient H_2 gas. After a few minutes of saturation, pure N_2 was allowed to flow through the cell, until the complete removal of the absorbed hydrogen. At first, the experiment was performed at 10% hydrogen. A positive ΔF was observed due to severe interference from other ambient gases (mainly O_2), which dominated detector response. On the other hand, concentrations 20% and higher exhibited negative ΔF as a function of time. Interestingly, for pure hydrogen, the saturation ΔF (ΔF_s) is ca. -53 Hz , i.e., greater than the saturation frequency $\Delta F_s = -40\text{ Hz}$ of the first exposure experiment (Fig. 1, $[\text{H}_2] = 100\%$ curve). This discrepancy indicates enhanced Pd sensitization, upon removal of the ambient oxygen and other gases following the first Pd-PQCMB exposure experiment. Figures 2 and 3 confirm the increase of the Pd surface activity, resulting in ΔF_s increases with increasing exposures to H_2 . In fact, comparing the shift frequency variations of Figs. 2 and 3, we note that ΔF_s at a given $[\text{H}_2]$ is greater for the latter. This is so because, in the case of the experiments presented in Fig. 3, the test cell was purged with N_2 until a constant base-line value was achieved before the introduction of H_2 . Sermon⁴¹ has previously mentioned this phenomenon concerning the reactivity of Pd surface after several exposures to hydrogen. The first experiment of Fig. 3 was performed with the introduction to the test cell of pure nitrogen (see Fig. 3, curve 0). The introduction of pure nitrogen to the test cell was found to increase F , due to its Pd surface cleaning role. The main result presented in Fig. 3 is that the introduction of 5% hydrogen gas in the test cell was capable of producing a negative ΔF shift of -7 Hz in counterbalancing the increase in ΔF due to the surface cleaning role of nitrogen, presumably, according to reactions (7a)–(7d). A concentration of 0.4% hydrogen was found to produce no ΔF shift from the zero base line. Figure 4 shows the magnitude of the variation of F for hydrogen concentrations ranging from 100% to 0.5%. The negative values of ΔF may be noted for all $[\text{H}_2]$ concentrations, except for $[\text{H}_2] = 0.5\%$. At that concentration, trace oxygen (and perhaps other gas impurity) interference becomes important in determining the value and sign of ΔF . Therefore, 1%–0.5% hydrogen was taken to define the sensitivity limit of the Pd-PQCMB sensor under flow-through conditions in nitrogen. This value represents a working figure of merit for comparison with the photopyroelectric detector of part I.³²

The relationship between gas concentration and Pd-PQCMB detector response, ΔF_s , is an important parameter for sensor characterization. Figure 5 shows the variation of saturation resonance frequency, ΔF_s , as a function of gas-phase hydrogen concentration, using data from Figs. 2–4. Unlike the prediction of Eq. (5), there are three apparent response regimes: a nonlinear one at concentrations between 20% and 70%, and two linear regimes at low ($< 20\%$) and high ($> 70\%$) concentrations, a region where all experimental curves converge. This convergence of all the experimental data can be explained by assuming that at high pressures the adsorbed and absorbed hydrogen dominates all other interfering phenomena. The presence of trace oxygen is thought to be partly responsible for the deviation of the

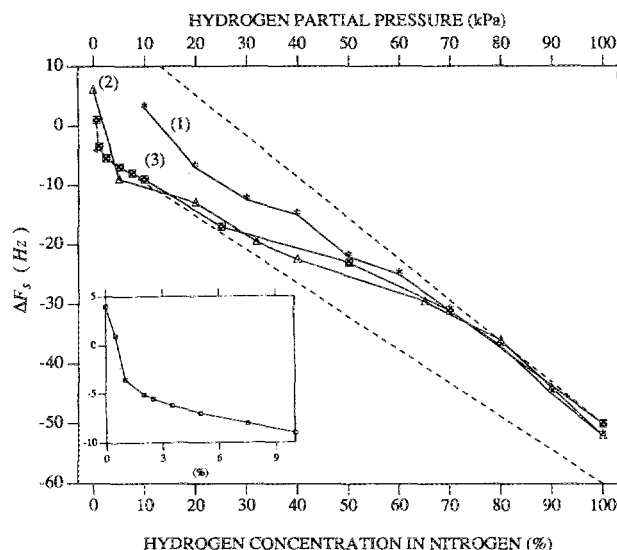


FIG. 5. Variation of the saturation resonance frequency shift ΔF_s with hydrogen concentration (or partial pressure); curve (1): data collected from Fig. 2; curve (2): data collected from Fig. 3; curve (3): data collected from Fig. 4. Inset: ΔF_s vs hydrogen concentration in the range of 0%–10%. Data collected from curve (3).

