

Hydrogen Sensor for Oil Transformer Health Monitoring

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Abstract – A hydrogen sensor for detection of H_2 dissolved in transformer oil has been developed for the use in a stand-alone dissolved gas analyzer (DGA) which will also assess the relative humidity saturation of oil. The sensor uses palladium nanoparticles as a sensitive material that is selective to hydrogen. The DGA will be capable of measuring dissolved hydrogen in concentrations from 50 ppm to 4000 ppm.

Keywords - hydrogen sensor; palladium nanoparticles; oil transformer health monitoring; dissolved gas analysis

I. INTRODUCTION

Hydrogen is a major fault gas observed in oil filled power transformers and is an indicator of possible corona discharge between the windings of the transformer coil. Timely detection of a change in concentration of dissolved hydrogen is critical in monitoring the transformer health and can prevent the transformer failure. There are a number of commercially available techniques currently used for the detection of hydrogen dissolved in transformer oil. They are based on gas chromatography, use of metal oxides, thermal conductivity, and fuel cell type combustible gas sensors [1]. All the techniques are based on the measurement of hydrogen concentration in a sample of gas obtained from oil rather than directly measuring H_2 in oil. Also, most of these technologies are either high cost or suffer from the issues of cross-sensitivity to combustible gases other than hydrogen.

It is known that palladium (Pd) metal can be used as sensitive material for detection of hydrogen in air. Palladium is intrinsically selective to hydrogen, since H_2 readily dissociates on the Pd surface and diffuses into Pd while changing the Pd lattice constant and forming palladium hydride. This process is often called a phase transition in palladium. However, at standard pressure and temperature, the phase transition takes place at rather high partial pressure of hydrogen [2], around 1% in air, that is not practical for dissolved gas analysis.

The sensor developed by Applied Nanotech, Inc. (ANI) uses Pd nanoparticles to lower the H_2 partial pressure at which this transition occurs. The surface effect in which hydrogen atoms occupy subsurface sites [3] prior to “bulk” phase transition makes it feasible to detect very low hydrogen concentrations. The “effective” phase transition in Pd nanoparticles is a smooth rather than a step function of hydrogen pressure [4], and allows detection of hydrogen in the range spanning over several orders of magnitude.

II. BACKGROUND

ANI has exploited the unique property of Pd nanoparticles' interaction with hydrogen at low concentrations in the miniature hydrogen sensor that is ideally suited for H_2 monitoring in power transformers. ANI is developing this hydrogen sensor as a part of a dissolved gas analyzer in partnership with a major supplier of equipment for energy utilities industry. The DGA includes temperature and humidity sensors for a broader assessment of the transformer operating conditions and will also be capable of operating with both

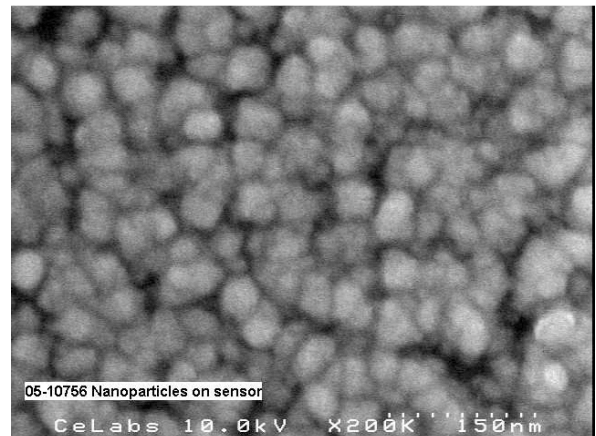


Fig. 1. SEM image of Pd nanoparticles deposited on a sensor substrate

nitrogen-blanketed and free-breathing types of transformers.

The ANI design approach uses a network of Pd nanoparticles deposited on a resistive substrate. An electroplating technique is used for Pd deposition in a chronoamperometric mode, where nanoparticle size and interparticle distance are controlled by the proper choice of plating parameters. Fig. 1 shows an SEM image of nanoparticles deposited on a substrate. An average nanoparticle size is approximately 30 nm, and the gaps between the particles appear to be on the order of 1 nm or less.

In the presence of hydrogen, Pd nanoparticles undergo a phase transition, increasing in their size and creating electrical contacts between each other. The change in the electrical resistance of the nanoparticle network is thus a function of hydrogen concentration (Fig. 2). Narrow gaps between nanoparticles ensure good sensor sensitivity to hydrogen concentrations as low as 10 ppm.

The sensor in its current design has a glass substrate and is mounted onto an 8-pin TO-5 package. Fig. 3 shows the sensor having both a working and reference elements; their terminals are wire-bonded to the package pins. The reference element keeps track of the changes that can be detected by a working element but not related to the presence of hydrogen, such as temperature deviations or any long-term drifts. In the standard configuration, the sensor is mounted on top of a miniature TEC module such that the temperature of the sensor can be controlled with good precision using an integrated feedback thermistor.

