H₂-Sensors for Automotive Fuel Cell Application

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Summary:

For the measurement of H_2 concentrations in the exhaust gas of automotive fuel cells and in its vehicle environment the development of an active diversified-redundant hydrogen gas sensor system has been started. The combination of a selective metal oxide semiconductor gas sensor and a thermal conductivity detector as well as suitable signal preprocessing enables an application-specific H_2 sensor system with high sensitivity, selectivity, stability and safety. Work status and current results of the development will be presented.

Keywords: H₂-sensor, fuel cell, ambient, exhaust, automotive, diversified-redundant

Sensor principles for H₂ measurement

Typical fields of application of H_2 sensors in automotive fuel cells are the measurement of H_2 concentrations in the exhaust gas of the fuel cell and in its vehicle ambient. For the measurement of hydrogen different functional methods depending on application are used. Known and proven methods include e.g. sensors based on catalytic, electrochemical, thermal conductivity, resistive, optical functional principles and combinations of these.

Application specific requirements

The application-specific automotive requirements for functionalities, safety, life-time and reliability of H₂ sensors necessitate accordingly ambitious target parameters of such sensors to be developed: e.g. H₂ measuring range from 1ppm to 10Vol%, accuracy values from measured value $\pm 30\%$ (≤1% H₂) and $\pm 10\%$ (>1% H₂), short time from 3s after switching on until operational readiness is reached (operational readiness after icing max. 5s), at least 45,000 on/off cycles, operating temperature range from -40°C up to +85°C/+125°C, resistance to a large number of chemical substances e.g. CO, C₆H₆, C₇H₈, NH₃, NO, NO₂, O₃, SO₂, HMDS, etc. as well as min. 8.000h operating hours, lifetime of at least 15 years, mileage of at least 300.000km.

Metal oxide (MOX) semiconductor gas sensors (resistive functional principle) are characterized by their high sensitivity in the ppm range and the very high selectivity for hydrogen when using specific filter-coated gas-sensitive layers.

The functional principle of a thermal conductivity detector (TCD) is based on different thermal conductivities of the gases. It is therefore particularly suitable for the detection of higher gas concentrations. Gas sensors, based on these functional principles have long been successfully used in vehicles for various applications.

H₂ sensor based on the Semicon[®] principle

To achieve the above mentioned objectives, a sensor system based on the Semicon® principle [1] was designed for H₂ measurement in the exhaust gas as well as in the environment. The H₂-Sensorsystem combines a thermal conductivity detector (TCD) and a metal-oxide semiconductive gas sensor (MOX). A TCD detects temperature changes resulting from the different thermal conductivities of individual gases and their concentrations. The functionality of a MOX gas sensor is based on the conductivitychange of the gas-sensitive MOX semiconductor layer/s at gas exposure, which can be externally measured and analysed. A specific MOX gas-sensitive layer reacts to oxidizing gases with increasing of the layer resistance and to reducing gases with decreasing of the layer resistance. Tab. 1 shows selected advantages and disadvantages of the TCD- and MOX-gas sensor principles [1] [2].

Tab. 1: Selected advantages and disadvantages of TCD- and MOX-gas sensors

Thermal conductivity detector (TCD)	MOX gas sensor
+ high linearity	+ high sensitivity

+ high accuracy	+ short response time
+ high stability	+ wide measuring range
+ pollution resistant	- low accuracy
- low selectivity	- low selectivity (de- pending on gas type)
- temperature sensi- tive	- pollution-sensitive

The innovative combination of a TCD and a MOX gas sensor combines the advantages and compensates the disadvantages of the two functional principles - Semicon[®] principle [1] [2].

Laboratory sample of the H₂ sensor

Fig.1 shows the block diagram of the H_2 sensor system for exhaust gas monitoring. The sensor system consists of the parts sensor head, currently with integrated H_2 MOX duo gas sensor element, TCD element, two platinum thin-film temperature sensor elements as reference elements and a separate sensor electronics module for sensor control, signal preprocessing, communication, interface and power supply. In a later development phase the MOX duo gas sensor element will be substituted by a new MOX gas sensor element with a multi-electrodes structure furthermore sensor head and electronics are to be integrated.

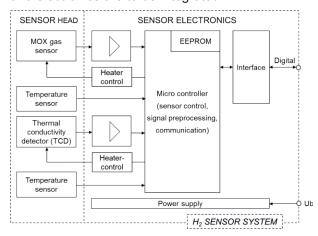


Fig. 1 Block diagram of the H_2 Semicon[®] sensor system for exhaust gas monitoring of an automotive fuel cell

Fig. 2 shows sensor elements, used for the first laboratory sample of the H_2 sensor for exhaust gas measurement.



Fig. 2 Ceramic TCD element 1,5x1,5mm (left) and MOX gas sensor element 2x2,3mm (right)

These MOX and TCD gas sensor elements are realized in hybrid-technology: ceramic carrier substrate (Al_2O_3) with a micro-structured platinum thin-film layer, covered with a passivation layer, specific layers for contacts and locking as well as a gas-sensitive metal oxide (MOX) layer for the MOX gas sensor element [3]. The H_2 sensor for the ambient monitoring will be realized with MOX gas sensor and the TCD element on one ceramic chip.

During a monitoring measurement in the laboratory test environment, a H_2 sensor system was exposed to various H_2 concentrations. c_H2 shows the H_2 concentration, c_s ensor H2 the output by the sensor. The deviations between c_H2 and c_s ensor H2 are within the specification (see Fig.3)

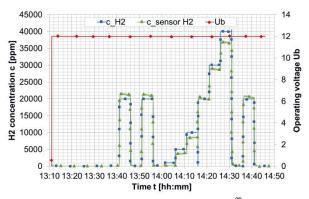


Fig. 3 Measurement of a H₂-Semicon[®] sensor system after use in the application

Results and outlook

The results show that the realized sensor system and it's components in connection with a suitable sensor head design and integrated electronics provide realistic basics for a successful continuation of the development work with the aim of future development of application-specific and customized H_2 sensors for automotive fuel cell applications.

References

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