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THERMOPHYSICAL RESPONSE OF A SOLID-STATE THERMAL-WAVE PYROELECTRIC-FILM SENSOR TO NATURAL GAS AND METHANE

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Abstract—A novel type of gas sensor based on a pyroelectric thin-film transducer under a.c. thermal excitation was studied. The pyroelectric film is deposited onto a dielectric material (substrate) and this film is sandwiched between two metal electrodes. The low frequency thermal wave is generated by passing a current through a strip-shaped resistive film that is deposited on the opposite side of the substrate. The response of the sensor to natural gas and high purity methane was examined. It was found to be reversible, reproducible, and symmetric when the natural gas was cycled. The sensor was able to detect a wide range of natural gas and methane concentrations in nitrogen (2.5–100% vol.) and its response was linear with increasing concentrations for both gases. The results have important implications for the monitoring of natural gas composition and the development of fuel management systems in natural gas fueled vehicles. Copyright © 1996 International Association for Hydrogen Energy

INTRODUCTION

The composition of natural gas varies widely across North America. This variation in composition has been well documented in the literature [1, 2]. The major component in natural gas is methane (typically 85–99%). Other light hydrocarbons (C_2–C_5), nitrogen, carbon dioxide, water, traces of sulfur and odorants such as ethyl mercaptan make up the difference. Recent legislation in the U.S. and Canada mandating the use of alternative fuels has provided an incentive for research and development of natural gas as an alternative fuel for vehicles. As this technology develops, it is important to take into account the variation of natural gas composition to provide reliable natural gas vehicle operation. Since gaseous fuels for vehicles have only emerged recently, it will take some time to develop suitable engine control systems. Most of the effort in this respect has been concentrated in adopting fuel management systems used in gasoline and diesel fueled vehicles [3]. However, some work has recently been done in the development of other gaseous fuel composition and quality sensors [4]. This paper examines a novel gas sensor based on a pyroelectric thin-film under a.c. thermal excitation [5] and its possible application to resolve natural gas composition. Among the advantages of this sensor are: its high signal-to-noise ratio since its pyroelectric signal can be easily measured by a lock-in amplifier; and its capability to detect a wide range of natural gas and methane concentrations in nitrogen.

SENSOR DESIGN AND EXPERIMENTAL ARRANGEMENT

The sensor, shown in cross section in Fig. 1, is based on a pyroelectric thin-film transducer operating under a.c thermal excitation. For this reason, it will be referred to as the Thermal Wave Pyroelectric Film Sensor (TWPFS). The pyroelectric film is deposited onto a dielectric substrate and is sandwiched between two metal film electrodes. It can be excited by a low frequency thermal wave. This thermal wave is generated by passing a current through a strip-shaped resistive film that is deposited on the opposite side of the substrate. The pyroelectric film material used in the sensor is an organic crystalline (spatially oriented) film which differs substantially from its commonly used inorganic analogs CdS, ZnO and AlN. From the molecular point of view, it is a polycyclic organic compound (POC) that includes $-NH_2$ groups. The POC crystals belong to the non-centrosymmetric polar mm2 point group and hence they possess both piezoelectricity and pyroelectricity. The film consists of spherolite blocks of typical dimensions 0.2–0.5 mm, each with its own orientation. In spite of the spatial inhomogeneity, the POC film exhibits very high pyro-

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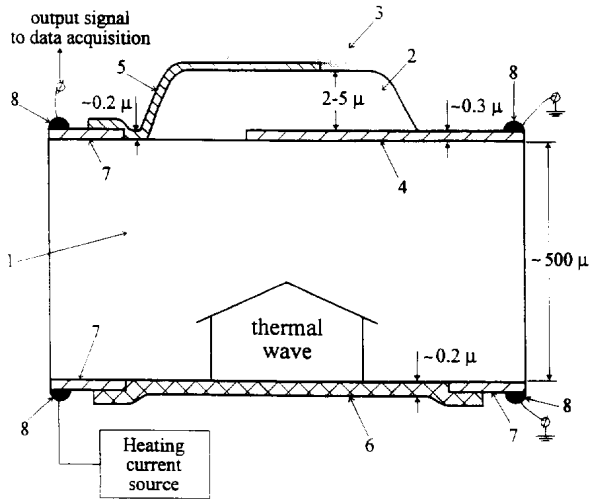