Pd-PQCMB sensor response at low concentrations. The purging history of the test cell plays an important role in determining the $\Delta F_s([H_2])$ curve at lower ($<70\%$) concentrations. In Fig. 5, curve (1) was obtained from the original exposure where the presence of ambient air before the onset of the experiment was significant: ΔF_s is consequently smaller than that of curves (2) and (3) where the cell was purged with N_2 before the experiment. In any event, all curves show significant deviations from linearity at low H_2 concentrations, which are a strong function of the cell's purging history. An important factor is the initial irreversible sensitization of the Pd-PQCMB surface with increasing degree of exposure to hydrogen flow. The low concentration anomalous behavior [between 20% and 70% [see Fig. 5, curves (2) and (3)]] could be due to a phase transition. The $\alpha \rightarrow \beta$ phase transition takes place around 20 kPa. According to Lundström and co-workers,⁵² it is probable that a phase transition from α to β may take place at low temperatures and high concentrations (1%–100%).⁵² This is in disagreement with several publications^{33,45} which show the possibility that at room temperature the phase transition takes place around 2% (2 kPa). It is also well known that the phase transition depends on the palladium thickness,⁴⁵ a complicating factor: Frazier and Glosser⁴⁵ used a PQCMB and showed that the phase change in Pd depends strongly on its thickness. Another problem for a quantitative analysis may be the presence of water on the Pd layer at room temperature. This could cause the Pd layer to be saturated at low pressures, as was observed in studies under UHV conditions.⁵²

Figures 6 and 7 show the variation of ΔF as a function of time, for various H_2 flow rates. It was found that the flow rate does not influence ΔF_s very much. Saturation occurs essentially at the same level, with the ΔF_s value being attained earlier at higher flow rates, as expected. The steeper

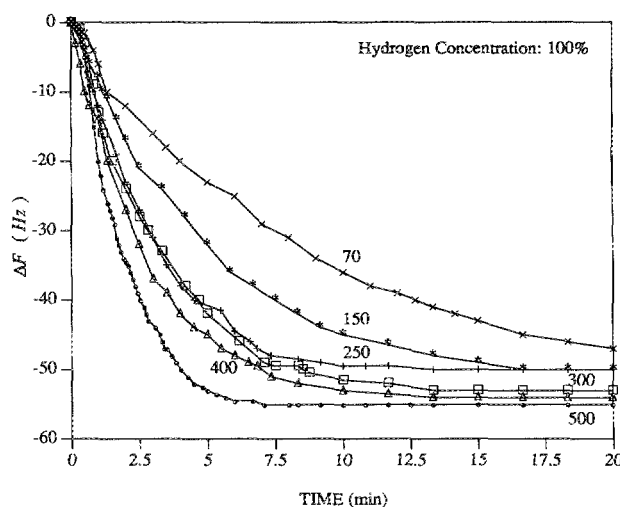


FIG. 6. Resonance frequency shift variation as a function of time at 100% H_2 for various flow rates: 70–500 $m\ell/min$. The hydrogen was turned on at $t = 0$ min ($T = 20^\circ C$).

ΔF decreases in the absence of contaminant ambient gases (Fig. 6) are consistent with the tendency of such gases, mainly oxygen, to prevent hydrogen retention thus raising the base-line resonant frequency (Fig. 7) in comparison to pure H_2 ambient after equal exposure intervals. We note that, while in Fig. 7 ($[H] = 5\%$) the saturation is between 8 and 12 min along the base line, in Fig. 6 ($[H] = 100\%$) the same degree of saturation has not been achieved even after 17–20 min. This phenomenon is quite surprising under the light of theory concerning the piezoelectric detection. However, this observation could be explained by the fact that it is possible that at low concentrations the presence of the impurities, which have a strong influence at low concentrations, produces adsorbed layers which saturate the Pd surface, leading to no possibility of further hydrogen adsorption.

