Abstract: An innovative hydrogen sensor based on palladium (Pd) nanoparticle networks is described in the article. Made by Applied Nanotech Inc. sensor has a fast response time, in the range of seconds, which is increased at 80°C due to higher hydrogen diffusion rates into the palladium lattice. The low detection limit of the sensor is 10 ppm of H₂, and the high limit is 40,000 ppm. This is 100% of a lowest flammability level of hydrogen. This range of sensitivities complies with the requirements that one would expect for a reliable hydrogen sensor.

Keywords: Hydrogen sensor; Palladium nanoparticle networks; Sensor controller

1. Introduction

As world economies convert from an emphasis on a petroleum based economy to a hydrogen fueled economy, hydrogen sensors have surfaced as an enabling technology. They are a critical part of hydrogen powered fuel cells and internal combustion engines in the hydrogen economy. They are needed to monitor the concentration of hydrogen used by fuel cells to prevent component failure. Hydrogen sensors are useful as well for leak detection in electrolyzers, reformers, biomass tanks, and other hydrogen storage devices.

Because hydrogen has the potential to burn and explode, sensors are needed to detect hydrogen leaks. The challenge is to develop a sensor that can detect the leak within the target timeframe at the desired detection level, assess the hazard, and trigger an alarm or activate a protective device.
2. Hydrogen Sensor Principles and Technology

Applied Nanotech Inc. (ANI) has introduced an innovative hydrogen sensor based on palladium (Pd) nanoparticle networks. Figure 1 shows ANI’s hydrogen sensor mounted on the engine module of an experimental hydrogen powered automobile.

![ANI’s hydrogen sensor mounted on the engine manifold of a hydrogen powered automobile.](image)

Hydrogen dissociates on the surface of palladium and dissolves into the palladium lattice causing a change in the crystal structure of the palladium metal. The change in the crystal structure induces a phase change resulting in an increase in conductivity of the metallic palladium nanoparticle networks. Traditional palladium thin film sensors operate due to a decrease in conductivity upon exposure to hydrogen. Their lower detection limit is approximately 0.5% hydrogen. ANI discovered that nanosized palladium clusters (Figure 2) undergo their crystal lattice phase change at much lower hydrogen concentrations than usually observed in bulk Pd films. This finding allowed ANI to develop a hydrogen sensor with a broad detection range. ANI’s nanoparticle network sensor has lower detection limits as low as 10ppm.

Hydrogen atoms can easily occupy sub-surface sites in the palladium lattice; however, their further diffusion into the bulk is hindered in bulk palladium films. The physics behind ANI’s sensor operation is the fact that the smaller particles have a relatively larger ratio of hydrogen atoms to palladium atoms. The low-concentration sensing effect is especially pronounced if nanoparticle size is equal or less than 30 nm. The 30nm size domain further extends the operating temperature range of the sensors. Based on the same surface effects, palladium nanoparticles change phase at higher temperatures than bulk palladium. The nanoparticle sensors operate up to 120°C versus the bulk sensors that are limited to 50°C operation.

Palladium nanoparticles are intrinsically selective to hydrogen, and sensors based on palladium nanoparticle networks do not produce false alarms in the presence of other gases, such as CO and hydrocarbons. Hydrogen sensors based on metal oxide, electrochemical and optical platforms are cross sensitive to other gases and require modifications for selectivity improvement.

ANI’s sensor has a fast response time, in the range of seconds (Figure 3). Response time is concentration dependent. The diffusion time constants of hydrogen throughout the palladium particles limit the response time of the sensor. ANI has achieved faster response time (< 5 seconds) by using smaller nanoparticles. It is important that the surface of palladium nanoparticle network is not contaminated with reactive chemical compounds. To avoid possible contamination, the sensor surface is maintained at 80°C. The hydrogen diffusion rate grows exponentially with temperature.
response time of the sensor is increased at 80°C due to higher hydrogen diffusion rates into the palladium lattice.

Fig. 2. SEM micrograph of Pd nanoparticle network. Fig. 3. Response time of ANI sensor to 10,000 ppm hydrogen

Hydrogen sensors that operate in harsh environmental conditions must be compensated for external drift over their lifetime. To improve the long-term stability of their device, ANI’s design includes two elements – a working element with deposited palladium nanoparticles and a reference element consisting only of a metal film (see Figure 4).