Fig. 1. Side view cross section of the thermal-wave pyroelectric film sensor (TWPFS) (1) Substrate; (2) pyroelectric thin film; (3) chemically sensitivity catalytic coating (optional); (4) bottom electrode (Cr–Au or Cr–Ni); (5) top electrode (Al); (6) resistive heater Cr–Ni strip; (7-8) electrical contact pads (Cr–Au or Cr–Ni).

electric and piezoelectric properties. It has been used for the pyroelectric detection of laser pulses and "hot" molecular beams [6, 7], and as the active element in high-frequency wide band piezoelectric transducers [8, 9]. The pyroelectric coefficient of POC is 5×10^9 C/cm^2 K [5]. The thickness of the POC film was 2 μm; the top electrode (0.15 μm) was an aluminium film, and the bottom electrode was made of a thicker gold layer (0.3 μm) with a very thin chromium sublayer (Cr–Au electrode). The morphology of the top electrode was not uniform but rather mesh-like, yielding a high specific surface area to facilitate the access of ambient gas molecules to the pyroelectric film. The active area, defined by the intersection between the top and bottom electrodes, was 4.0 mm^2 [5]. The output pyroelectric signal is caused by a thermal wave, the amplitude and phase of which are easily measured by a lock-in amplifier with the added benefit of the high signal-to-noise ratio afforded by this narrow band demodulation scheme. When the device is exposed to high purity methane or natural gas a purely thermophysical response is observed. This is consistent with a change in the boundary conditions (thermal coupling coefficients) of the thermal wave field in the active element due to the increased thermal effusivity of natural gas which displaces other ambient gases (i.e. nitrogen, air) on the sensor surface [10, 11]. For the POC sensor no detailed thermal-wave model has been developed; however, the amplitude increase is expected to be partly the result of the increased temperature gradient between the front (top) and the back (bottom) surfaces of the pyroelectric thin film due to the cooling of the top surface of the substrate on which the film rests upon exposure to ambient natural gas or methane. Thus, the POC element acts as a pyroelectric thermometer [12]. No chemical coating on the pyroelectric film is needed for this mode of operation. Through proper choices of the thermal-wave field (frequency and

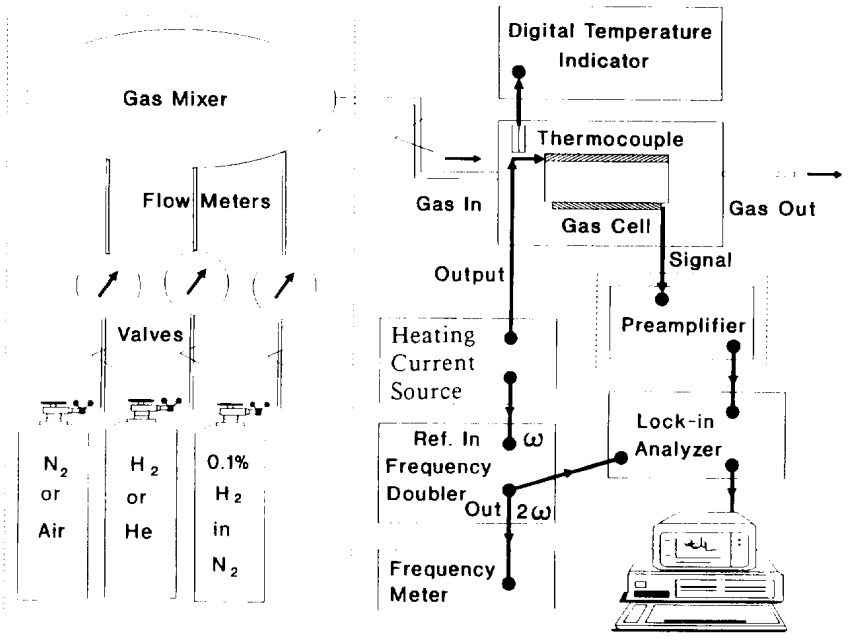

Fig. 2. Schematic of experimental arrangement.

amplitude of the heating current) and sensor characteristics (i.e. substrate materials and dimensions), it is possible to obtain strong responses to the introduction of different concentrations of natural gas and methane. A ceramic material ("sitall") was used as a thermally conductive substrate; it is based on SiO_2–Al_2O_3 and its thermal conductivity (k) is 0.015 W/cm K. Conventionally, this ceramic is used in the Russian electronics industry [5].

