Hydrogen Concentration Sensor Selection for the Renewable Energy Vehicle

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ABSTRACT: This paper discusses the selection of a hydrogen concentration sensor for the use in the University of Western Australia’s Renewable Energy Vehicle (REV). Prior to selecting a sensor, it is important to consider the available sensing methods and the specific properties of the measurand, hydrogen. The selection process leading up to the purchase of two different hydrogen sensors from Neodym Technologies, is documented and finally the method of sensor calibration is outlined.

1 INTRODUCTION
The University of Western Australia’s Renewable Energy Vehicle (REV) project aims to show the viability of using renewable energy as a means of transport. The vehicle will resemble the cars of today, but will be solely powered by a hybrid of hydrogen fuel and solar energy. The proposed car’s completion date is late 2005, allowing it to be driven around Australia in 2006.
The REV requires numerous amounts of measured physical quantities for both data logging and controlling the car’s systems. For each measured physical quantity, a sensor is required to convert this quantity into an electrical signal.
Safety is always first priority, and for this reason hydrogen leak safety sensors were given the highest priority on the list of required sensors.

2 HYDROGEN CONCENTRATION MEASUREMENT
Hydrogen gas is extremely flammable having an EL\(^1\) of 4.1–74.8\% by volume in air. The minimum energy of hydrogen gas ignition in air at atmospheric pressure is about 0.02 mJ and it has been shown that escaped hydrogen is very easily ignited [1], the ignition temperature in air is 520–580\(^\circ\)C. In high concentrations, hydrogen may exclude an adequate supply of oxygen to the lungs, causing asphyxiation. Hydrogen gas is colourless, odourless and insipid, so the victim may be unaware of its presence. It is therefore, crucial that any hydrogen leaks are detected quickly and accurately.
Hydrogen gas does react with oxygen to form water, though this reaction is extraordinarily slow at ambient temperature. At high temperatures or with an appropriate catalyst, hydrogen and oxygen gas are highly reactive. The standard hydrogen concentration in air at standard pressure is 0.00005 %, but hydrogen emissions from lead acid batteries [2] and fossil fuel burning may result in higher levels. A hydrogen sensor needs to detect over the general level of ambient hydrogen levels (0.00005 %) and in a variety of environments.
Hydrogen gas is the lightest element having a relative density of 0.07. This means the gas is extremely buoyant and will accumulate near the ceiling of an airtight room. Hence, the sensors will need to be mounted in the apex of the monitored space, as this is where the highest concentrations of hydrogen occur. If a sensor was positioned at ground level, it may detect hydrogen gas as low concentrations as it passes, but dangerous levels would accumulate at the roof, which would remain undetected. Three hydrogen gas sensors will be needed; one general leak detector for the hydrogen workshop; two safety leak detectors in the driver’s cabin and the fuel cell compartment of the car.

3 SENSING PRINCIPLES
There are a number of sensing principles used to detect hydrogen gas, the common sensing principles are Metal Oxide Semiconductor, Catalytic Bead, Thermal Conductivity, Electrochemical, and Acoustic Wave. Each have their advantages and disadvantages and these are discussed below.

3.1 METAL-OXIDE SEMICONDUCTOR
Metal-oxide semiconductor (MOS) sensors are composed of a heater resistor to warm the sensor to its working temperature (between 200–500\(^\circ\)C[3]), and a sensitive resistor made of a metal-oxide layer deposited on the heater. The electrical resistance of the metal-oxide layer changes, depending on the temperature and the hydrogen content in the surrounding air. MOS sensors suffer from several problems including lack of selectivity, stability and sensitivity, and long response times [4].

\(^1\)Explosive Limit – the concentration at which an air–hydrogen mixture becomes explosive.
3.2 CATALYTIC BEAD

Catalytic bead sensors consist of two beads surrounding a wire operating at high temperatures (450 °C). One bead is passivated, so that it will not react when it comes into contact with hydrogen gas molecules, the other is coated with a catalyst to promote a reaction with the gas. The beads are generally placed on separate legs of a Wheatstone bridge circuit (Figure 1).