Pd Phase Transition

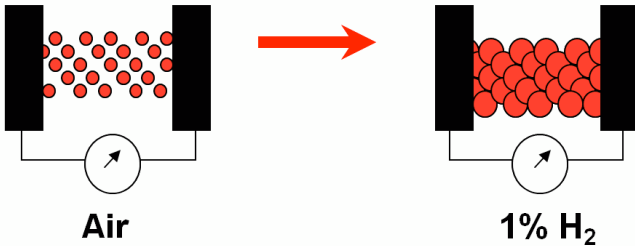


Fig. 2. Phase transition in Pd nanoparticles results in the detection of H₂

The palladium metal is a catalyst that promotes the reaction of hydrogen oxidation and formation of water molecules [5]. This means that the amount of hydrogen dissolved in palladium also depends on the concentration of oxygen present. During the catalytic reaction, oxygen takes away hydrogen atoms from the surface of palladium nanoparticles. In the DGA design, we use ambient air with the known oxygen concentration.

The DGA sampling system consists of two sampling

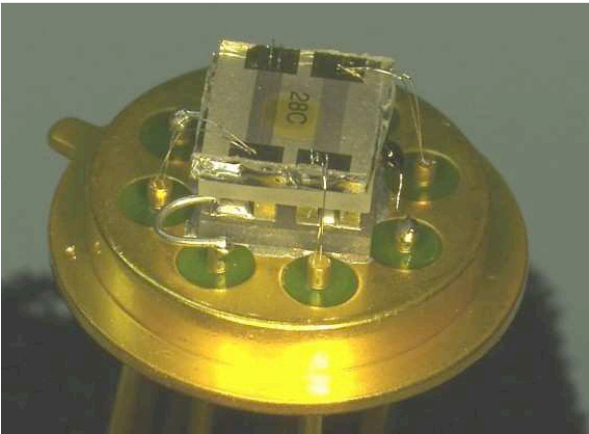


Fig. 3. Hydrogen sensor mounted on a TO-5 package.

volumes: one for air and one for oil, separated by a gas separation membrane. Changing the sampling volume ratio, it is possible to adjust the sensor sensitivity span for H₂ in air to the range of concentration of hydrogen typically expected in transformer oils. This approach allows measuring

concentrations of dissolved hydrogen from 20 to 5000 ppm, which extends beyond the range of interest for this application.

For the consistency of the measurements, stability of the sensor operation, and due to the fact that at different temperatures the amount of hydrogen that can be dissolved in oil is different, the oil sample as well as the hydrogen sensor are kept at a fixed temperature of 80°C. Keeping the sensor at a fixed temperature using a PID algorithm helps significantly simplify the sensor calibration at the production stage as well as easing the spot check calibration process in the field. Since at fixed temperature the Ostwald (partition) coefficient for an oil-hydrogen system is a constant value, the sensor can be calibrated in an air-hydrogen mixture.

III. EXPERIMENTAL RESULTS

The sensitivity range of the sensor spans over several orders of magnitude. The sensor is typically sensitive to the H₂ concentrations in air to as low as 10 ppm. The response of the sensor changes monotonously up to the concentration of 1% and higher (see Fig. 4), and saturates at nearly 4% H₂ in air.

The sensitivity curve shown above can be fitted fairly well

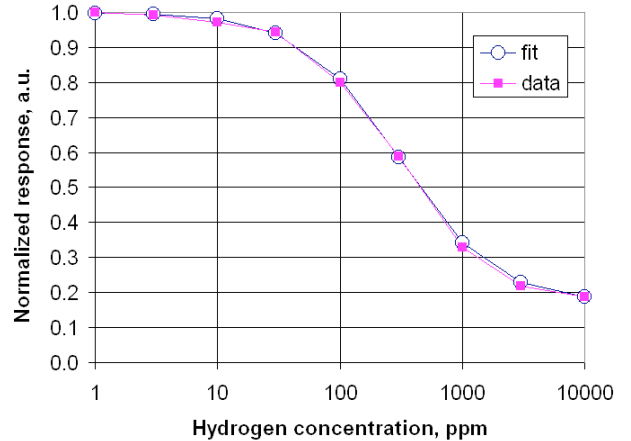


Fig. 4. Sensor response to hydrogen in air

with a logistic function. This function describes initial exponential growth of some parameter, followed by the inflection in the growth curve and finally exponential saturation. The logistic function best fits the sensitivity curve for a hydrogen concentration in a log scale. The equation for the normalized response R (drop in the sensor resistance) can be written in the following form:

$$R = R_{MIN} + \frac{1 - R_{MIN}}{1 + \left(\frac{C}{C_0}\right)^a}, \quad (1)$$

where R_{MIN} is the normalized minimum resistance achieved at sensor saturation, C is the hydrogen concentration, C_0 is the inflection concentration, and a is a power coefficient describing the curve slope at the inflection point. The inflection concentration is the hydrogen concentration at which the exponential growth of the sensor response to increasing

hydrogen concentration changes to sensor saturation. The power coefficient is related to the phase transition miscibility gap: the higher the power coefficient, the narrower the miscibility gap. For a bulk Pd the miscibility gap is very narrow, and the sensor based on large particles would operate like a hydrogen-driven switch. A broad gap (low a) indicates that particles of palladium have very small dimensions, as well as rather wide distribution of the nanoparticle sizes.