The experimental arrangement, shown in Fig. 2, consisted of a gas cell, gas delivery system, thermal wave generator, and the signal detection and data acquisition instrumentation. The gas cell was a 40 cm^3 half-cylinder made of plexiglass. The sensor was mounted on four contact plates and fixed by four copper clamps which acted as electrical contacts: two to deliver the heating current and two to pick up the pyroelectric signal. The gas delivery system included a natural gas tank (93% CH_4), high purity methane (99.97%), and nitrogen (zero grade) from Matheson Gas Products. The gas flow meters were one high precision (1–11 ml/min) gauge and two high flow rate (60–500 ml/min) gauges. The heating current source was a low-frequency function generator (Kron-Hite, model 5100A). The generator output signal was monitored by an oscilloscope Tektronix T912. The same generator was the source of a square-wave 5 V peak-to-peak lock-in reference signal. The pyroelectric output is at double the frequency when compared to the generating signal owing to the Joule heating effect. Thus, a frequency doubler was required. A EG & G PARC, model 5210, lock-in amplifier was used to measure the output pyroelectric signal at the fundamental frequency. The data acquisition was facilitated by a personal computer connected to the lock-in amplifier through a RS232 port.

RESULTS AND DISCUSSION

Response-time profiles of the TWPFS were obtained for natural gas and high purity methane in nitrogen. Both amplitude and phase channels were monitored and both exhibited similar quality and signal-to-noise ratios. For conciseness only amplitude data will be presented here. The signal change in mV with respect to different natural gas concentrations (% vol.) in nitrogen is shown in Fig. 3. The base line is 100% nitrogen. When the natural gas was turned on, the signal amplitude increased until it reached saturation. When the natural gas was turned off, the signal always returned to the base line. These measurements were done at total flow rates of 500 ml/min. The thermal wave generator input voltage was 20 V peak-to-peak at a frequency of 4 Hz. These values gave an optimal signal and were determined empirically. The results showed a proportional increase of the signal as the concentration increased. A similar result was obtained when high purity methane was introduced to the gas cell. The amplitude change was higher in the case of high purity methane than for natural gas. This is expected since the thermal conductivity for high purity methane (0.0343 W/mK) is higher than for natural gas and the

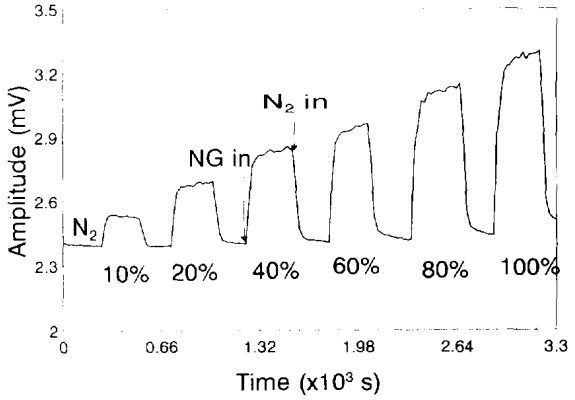

Fig. 3. TWPFS thermophysical response to natural gas concentrations in nitrogen. The arrows indicate the onset of gas introduction.

latter is higher than the thermal conductivity of nitrogen (0.0256 W/mK) [13]. Linear isotherms for natural gas and high purity methane were obtained from these measurements and they are shown in Fig. 4. The isotherm points were determined by reading the saturation level of the sensor response at different concentrations. The slope of the isotherms for natural gas was lower than the one for high purity methane. This is due to the difference in thermal conductivities between the two gases. The TWPF sensor was able to detect a minimum concentration of 2.5% by volume in nitrogen, equivalent to about half the lower explosive limit for methane in air (5% vol.). The sensor response to 2.5 and 5% of natural gas in