![Wheatstone bridge circuit](image)

Figure 1: Wheatstone bridge circuit. $R_2$ keeps the bridge balanced, $R_1$ and $R_2$ are selected with relatively large resistance values.

When hydrogen is present there is an increase in resistance on the catalysed bead and no change on the passivated bead. This changes the bridge balance and changes $V_{out}$.

3.3 THERMAL CONDUCTIVITY

Thermal conductivity (TC) sensors are similar to catalytic bead sensors in that they compare the properties of a sample consisting of hydrogen in air to that of just air, which is used as a reference. TC sensors work by comparing the thermal conductivity of the sample to the reference. A heated thermistor is placed in the sample and another as a reference placed in the reference gas.

If the sample has a higher thermal conductivity than the reference, heat is lost from the exposed element and its temperature decreases, whilst if the thermal conductivity is lower than that of the reference, the temperature of the exposed element increases. Again, a Wheatstone bridge is used to measure the different resistance as a result of the temperature changes (Figure 1).

3.4 ELECTROCHEMICAL

Electrochemical sensors work on the same principle as fuel cells. They consist of an anode and cathode separated by a thin layer of electrolyte. When hydrogen passes over the electrolyte, a reversible chemical reaction occurs which generates a current, proportional to the gas concentration. Electrochemical sensors require very little power to operate, their power consumption is the lowest amongst all sensor types. Electrochemical sensors have high sensitivity, short reaction time, high reproducibility after calibration, linearity, zero point stability and relative low cross sensitivity. They are useful in safety and process control applications. One of the major drawbacks of electrochemical sensors is that the sensitivity decreases in the course of time, due to the loss of catalytic surface. [5].

3.5 SURFACE ACOUSTIC WAVE

Surface acoustic wave (SAW) sensors can be used in a number of applications, such as gas, fluid and biological sensing. SAW sensors work by creating an acoustic wave on two surfaces, with a piezoelectric transducer that propagates through the material, where it is then received by a second piezoelectric transducer that converts it back into an electrical signal. One surface is coated with a hydrogen reactive film that changes the properties of the material when hydrogen is present, the other surface is left uncoated and is used as a reference. This change in properties causes the received acoustic wave to change in frequency or amplitude, proportional to the concentration of hydrogen [6]. SAW sensors are reasonably priced, inherently rugged, very sensitive and intrinsically reliable [7]. SAW sensors have been successfully shown to measure hydrogen gas concentrations in an experimental setup [8][9].

4 SENSOR SELECTION

When selecting a hydrogen sensor, the main factors are sensing range, resolution, operating conditions, and interference gasses. Depending on the sensing range, the data sheet can either specify the concentration in percent in volume or ppm, where 1 % is equal to 10 000 ppm. After searching for sensors and getting quotes of $1350 and AU$3500, the company Neodym Technologies [10] was discovered that produced hydrogen sensors specifically for the fuel cell applications at a low cost.
4.1 MINIKNOWZ
The MiniKnowz is Neodym Technologies’ cheapest combustible gas sensor between $68 – $106, depending on features, and was initially chosen for this reason (Figure 2). The MiniKnowz uses a MOS sensing element, this provides a typical response time of 4–10 seconds and a typical accuracy of ±800 ppm.

Figure 2: MiniKnowz, uses the metal-oxide semiconductor sensing principle.

The distinct drawback of this sensor is that the sensor may be permanently damaged even by brief exposure to extremely high concentrations of hydrogen gas (typically > 5 times the maximum sensing range)[11]. The sensors maximum sensing range is 20 000 ppm, meaning any concentrations greater than 10% by volume in air, will cause damage. This level is not suitable for use in a hydrogen workshop where it is quite possible that these concentrations could occur. It is useful as a driver’s cabin sensor where any hydrogen will be rare, and used only as a safety measure. Due to its cheap price, the MiniKnowz may also be used as an exposable sensor. If a large leak occurred and the sensor was over exposed, it would go into its error state of 0 V, which is different from its normal working state of 0.5 V. The sensor would then either have to be replaced or the sensor head replaced and the sensor recalibrated.