The physics and chemistry of Pd-H interactions in the sensor is quite complex, and even a good fit with an analytical function does not yield readily a simple model for hydrogen sensing effect. However, this approximation can be useful for the sensor characterization and calibration. For example, in case of consistent distribution of nanoparticle sizes, which gives us an estimate for a power value a , that can also be considered a constant, sensor calibration can be done only at two points – one at saturation point in order to determine R_{MIN} and the other one near the inflection point, from which the real position of the inflection concentration C_0 can be easily determined. As far as this approximation works well in the semi-log scale, it can be used for sensor calibration over several orders of magnitude of concentration values.

The sensor response and recovery times (t_{90}) in hydrogen-air mixtures are usually below 10 seconds (see Fig. 5) for low and high hydrogen concentrations. However, at concentrations near 100–300 ppm, we observe an increase in the response time that can be as long as several minutes. Interestingly, this feature coincides with the inflection point on the concentration curve. This may be explained by a transition from “surface” sensitivity to “bulk” sensitivity, where two processes compete at intermediate H_2 concentration.

The nature of such a competition can be clarified if we take into account an observation that the sensor saturates at much

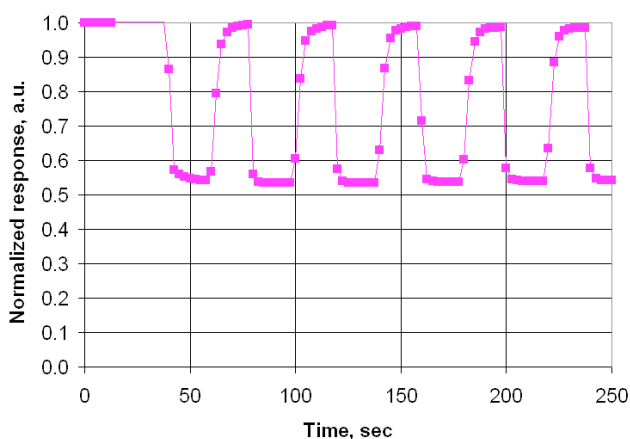


Fig. 5. Hydrogen sensor response to 1000 ppm H_2 in air.

lower hydrogen concentrations in the lack of oxygen. In pure nitrogen-hydrogen mixtures, the sensor will max out at H_2 concentrations in the low ppm range. This means that oxygen plays a crucial role in the phase transition in nanoparticles. Most likely, the hydrogen trapped in a loosely packed sub-surface Pd lattice reacts with oxygen at a rate high enough to

deplete H_2 in the bulk. When oxygen is not present, hydrogen quickly diffuses into the bulk resulting in the phase transition even at very low H_2 concentrations. The bulk-to-surface gradient in the packing density of Pd atoms may be taken into account as well, though it should not lead to any dramatic changes in the outcome of such a model. Thus, we can assume that at the inflection concentration, there is a balance between the diffusion rate and the water formation rate.

In the transformer DGA, however, the response time is limited by the hydrogen diffusion throughout the oil sample and the area of the gas separation membrane. In most cases, the response time of the sensor during the measurements in oil is less than 30 minutes.

The sensor design is rugged and withstands wide variations in ambient temperature and atmospheric pressure. It has water-proof housing and is designed to be easily mounted on an oil drain valve at the bottom of the transformer oil tank. The DGA has an RS-232 user interface and current loop outputs for hydrogen concentration (in ppm by volume) and relative humidity saturation (in %) values. In addition to this, water concentration in the units of ppm (by weight), as well as the oil temperature (in $^{\circ}C$) values can be directly obtained via RS-232 port. The embedded firmware enables the user to read the measurement status, change constants and calibration data, and also perform field calibration of the sensor if necessary.

IV. CONCLUSIONS

A Pd nanoparticle hydrogen sensor for detection of H_2 dissolved in transformer oil has been developed for the use in a stand-alone dissolved gas analyzer (DGA) which will also assess the relative humidity saturation of oil. The sensor can be used for many other applications where detection of hydrogen at concentrations below the lower flammability level (4% H_2 in air) is required. These include leak detection, hydrogen storage, hydrogen production, fuel cells and other industrial and automotive applications.

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