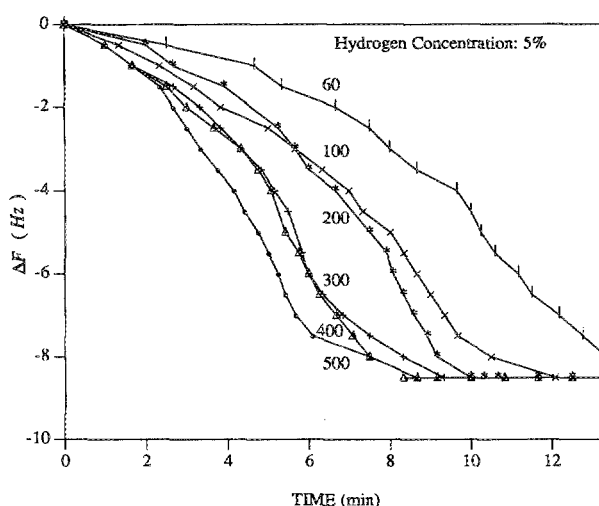


FIG. 7. Resonance frequency shift variation as a function of time at 5% H_2 for various flow rates: 60–500 $m\ell/min$. The hydrogen flow was turned on at $t = 0$ min ($T = 20^\circ C$).

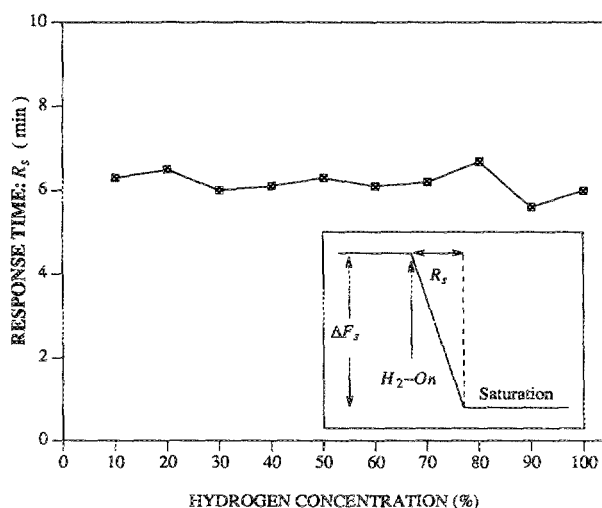


FIG. 8. Variation of response time R_s as a function of H_2 concentration ($T = 20^\circ\text{C}$). Inset: definition of R_s .

Figure 8 shows the response time R_s as a function of H_2 concentration. The response time is defined as the time which is required for the rising signal to reach steady state. The H_2 concentration does not drastically influence the response time. On the other hand, the flow rate of carrier gas has a direct effect on response time (Fig. 9): The response time R_s of the sensor increases monotonically with decreasing flow rate between 500 and 60 ml/min. These observations indicate that dynamic processes related to the hydrogen residence time on, and removal from, the Pd-surface may be rate limiting of mass transport to the Pd-bulk where gaseous mass accumulation is expected to generate the signal. On the other hand, the front exposed surface is continuously in equilibrium with the ambient hydrogen and the Pd-quartz interface and thus with the entire bulk, as well. The equilibrium reactions have been described by Lundström in great detail.⁵²

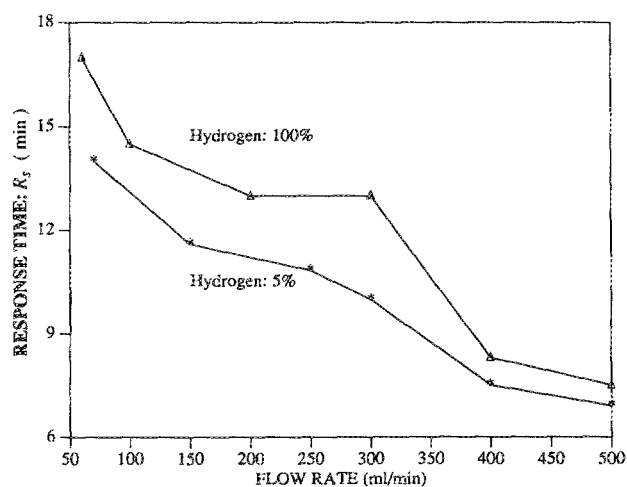


FIG. 9. Variation of response time R_s as a function of flow rate. $T = 20^\circ\text{C}$.

V. CONCLUSIONS

In this work we have studied the hydrogen detection characteristics of a palladium-coated piezoelectric crystal at room temperature. In addition, we have discussed the absorption properties of hydrogen by palladium deposited on the sensor and identified for the first time the limitation of the sensor sensitivity to H_2 under flow through conditions, due to its nonselective response to the absorbed mass of other ambient gases.