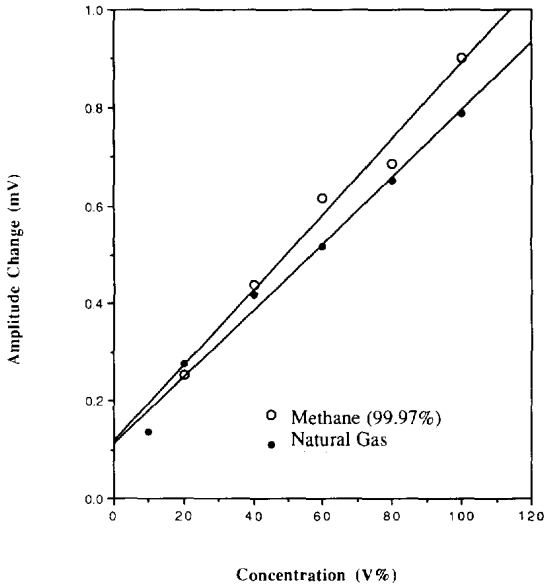

Fig. 4. TWPF sensor isotherms for natural gas and high purity methane in nitrogen. Linear fit to data: $Y(NG) = 0.1117 + 6.834 \times 10^{-3}$ [NG] $Y(CH_4) = 0.1166 + 7.71 \times 10^{-3}$ [CH_4].

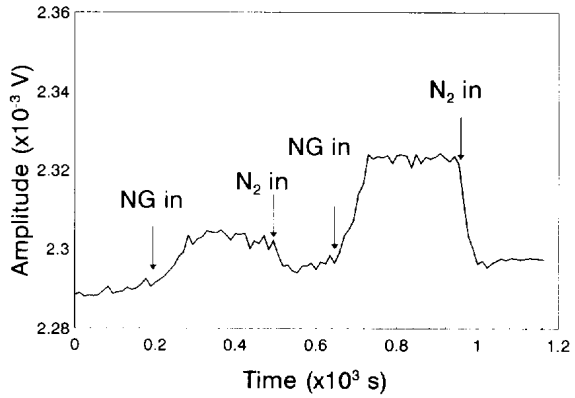

Fig. 5. TWPFS thermophysical response to 2.5% and 5% (vol.) of natural gas in ambient nitrogen.

nitrogen is shown in Fig. 5. The signal is clearly above the base line (100% nitrogen). The rise times for these signals were around 90 and 75 seconds, respectively. These slow times were limited mostly by the gas delivery system. Rise times of the order of 15 seconds are expected without this limitation [5]. Further rise time minimizations are under way. The sensor was able to distinguish between high purity methane and natural gas. For this test, natural gas (100%) formed the base line. In the presence of high purity methane the signal increased reversibly to a saturation value, Fig. 6. When the high purity methane was turned off, the signal always returned to the base line. In the foregoing measurements, the TWPF sensor exhibited a wide dynamic range (2.5–100%) for natural gas and high purity methane. Since the TWPF sensor operating mechanism originates from the dependence of the pyroelectric signal on the thermophysical gas properties, increasing the methane concentration in nitrogen increases the heat transferred away from the surface of the pyroelectric film. In this respect, the heat transfer from the pyroelectric film was found to be mildly dependent on the flow rate of the gas [14]. The ability

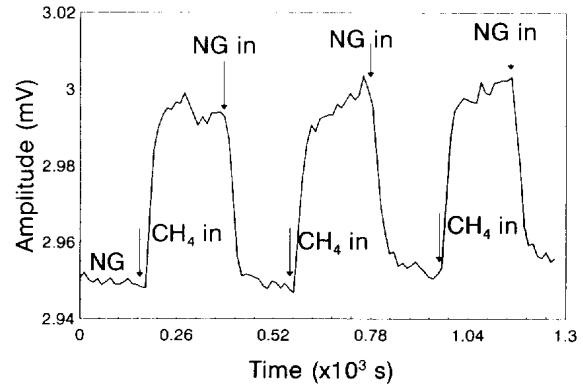

Fig. 6. TWPFS thermophysical response to natural gas and methane (100%). The arrows indicate the onset of gas introduction.

of the TWPF sensor to respond to different natural gas concentrations suggests the possibility of using this sensor in a gas quality and composition monitoring system for natural gas vehicles. However, further research is required under conditions simulating the actual air fuel mixtures for natural gas vehicles. Since the TWPF sensor responds to concentrations of methane and natural gas in nitrogen equivalent to half the lower explosive limit of methane in air, the possibility of developing a sensor for safety purposes exists. This will be useful in many circumstances ranging from industrial to residential applications.

CONCLUSIONS

A novel thermal wave pyroelectric film sensor (TWPFS) was used to resolve different concentrations of natural gas and high purity methane in nitrogen. The sensor response was reversible, reproducible, and symmetric with respect to the onset and cut off of the natural gas or methane flow. The sensor response was proportional to the natural gas and methane concentration in nitrogen. The detection range of the sensor was from 2.5–100% by volume of natural gas and methane in nitrogen.

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