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Photopyroelectric detection of hydrogen/oxygen mixtures

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It has been found that the photopyroelectric (PPE) sensor made of thin film polyvinylidene fluoride (PVDF), sputter-coated with palladium, can detect trace hydrogen gas in the presence of pure oxygen without significant drift and stabilization problems. Presently, hydrogen concentration as low as 0.1% in flowing 99.9% oxygen has been detected under STP conditions. The detector has been used without a reference sensor (single-ended mode) which simplifies the sensor system compared to previous work.

I. INTRODUCTION

Sometime ago, in our laboratory, we undertook the task of developing and optimizing a fast, sensitive, and inexpensive photopyroelectric (PPE) sensor for trace hydrogen gas detection at room temperature [1-6]. During that time the base objective was to discover and prove the hydrogen sensing ability of the new device under ideal experimental conditions such as: (a) clean palladium surfaces; (b) room temperature; and (c) the minimization of any environmental impurities, in order to detect hydrogen in nitrogen ambient [1,2]. In 1990 in an extensive review paper a critical comparison between the new PPE hydrogen sensor and other conventional devices was presented [7]. Significant progress has been made both in the development and in the optimization of the new device [8], as well as towards the understanding of the relevant physical mechanisms [9]. The PPE detector was found capable of operating within a broad range of temperatures (+53 to -60°C) with good prospects down to that of liquid nitrogen [8-10]. Broader interest in this photothermal device has been shown and different versions of our PPE sensor were already constructed and used [11].

Recently, hydrogen detection was studied under simulated ambient air conditions. This paper describes new results concerning PPE hydrogen sensor used for detection of various hydrogen concentration in oxygen.

2. EXPERIMENTAL APPARATUS

An experimental system that allowed us to test the response of the Pd-PVDF photopyroelectric sensor to flows of hydrogen, oxygen, nitrogen, and hydrogen/oxygen mixtures, with hydrogen concentrations ranging from 1000 ppm to pure hydrogen has been constructed. The system consists of four parts; gas control; external temperature control, and test cell (internal) temperature control; fiber optic and laser system; and

finally signal generation and analysis as shown in Fig. 1. Three different types of signals have been monitored:

$$S_A = \frac{A}{R} \quad \Delta S_R = \frac{A - B}{R} \quad \text{and} \quad \Delta S_B = \frac{A - B}{B} \quad (1)$$

where A and B are the signals obtained by the active and reference detector, respectively, and R is the *a.c.* laser power reference output obtained from a photodiode. More details on the signal generation and analysis are given in previous reports [1,2].

Fig. 1 Schematic diagram of PPE gas sensor set-up.

3. DETECTION OF HYDROGEN/OXYGEN MIXTURES

Figure 2 shows a typical PPE response as a function of time. Before each experiment the detector was cleaned for 30 minutes with pure oxygen. Then hydrogen (500 ml/min) at the prescribed flow rate was admitted to the test cell. Similar results were obtained through cycling with other $[H_2]/[O_2]$ ratios. In Fig. 2 it is seen that after the interruption of H_2 and introduction of pure oxygen, there appears an intermediate signal "induction" period before the signal reaches the saturation level(s). At low $[H_2]$ concentrations in hydrogen/oxygen mixtures, the presence of this induction period is not well pronounced. It is probable that this signal saturation delay observed in the case of high concentrations of hydrogen in oxygen is due to the production of water on the Pd surface. If so, there is no evidence of cumulative surface water effect on the reversibility of the signals. Another possibility for the observed induction period might be the phase transition of Pd (from α to β) form in the presence of hydrogen in the bulk. This effect, however, is known to occur at lower hydrogen concentrations (≤ 2000 ppm) [12] and has not been observed with the photopyroelectric sensor in H_2/N_2 mixtures in the concentration range of 0.1 - 100% [2]. Fig. 3 shows the variation of the saturated photopyroelectric signal, $\Delta S_s = (S_A)_s$, as a function of hydrogen concentration. Note that ΔS_s increases monotonically when hydrogen concentration increases, while the signal associated with the lowest (0.1%) hydrogen concentration is not believed to be an absolute minimum. Differential signal detection is expected to improve this sensitivity limit.

The Pd -PPE sensor shows excellent reproducibility of the PPE saturated signal ΔS_s after many cycles of exposure to hydrogen ($[H] = 50\%$) at room temperature and opens the way for photopyroelectric measurements under real, rather than simulated ambient conditions. The sensitivity of 1000 ppm in O_2 under simulated dynamic flow-through ambient air conditions is a very promising step toward the establishment of a continuously monitoring H_2 sensor operating at room temperature and atmospheric

conditions including the outdoors. The experiments performed under several hours and duty cycles prove that such a device could serve as a valuable, real-time detector of hydrogen. Signal stability improves in time following the system turn on.

Fig. 2 Photopyroelectric signal ratio (A/R) as a function of time for gaseous mixture containing 50% hydrogen in oxygen.

Fig. 3 Photopyroelectric saturated signal (ΔS_s) as a function of hydrogen concentration $[H]$. The solid lines represent error at low and at high concentrations.

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