

Dynamic measurement methods for solid electrolyte gas sensors

*Daniela Schönauer-Kamin¹, Nils Donker¹, Anastasiya Ruchets², Jens Zosel²,
Ulrich Guth² und Ralf Moos¹*

¹Lehrstuhl für Funktionsmaterialien, Universität Bayreuth, 95440 Bayreuth, Deutschland

²Kurt-Schwabe-Institut für Mess- und Sensortechnik e.V. Meinsberg, 04736 Waldheim, Deutschland

Summary

Dynamic measurement methods are an appropriate tool for the realization of highly selective solid-electrolyte based gas sensors. Three dynamic methods are used in this work to investigate Pt|YSZ-based sensors. The polarization of Pt|YSZ sensors with alternating voltage pulses and the measurement of the resulting self-discharge behavior leads to a very sensitive and selective NO_x sensor. By using the dynamic cyclic voltammetry method, it is possible to detect H₂ and O₂ simultaneously and selectively in low concentration ranges under certain measuring conditions. The third method, the coulometric measurement method, is used for the determination of the amount of exchanged oxygen during polarization of the system Pt|YSZ. For 400 °C, an uptake of O₂ of the polarized Pt|YSZ sensor was found.

Keywords: dynamic sensor systems, solid-electrolyte, Pt-YSZ, gas sensor

Novelty

Dynamic methods provide a great potential to realize sensitive and highly selective electrochemical gas sensors. This study shows examples for applications of dynamic methods. The pulsed polarization method of Pt-YSZ sensors to detect NO_x and dynamic cyclic voltammetry, a tool for selective measurement of H₂ and O₂ in non-equilibrated gas mixtures by commercial solid electrolyte gas sensors based on Pt-YSZ are presented.

Introduction

The detection of various gas concentration, e.g. NO_x, is still a huge task considering exhaust-aftertreatment systems and air quality monitoring applications. Typical gas sensing devices measure during stationary equilibria meaning the sensor is in equilibrium with the surrounding atmosphere and a static electrical property like resistance or potential difference is measured in dependence on the analyte concentration. A new approach utilizes dynamic interactions between gas phase and polarized electrodes of solid electrolyte based sensors, here in the system Pt|YSZ. The dynamic behavior provides on the one side a possibility to improve the sensing characteristics like sensitivity and selectivity and on the other side enables investigation of processes occurring at the three-phase boundary Pt|YSZ|gas, at the electrode and at the electrolyte. Here, the dynamic pulsed

polarization method [1], the cyclic voltammetry (CV) analysis of solid electrolyte sensors [2] and the coulometric measurement of oxygen exchange [3] are combined for investigation of the dominating processes.

Experimental

The dynamic behavior of the system Pt|YSZ is investigated by pulsed polarization technique and by dynamic cyclic voltammetry.

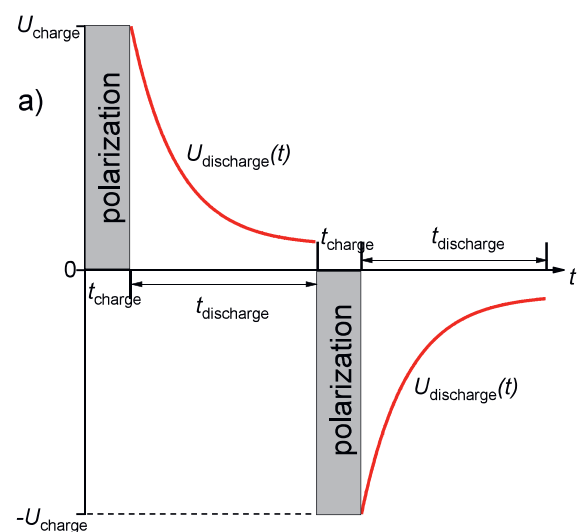


Fig. 1: Scheme of pulsed polarization method with constant voltage polarization, adapted from [1].

Fig. 1 shows a scheme of the pulsed polarization technique. A sensor consisting of two Pt electrodes screen-printed on both sides of an 8YSZ disk (Pt|YSZ|Pt) is heated in a tube furnace to 400 °C. The base gas consists of 10 % O₂, 2 % H₂O and N₂ as balance. The sample is polarized by alternating voltage pulses of 1 V for 1 s and the self-discharging (depolarization voltage) of the sensor is measured during 10 s of depolarization [1]. The dynamic response is analyzed for varying O₂ concentrations in dependence of the NO concentration.