The nanoparticles are deposited on the working element using a metal electrodeposition process. The reference element is masked during this process (Figure 5). The electrical conductivity of the deposited nanoparticle networks increases when exposed to hydrogen. The increase in electrical conductivity is due to the bridging of the electrical pathways between individual nanoparticles.

Fig. 4. Layout of the sensor architecture Fig. 5. SEM image of the Pd nanoparticle deposited on the working sensor element

The sensor can be fine tuned to different concentration ranges by precisely controlling the size and the distance between the nanoparticles. The sensor contains a variety of nanoparticle networks that provide broad dynamic sensitivity range for hydrogen (10 ppm to 40,000ppm). The sensor has a logarithmic response to hydrogen.
3. Sensor Realization

The resistance of ANI’s sensor in a hydrogen-free atmosphere is approximately 2200 Ohms. In order to measure this resistance, a probe current of less than 20 ìA is used. Total power dissipated by both the working and the reference elements of the sensor is less than 2 mW.

ANI’s current sensor chip is 4x4 mm$^2$ and fits on a TO-5 package (Figure 6). The sensor terminals are wire-bonded to the package leader leads. A sensor die is attached to a Thermo Electric Cooler (TEC) element that maintains constant sensor temperature. If the outside temperature is below 80°C, the TEC operates as a heater. On the other hand, it cools the sensor down to 80°C in a warmer environment. The TEC element ultimately enables stable operation of the sensor and drastically simplifies its calibration, eliminating the need to account for the sensor response at different temperatures.

Typical power needed to warm the sensor from room temperature to 80°C is about 0.5W. Temperature stability is provided using a simple TEC driving circuit controlled by a feedback signal from a 10-kÙ thermistor mounted near the sensor. Temperature deviations of the sensor mounted on the TEC do not exceed 1°C. The specified operating temperature range of the TEC-based sensor is -30°C to 120°C.

4. Sensor Controller

ANI has developed and provides a controller for their sensor. The controller (Figure 7) measures resistances of working and reference elements, calculates their normalized values, accesses calibration data in order to calculate the concentration of hydrogen in a gas mixture, and shows the concentration on an LCD display (Figure 8).
Fig.8. Picture of ANI’s sensor mounted on the controller.

The dual measurement scheme with working and reference elements compensates for uncontrolled drifts. The controller includes a TEC driver to maintain the preset sensor temperature. A serial RS-232 port enables a connection to a computer for data acquisition and calibration data upload. The data transmitted from the controller to computer include time stamps, absolute values of the resistance in Ohms, normalized resistance, and hydrogen concentration data in parts per million (ppm).

ANI’s sensor can be readily configured to TO-8 package, PCB for sensor surface mount, or ceramic with side-brazed leads. Other packaging options are available for specific applications. The standard TO package configuration includes a metal mesh to mechanically protect the sensor. A polymer membrane can also be installed for applications requiring detection of hydrogen in fluids.

5. Experimental Results and Applications

The low detection limit of the sensor is 10 ppm of H_2, and the high limit is 40,000 ppm. This is 100% of a lowest flammability level (LFL) of hydrogen (Figure 9). This range of sensitivities complies with the requirements that one would expect for a reliable hydrogen sensor.

Fig. 9. Detection limit for hydrogen sensor.

Because of the sensor’s dynamic range it is applicable for detection of hydrogen concentrations in oil-filled power transformers for incipient fault detection (Figure 10). ANI’s sensor is very stable in this harsh environment. Furthermore, ANI’s sensor differentiates itself from the rest of the market because it can detect hydrogen directly in the transformer oil. The stability of the sensor is very important in this harsh environmental condition. ANI’s sensor monitors the rate of the H_2 release. This is critical for
determining transformer health. ANI’s cost effective hydrogen sensor eliminates considerable labor and equipment costs when used for this application.

Fig. 10. ANI hydrogen sensor response for transformer incipient fault detection.

In addition to automotive, fuel cell and electric transformer applications, hydrogen sensors developed at ANI can be used in many other applications, such as

- Hydrogen leak detection in electrolysers
- Monitoring of hydrogen annealing furnaces
- Hydrogen reformers and hydrocracking
- Aerospace applications
- Personal safety monitors
- Monitoring processes with hydrogen as a by product
- R&D applications