Interference gas is another concern. Detectors will read accurately in the presence of homogeneous hydrogen gas/air mixtures, but will also produce readings in the presence of other inorganic and organic vapours. “Heterogeneous gas mixtures generally have a synergistic effect on the sensor, and in the absence of a target gas presence, the interference gases will manifest themselves as ‘false’ readings” [11]. The car will be subject to various degrees of hydrocarbons from other vehicles exhaust. When emailed about this, Neodym Technologies stated “the sensor will pick up the unburnt hydrocarbons from gasoline engines if it is exposed to the direct exhaust stream. This has not been a problem for any of our automotive customers to date. Perhaps, because the inside of their fuel cell enclosures are positively ventilated” [12]. The sensor was tested to see the effect of hydrocarbons, and it was concluded that hydrocarbons had an insignificant effect on the sensor.

4.2 PANTERRA
The Panterra is a range of gas sensors which use a variety of sensing technologies to sense a variety of gasses. The distinct advantage over the MiniKnowz is that they can operate in harsher environmental conditions, but this comes at a higher cost of approximately $325 per sensor, again depending on options.

The main advantage of the Panterra range is their ability to withstand high concentrations of hydrogen without permanent damage. This makes them usable as a general leak detector and makes them suitable for use in the hydrogen workshop, where high hydrogen concentrations could occur. Initially, the SONIC class based on acoustic sensor technology was chosen due to its large sensing range of 0–100% and inexpensive price, but was rejected after receiving a reply from Neodym Technologies stating “the sensor is still in beta and not ready for an automotive beta application” [12].

The choice of sensor came down to either the Panterra-CAT based on catalytic sensor technology or the Panterra-TCOND based on thermal conductivity sensor technology. The Panterra-TCOND has a sensing range of 0–100% and the Panterra-CAT 0–40 000 ppm. The Panterra-TCOND has the advantage that the sensor can be operated in anaerobic and no-moisture environments, and are not affected by silicones [13], but due to its larger sensing range has a lower sensing resolution and accuracy when compared to the Panterra-CAT. It was decided that the Panterra-CAT was the most suitable option due to its high sensing resolution and accuracy, making it more useful detecting hydrogen concentrations up to the critical EL, where anything greater is considered dangerous (Figure 3).

5 CALIBRATION CHECKING
The only method to check sensor accuracy and proper operation is via exposure of the sensor to a reference gas concentration and to measure the sensors output voltage. Neodym Technologies recommends that calibration checking should be performed as often as is practical, and no less frequently than once every six months [11]. Neodym Technologies’ recommended method for generating calibration test gas mixtures is to dilute pure
target gas with clean, normal air in a leak-free chamber of fixed, known volume [11]. To calculate the actual concentration of hydrogen gas in air, the volume of the syringe (specified in cubic centimeters) is divided by the container volume (in mL) and then multiplied by 1000000. This gives a concentration in part per million.

Given the sensors output voltage, equation (1) can be used to calculate the concentration.

\[
\text{Concentration} = \frac{(V_{\text{out}} - V_{\text{offset}}) \times \text{Resolution}}{\text{StepSize}}
\]

where

- \( \text{Concentration} \) = hydrogen concentration in ppm
- \( V_{\text{out}} \) = output signal voltage
- \( V_{\text{offset}} \) = zero offset voltage
- \( \text{StepSize} \) = step voltage
- \( \text{Resolution} \) = sensor resolution

6 CONCLUSION

In this paper, the selection of a hydrogen concentration sensor in an automobile application has been presented. The available sensing methods discussed and why two sensors, the MiniKnowz and Panterra-CAT were finally purchased. The calibration technique has finally been outlined.

7 REFERENCES