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Solid state mixed-potential sensors as direct conversion sensors for automotive catalysts

Thomas Ritter, Gunter Hagen, Julia Lattus, Ralf Moos*

Bayreuth Engine Research Center (BERC), Zentrum für Energietechnik (ZET), Department of Functional Materials, University of Bayreuth, 95447 Bayreuth, Germany

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ABSTRACT

In order to determine directly the quantity "conversion of a catalyst", we developed a new YSZ solid-electrolyte based mixed-potential sensor that enables to compare electrochemically two gas compartments. Core of the sensor is a self-heated YSZ disc that provides in the center sufficiently high temperatures for sensing. At the sensor rim, the temperatures are low enough to allow for applying polymer sealings to separate both gas chambers gas tightly. In this study, the YSZ sensor disc compares two gas mixtures emulating the propene concentrations that occur up- and downstream of a diesel oxidation catalyst (DOC). At a temperature of 500 °C at the center of the disc, the changing propene concentrations on one side of the sensor, which emulate a changing propene conversion of the catalyst, are reflected by the sensor signal. Up to a conversion of 90 %, the sensor signals follow a theoretical equation that is derived from mixed-potential theory. For higher propene conversions, the signal differs from that theory. An initial explanation for this may be the catalytic activity of the platinum electrode at these high operation temperatures. This is supported by the fact that when reducing the catalytic activity, which is achieved by reducing the sensing temperature, the sensor signal is meeting more and more the theoretically derived equation. At 425 °C and below, there is no more dependency on the feed gas concentration, and all measured data fit exactly with the above-derived theory, i.e., the sensor signal depends only on the "conversion of the catalyst" and not on the propene concentration. As result, a sensor that measures directly the quantity "conversion" is obtained.

1. Introduction

For today's automotive exhaust gas aftertreatment systems it is required that malfunctions of any emission-relevant device are reported. These procedures are known as on-board diagnostics (OBD) [1]. If a component of the exhaust gas aftertreatment system fails or does not behave correctly, the dashboard malfunction indicator lamp illuminates. Commonly, exhaust gas sensors are applied downstream of a catalyst to monitor its conversion (see e.g. [2–4]). With increasingly tightening emission standards, the accuracy of such sensors has to be increased as well. Many overviews report on the status of present and future technology for gas sensors OBD purposes [5–8]. It has also been emphasized that only zirconia-based devices provide the required long-term stability for application in the harsh automotive exhaust environment [9].

In the past years, many studies on zirconia-based mixed-potential sensors have been published. Sensors following this principle are considered as sufficiently selective and sensitive to measure certain gas components, see, e.g., the recent review [10]. In the case of mixed-potential sensors, the operating temperature is that low that the gas mixture to be analyzed is far away from the equilibrium in the gas phase. Typically, such mixed-potential sensors comprise two different electrodes that are applied on ceramic yttria stabilized zirconia (YSZ) substrates. At an operation temperature between ca. 400 and 600 °C, a mixed-potential forms at each electrode, which depends on the analyte concentrations. The gas phase analyte can be oxidized or reduced at the three-phase boundary gas|electrode|YSZ. Competing reduction and oxidation reactions form the mixed-potentials and the potential difference between both electrodes is the sensor output signal.

Many studies report on the selective measurement of certain gas components that are relevant for automotive exhaust application. For example, nitrogen oxides (NO_x) abatement systems require selective NO_2 [11–15] or NO_x [16–20] sensors, whereas selective reduction catalysts (SCR) require ammonia (NH_3) sensors, as investigated for instance in [21–25]. Especially during cold start conditions, the concentrations of hydrocarbons (HC) (investigated sensors in [26–30]), or carbon monoxide (CO) ([31–33]), are of interest. Other exhaust components of general interest are

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* Corresponding author.

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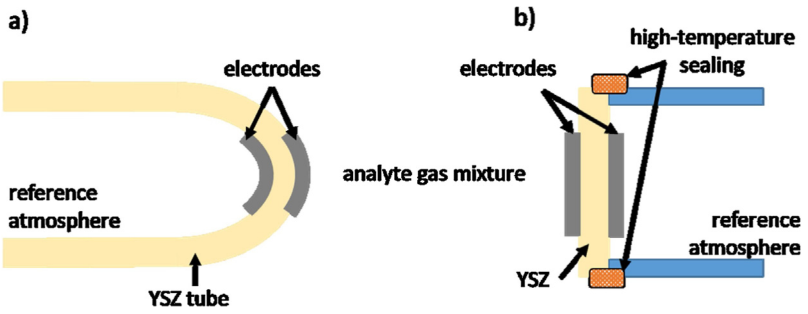

Fig. 1. Typical setups for an electrochemical comparison of two gas mixtures for electrode kinetics characterization in form of (a) an single-side-closed YSZ tube as applied in [41,42] and (b) a setup made from ceramic or metal tubes bonded together by a high temperature sealing as applied in [43,44].

hydrogen (H_2) or sulfur dioxide (SO_2). They can be monitored with mixed-potential sensors as well, as shown in [34–36] or [37,38], respectively.