The main results of this study can be summarized as follows: (1) From the point of view of the mechanism of the Pd-PQCMB detector operation, a qualitative understanding has been achieved by showing agreement of simple gas-surface interactions with our experimental observations of the effects of ambient gaseous impurities, such as O_2 , on the resonant frequency shift of the detector. This frequency shift is quite difficult to model especially at low concentrations at room temperature as is the case with some of our experiments, since the presence of water on the Pd layer is probable. (2) The influence of ambient gases, especially O_2 on the piezoelectric quartz sensor response indicates an important disadvantage of this sensor. In fact, the piezoelectric sensor could give a false alarm if used under ambient conditions where oxygen abounds. This problem could only be solved by venting the area of interest (room, building, etc.) with a neutral gas (such as N_2) for 1 or 2 h before the setting up of this sensor as an alarm. This is, of course, simple for laboratory conditions, but cumbersome if not entirely unrealistic for field applications. Another solution would be to use a molecular diffusion oxygen filter. However, that could also slow down the access of hydrogen to the sensor, which surely would delay the response time of the sensor. Furthermore, it is not certain that other ambient gases besides O_2 do not contribute to sensor response, rendering its selectivity to trace H_2 gas altogether questionable. The present ambient gas interference effects confirm observations made by Sermon⁴¹ such as the effects on the surface condition of a Pd sample, which is covered initially by a monolayer of chemisorbed oxygen. (3) In terms of its sensitivity, the sensor presents a lower limit under flow-through conditions around $[H_2] = 0.5\%$, which is too high compared to the P²E hydrogen detector (part I)³² and other solid-state detectors.

The two parts of this work make possible the direct comparison of the piezoelectric and photopyroelectric sensors: The two sensors were in the same test cell and thus all experiments were performed under the same conditions. A quantitative comparison of the important parameter sensitivity of the sensor shows directly the superiority of the P²E device over the piezoelectric one: The experimental sensitivity of the photopyroelectric sensor appears to be 200 times higher than that of the piezoelectric device at room temperature. In addition, the interference of oxygen (20.94% in air), and perhaps other trace ambient gases (such as CO_2 , 0.033% in air) with the signal generation mechanism of the Pd-PQCMB sensor, renders the P²E device much more desirable for trace hydrogen environmental applications due to its superior H_2 gas selectivity.

The main discussion in these two papers (parts I and II) concerned the functional dependence of the photopyroelec-

tric and piezoelectric responses on hydrogen concentration: In part I we hypothesized that the P²E response was caused by concentration of the hydrogen atoms in the bulk, a function of the heat of dissociation of the H₂ molecule at the Pd surface, and selective interaction with the dipolar field at the Pd-PVDF interface. It appears that the very high selectivity of the P²E sensor to trace H₂ gas is due to the Pd-PVDF interfacial character of the interaction with atomic H or H⁺, with all other interfering ambient gases having been screened out by the bulk Pd film lattice in a manner similar to the Pd-MOSFET interface.⁵² On the other hand the piezoelectric response depends on the weight of any absorbed atom. Therefore, it is obvious that in the presence of interfering gases interacting with the Pd surface, the piezoelectric sensor could be definitely influenced by their molecular weights as a gas-Pd surface active device.

