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A new approach to self-monitoring of amperometric oxygen sensors

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ABSTRACT

A new approach for self-monitoring of amperometric oxygen sensors based on ZrO_2 utilizing a dynamic operation mode is presented. The sensors are characterized statically and dynamically before and after degradation induced by exposure to silicone. It is shown that dynamic operation reveals several features in current–voltage characteristics that can be attributed to, e.g., a silica covered membrane. Thus, it is possible to use dynamic characterization as a simple and effective method to assess the degradation state of the sensor. Those features are independent of the oxygen partial pressure, i.e. no gas test is needed, allowing continuous estimation of the sensor performance, which is especially important for safety applications. A classification of degraded and non-degraded states is done by pattern recognition via Linear Discriminant Analysis, which is validated using 10-fold cross-validation. We also attempt a quantitative evaluation of the poisoning using linear regression (Partial Least Squares Regression) to account for the usually continuous nature of degradation processes. In practical applications this could allow estimation of the remaining sensor lifetime in a given environment.

1. Introduction

Zirconium oxide (ZrO_2) is a pure oxygen ion conductor at elevated temperatures making it an important material for oxygen sensors. Two sensor designs are currently prevalent: the potentiometric and the amperometric design [1,2]. While the potentiometric design is used for the measurement of partial pressure variation over several orders of magnitude, e.g. for λ-probes; the amperometric design is used for the measurement of small variations of the oxygen partial pressure in ambient air e.g. in fire-proof buildings with the ambient oxygen concentration. Furthermore there exist combinations of the potentiometric and the amperometric principles e.g. the Universal Exhaust Gas Oxygen (UEGO) sensors [3]. These are used e.g. for combustion engines that are intentionally driven with a fuel lean ($\lambda > 1$) or rich ($\lambda < 1$) mixture [4]. In this paper, amperometric ZrO_2 sensors for the measurement of ambient oxygen pressure are investigated. The amperometric principle is based on the measurement of the oxygen ion current through a ZrO_2 membrane while the cathode side is equipped with a diffusion barrier, e.g. a cap with a small pinhole (Fig. 1) [5]. The amount of oxygen that diffuses through the barrier is completely pumped through the ZrO_2 membrane, typically using a constant voltage. The cavity formed by the membrane and the diffusion barrier is almost depleted of oxygen as the pumping voltage is many times higher than the Nernst voltage. Hence, the sensor signal is proportional to the oxygen concentration outside of the diffusion barrier which can be derived by Fick's Law. The described sensor principle is vulnerable to contaminations that inhibit the oxygen transport, e.g. organic silicones which are emitted e.g. by lubricants, polishes [6], cable sheeting or silicone rubber. Silicones dissociate at the high working temperature of the sensor and form nonvolatile reaction products (silica) [6]. In this context, silica adsorbates have been proven to block the oxygen uptake of the ZrO_2 [7], especially adsorbates at the three phase boundary between air, electrode and ZrO_2 [8]. Thus, the electrodes of the sensor degrade gradually leading to an increased overpotential and thereby to a reduction of the effective pumping voltage. As long as the cavity is almost depleted the degradation is not affecting the sensor signal, but when the effective pumping voltage approaches the Nernst voltage, the sensor signal changes very rapidly.

For safety applications the function of the sensor must be tested and, if necessary, recalibrated in order to maximize the operating time. As is it also a legal requirement in many countries to monitor ZrO_2-based oxygen sensors in cars, many strategies have been developed to identify degradation and malfunction. The most intuitive method is to apply a known oxygen concentration and compare the sensor reading to a known, correct value [9].

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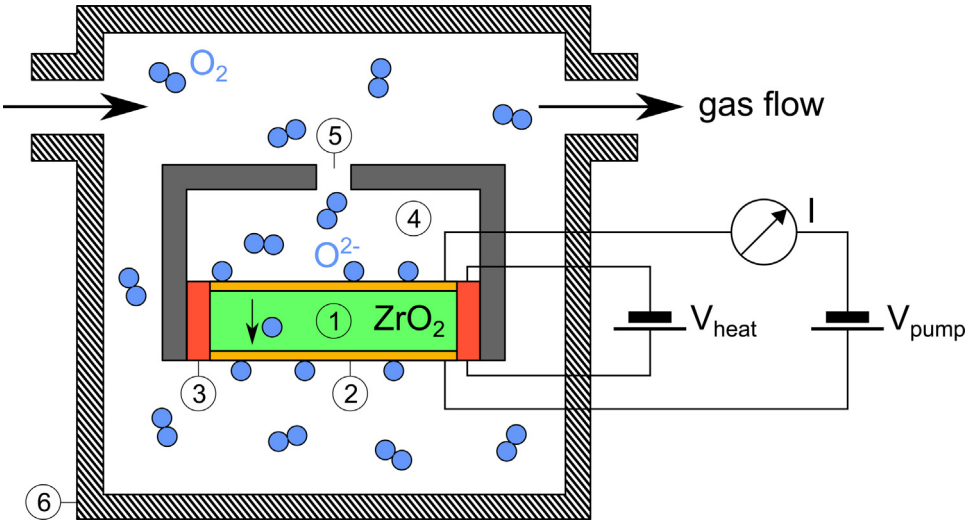

Fig. 1. Schematic of sensor and measurement setup. The sensor consists of a ZrO_2 membrane (green, 1) with electrodes (orange, 2) on top and bottom, a heater (3), a cavity (4), a diffusion barrier realized as a pinhole (5) and is fully enclosed by a leak-proof chamber (6).