With a single sensor device that is mounted into the exhaust pipe downstream of the catalyst to be monitored, one can get only information about the absolute concentration of the analyte. Therefore, monitoring the functionality of a catalyst is limited by this method, since only the concentration downstream of the converter is known and not its conversion behavior. Therefore, either a raw emission model, which has accuracy limitations, or a second gas sensor upstream of the catalyst, which is expensive, is needed. The latter approach requires sensors with different sensitivities (low sensitivity upstream and high sensitivity downstream) but with the same time response behavior. This is a difficult task regarding temperature control, sensor ageing, and cross sensitivities.

To overcome these drawbacks, we recently proposed a new mixed-potential sensor-based method to determine directly the quantity "conversion of a catalyst" (which is typically given in %) [39,40], with one single sensor device. In the following sections, the basic idea behind this sensing principle is shown. The applied setup to conduct the basic characterization of the "conversion sensor" without a real catalyst is also described. Then, it is shown that the sensor provides fast, stable, and reproducible signals, while it is possible to determine the catalyst conversion independently of the feed gas concentration, i.e. the sensor output signal is a function of the pollutant conversion (in %) and not of the concentration of the pollutant. This study also shows how precise the novel method to compare two gas species electrochemically can be. This sensor is also employed for basic measurements that help to understand the sensor behavior and to support the mixed-potential theory.

2. Setup to compare two gas mixtures electrochemically

Typical setups to derive half-cell data to describe mixed-potential sensors expose one electrode to a gas mixture containing the analyte, whereas a second electrode is in contact with a reference atmosphere, as illustrated in Fig. 1. These setups are either designed as solid electrolyte tubes that are closed on one side at which the electrodes are deposited (Fig. 1a). Typically, the whole tubes are made of yttria-stabilized zirconia (YSZ) serving as electrolytes [41,42]. The inner sides of the tubes contain mostly the reference atmosphere (e.g., air). The outer sides face the analyte gas mixture.

Not depending on the chosen setup, separating the two gas mixtures is an important but complex task. In setup (b) in Fig. 1b, a gas-tight glue (high-temperature sealing; typically glass) holds the tube and the solid electrolyte together [43,44]. Even if the gases can be separated elsewhere by using setup (a), often a high temperature sealing is needed since the whole system is placed in a furnace to provide that high temperatures that both the ionic conductivity of the solid electrolyte and the electrode activity are sufficient. Manufacturing the electrodes and wiring and bonding is difficult, too, especially for the setup in Fig. 1a. Dismantling of these setups after testing and applying new electrodes is hardly possible.

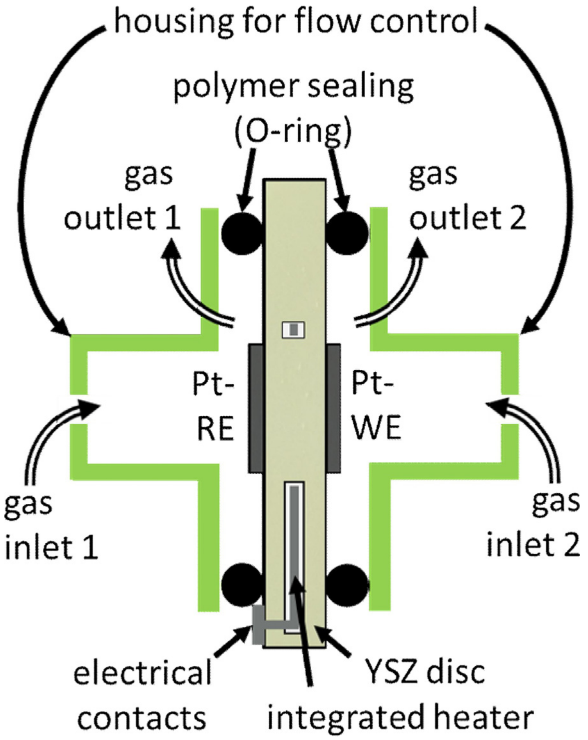

Fig. 2. Scheme of the sensor setup. Two plastic O-rings seal the sensor disc that separates two gas chambers. The sensor disc is self-heated. The disc is electrically contacted outside of the housing. Gas inlet 1 is connected with the upstream side and gas inlet 2 with the downstream side of the catalyst.

A very initial setup to investigate the novel method to measure the quantity "catalyst conversion" was described in [39]. This device, however, requires much space, is passively heated, and shows a poor kinetics since it is heated in an external furnace. Nevertheless, variable, but double-sided mostly identical electrodes were screen-printed on YSZ discs as shown in Fig. 1b, with all the problems for high-temperature sealing as reported above. A more sophisticated setup is shown in Figs. 2–4.

Heart of the sensor is a YSZ disc with vertically arranged electrodes in its center (Fig. 3). A planar platinum heating element is buried in the solid electrolyte that meanders around the circular electrodes. To prevent electrochemical blackening, the electrical heater tracks are buried in an alumina insulation layer. The whole device is manufactured in multilayer high temperature co-fired ceramics (HTCC) technology as industrially applied for planar lambda probes [9]. Details of manufacturing process and FEM-