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- ¹W. H. King, *J. Anal. Chem.* **36**, 1735 (1964).
- ²W. H. King, *Res. Dev.* **20**, 28 (1969).
- ³W. H. King, *J. Environ. Sci. Technol.* **4**, 1136 (1970).
- ⁴W. H. King, in *Vacuum Microbalance Techniques*, edited by A. W. Czanderna (Plenum, New York, 1981), Vol. 8, p. 183.
- ⁵G. Z. Sauerbrey, *Z. Phys.* **155**, 206 (1959).
- ⁶G. Z. Sauerbrey, *Z. Phys.* **178**, 457 (1964).
- ⁷A. L. Roman and G. G. Guilbault, *Anal. Lett.* **5**, 225 (1972).
- ⁸M. W. Frechette and J. L. Fasching, *Environ. Sci. Technol.* **7**, 1135 (1973).
- ⁹F. W. Karasek and J. M. Tiernay, *J. Chromatogr.* **89**, 31 (1974).
- ¹⁰J. L. Cheney and J. G. Homolya, *Anal. Lett.* **8**, 175 (1975).
- ¹¹K. H. Karmarkar, L. M. Webber, and G. G. Guilbault, *Anal. Chem. Acta* **81**, 265 (1976).
- ¹²K. H. Karmarkar and G. G. Guilbault, *Anal. Chem. Acta* **75**, 111 (1975).
- ¹³J. Hlavay and G. G. Guilbault, *Anal. Chem.* **50**, 965 (1978).
- ¹⁴W. M. Shackelford and G. G. Guilbault, *Anal. Chem. Acta* **73**, 383 (1974).
- ¹⁵F. W. Karasek and J. M. Tiernay, *J. Chromatogr.* **89**, 31 (1974).
- ¹⁶E. P. Scheide and G. G. Guilbault, *Anal. Chem.* **44**, 1764 (1972).
- ¹⁷G. G. Guilbault and Y. Tomita, *Sensors Actuators* **2**, 43 (1981).
- ¹⁸Y. Tomita, M. H. Ho, and G. G. Guilbault, *Anal. Chem.* **51**, 1475 (1979).
- ¹⁹M. Janghorbani and H. Freund, *Anal. Chem.* **45**, 325 (1973).
- ²⁰M. R. Deakin and H. Byrd, *Anal. Chem.* **61**, 290 (1989).
- ²¹T. Seiyama and S. Kagawa, *Anal. Chem.* **38**, 1069 (1966).
- ²²P. J. Shaver, *Appl. Phys. Lett.* **11**, 255 (1967).
- ²³H. Obayashi, Y. Sakurai, and T. Gejo, *J. Solid State Chem.* **17**, 299 (1976).
- ²⁴K. I. Lundström, M. S. Shivaraman, and C. M. Svensson, *J. Appl. Phys.* **46**, 3876 (1975).
- ²⁵K. I. Lundström, M. S. Shivaraman, and C. M. Svensson, *Surf. Sci.* **64**, 497 (1977).
- ²⁶M. C. Steele and B. A. MacIver, *Appl. Phys. Lett.* **28**, 687 (1976).
- ²⁷T. Yamamoto and M. Morimoto, *Appl. Phys. Lett.* **20**, 269 (1972).
- ²⁸T. L. Poteat and B. Lalevic, *IEEE Trans. Electron Devices* **ED-29**, 123 (1982).
- ²⁹A. D'Amico, A. Palma, and E. Verona, *Appl. Phys. Lett.* **41**, 3 (1982).
- ³⁰M. A. Butler, *Appl. Phys. Lett.* **45**, 10 (1984).
- ³¹A. Mandelis and C. Christofides (unpublished).
- ³²C. Christofides and A. Mandelis, *J. Appl. Phys.* **66**, 3975 (1989).
- ³³F. A. Lewis, *The Palladium/Hydrogen System*, (Academic, New York, 1967).
- ³⁴J. R. Lasher, *Proc. R. Soc. London* **161**, 525 (1937).
- ³⁵D. H. Everett and P. Nordon, *Proc. R. Soc. London A* **259**, 341 (1960).
- ³⁶J. W. Simons and T. B. Flanagan, *Can. J. Chem.* **43**, 1665 (1965).
- ³⁷J. W. Simons and T. B. Flanagan, *J. Phys. Chem.* **69**, 3773 (1965).
- ³⁸V. Ponc, Z. Knor, and S. Cerny, *Discuss. Faraday Soc.* **41**, 149 (1969).
- ³⁹J. Llopis, *J. Catal. Rev.* **2**, 161 (1968).
- ⁴⁰M. A. Vannice, J. E. Benson, and M. Boudart, *J. Catal.* **16**, 348 (1970).
- ⁴¹P. A. Sermon, *J. Catal.* **24**, 460 (1972).
- ⁴²G. A. Frazier and R. Glosser, *J. Phys. D* **12**, L113 (1979).
- ⁴³R. V. Bucur, V. Mecea, and T. B. Flanagan, *Surf. Sci.* **54**, 477 (1976).
- ⁴⁴R. V. Bucur, V. Mecea, and E. I. Indrea, *J. Less-Common Met.* **49**, 147 (1976).
- ⁴⁵G. A. Frazier and R. Glosser, *J. Less-Common Met.* **74**, 89 (1980).
- ⁴⁶R. V. Bucur, *J. Catal.* **70**, 92 (1981).
- ⁴⁷B. Kasemo and E. Tornqvist, *Phys. Rev. Lett.* **44**, 1555 (1980).
- ⁴⁸V. Mecea and R. V. Bucur, *J. Vac. Sci. Technol.* **17**, 182 (1980).
- ⁴⁹S. Abe and T. Hosoya, in *Proceedings of the 5th World Hydrogen Energy Conference*, Toronto, Canada, 15–20 July 1984, Vol. 4, p. 1893.
- ⁵⁰A. Kindlund and I. Lundström, *Sensors Actuators* **3**, 63 (1982).
- ⁵¹J. N. Zemel, in *Solid State Chemical Sensors*, edited by J. Janata and R. J. Huber (Academic, New York, 1985), p. 163.
- ⁵²I. Lundström, M. Armgarth, and L. G. Petersson, *CRC Crit. Rev. Solid State Mater. Sci.* **15**, 201 (1989).