However, this kind of gas tests requires a lot of effort and access to the sensor. Another method uses large steps of the driving voltage and measures the height of the resulting current peaks which relate to the degradation of the cathode [10]. Nevertheless, to calculate an acceptable limit for these peaks, knowledge about the outer oxygen concentration is necessary. A third method [11] applies a sine wave to the pumping voltage which should keep the sensor in the current-limited region, i.e. the sensor signal should not change. If it does, the sensor is defective; however, it is not possible to detect imminent malfunction.

In this work we describe a method for assessing the degradation state of the sensor without using a gas test. This method is based on a dynamic variation of the sensor operating condition, i.e. voltage, and pattern recognition via Linear Discriminant Analysis (LDA) [12,13]. 10-fold cross-validation (10-FCV) is used to validate the results [14]. Additionally, a linear model is built from the data using Partial Least Squares Regression (PLSR) [15,16], which has the advantage of easy interpolation, to estimate the degradation state and thus the remaining lifetime of the sensor.

2. Experimental details

2.1. Data acquisition

To apply a certain oxygen concentration to the sensor, a gas mixing unit (GMU) is used. It provides two separate, software controlled mass flow controllers (MFCs), each with a maximum flow of 500 ml/min. One of them is fed with nitrogen, and the other with air (i.e. 20% oxygen), thus allowing to create oxygen concentrations between 0 and 20%. The sensor is electrically connected and mounted into a leak-proof chamber which is then connected to the gas flow.

A similar setup is used for poisoning the sensor, i.e. degrading it by exposure to hexamethyldisiloxane (HMDSO). In the poisoning setup, both MFCs are fed with air, but one of the gas flows is run through a bubbler with distilled water and thus saturated with water vapor, which makes it possible to choose a relative humidity between 0 and 100% over the sensor. A third MFC (max. 10 ml/min) is connected to a bubbler with HMDSO. The concentration of HMDSO in the gas phase was determined as 70,000 ppm by using a calibration based on weighing the HMDSO flask before and after a time span with a defined gas flow.

Two ZrO_2 sensors from Fujikura Ltd. (Japan), type FCX-UC [5], were used. Sensor control and read-out are realized with LabVIEW and a custom-made circuit board (emitter follower with shunt resistor for heater driving and control, and OP-Amp-I-V-converter) attached to a LabJack U12 for data acquisition. The sensors are operated at a constant heater power of 1.5 W, which is software controlled, corresponding to 450 °C [17].

Basic electrical characterization of the devices was done in a previous work [18]. The static IV-characteristic of the device was determined in the range from 0 to 1.15 V in steps of 50 mV. Static measurement means recording a stationary current, therefore current is measured 30 s after each voltage increase (Fig. 2). This shows that an operating voltage of 1 V is sufficient to achieve stable operation over the whole concentration range. For the dynamic characterization, a voltage ramp (0–2 V) with a slope of 20 mV/s was applied (Fig. 3, discussion in Section 3.1).

The two sensors were treated differently for testing degradation by silicones. One sensor (operated statically at 1 V) is exposed to a gas flow (50 % relative humidity) consisting of air with 70 ppm HMDSO for 370 min resulting in a dose of approx. 430 ppm h. Before and after this exposure, characterization measurements as described above were performed in 5, 10, 15 and 20% oxygen in dry nitrogen as background.

The second sensor (dynamically operated, cf. Fig. 3) was exposed to a gas flow (50% relative humidity, r.h.) consisting of air with 350 ppm HMDSO for a total of 72 h resulting in a dose of 25,200 ppm·h. Every 18 h, corresponding to a HMDSO dose of 6300 ppm·h, dynamic measurements were performed in 5, 10, 15 and 20 % of oxygen in dry nitrogen for one hour each.

2.2. Data treatment

Linear Discriminant Analysis (LDA) is a supervised learning method, i.e. the desired classification, here the state of degradation, is known for each observation, here each voltage ramp [12,13]. For pattern recognition by LDA, the obtained data is preprocessed by normalization and feature extraction.

In this case, the data are normalized by mapping each voltage ramp to a range from 0 to 1 and equally spaced ranges (15 in total) are defined for several sections of the ramp (Table 1). Signal mean value, slope and maximum are computed for each range and, subsequently, LDA projections are computed with these 45 features into a two dimensional plot (Figs. 6–8). The LDA