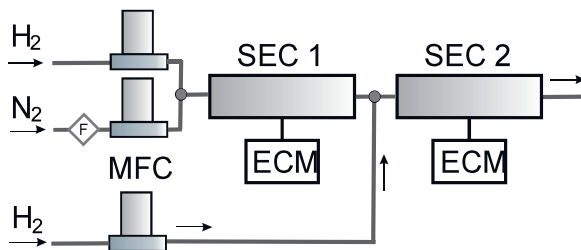


Fig. 2: *Experimental setup for dynamic CV measurements, SEC = solid electrolyte cell, ECM = potentiostat, MFC = massflow controller*

The experimental setup for dynamic CV measurements (Fig. 2) shows two commercial solid electrolyte Pt|YSZ|Pt cells (SEC). Main added gases are N₂ and H₂. SEC 1 is polarized by a defined pumping voltage to adjust the O₂ concentration. SEC 2 is the measuring cell, measuring by CV [2] in dependence of O₂ and H₂ concentrations. Another setup for the coulometric determination of the oxygen exchange of a heated Pt|YSZ sensor presents Fig. 3 [3]. Here, defined O₂ concentrations are adjusted by cell 1 (SEC) (e.g. 1 ppm O₂). A voltage pulse of 1 V is applied for 1 s to the Pt|YSZ|Pt sensor (at 400 °C) to activate the O₂ exchange reactions and the resulting O₂ concentration (sum of dosed CO₂ and O₂-uptake or release of the polarized sensor) is measured downstream by cell 2.

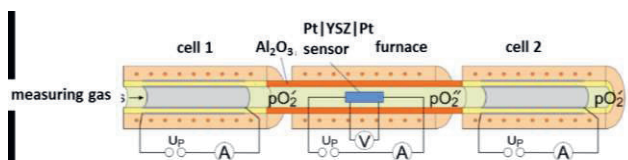


Fig. 3: *Setup for coulometric measurement of oxygen exchange of heated Pt|YSZ|Pt sensor, adapted from [3].*

Results and Discussion

Fig. 4 shows the discharge voltages after positive polarization pulse of the Pt|YSZ|Pt sensor for different NO concentrations and for different signal evaluation times (1, 2, 4, and 8 s) at 400 °C. The discharge voltage decreases with increasing NO concentration. That means that NO accelerates the self-discharge behavior resulting in a faster discharge. Additionally, the O₂ concentration shows a comparable effect, the discharging is faster with increasing O₂ concentration. Various effects contribute to the sensing mechanism, which is not fully understood yet.

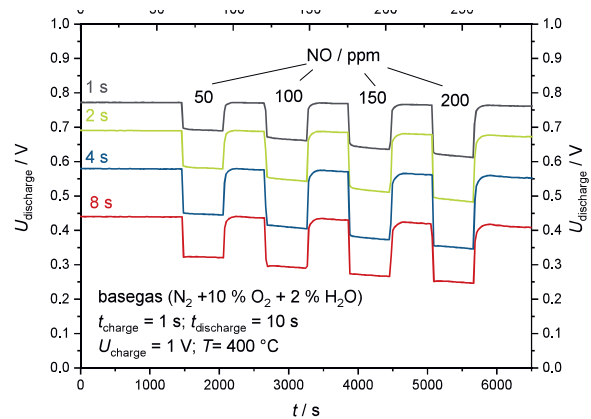


Fig. 4: *Discharge voltage curves for varying evaluation times of discharge curves and different NO concentrations of Pt|YSZ|Pt sensor at 400 °C.*

The results in Fig. 5 show the CV analysis of SEC 2 of the setup shown in Fig. 2 at 750 °C. A hydrogen related peak appears in anodic scan direction at low scan rates and an oxygen related peak occurs at higher scan rates in cathodic direction. This clear difference between O₂- and H₂-related peaks allows determining the concentration of the both gases simultaneously with high selectivity. Additionally, reaction steps on electrode processes can be analyzed.

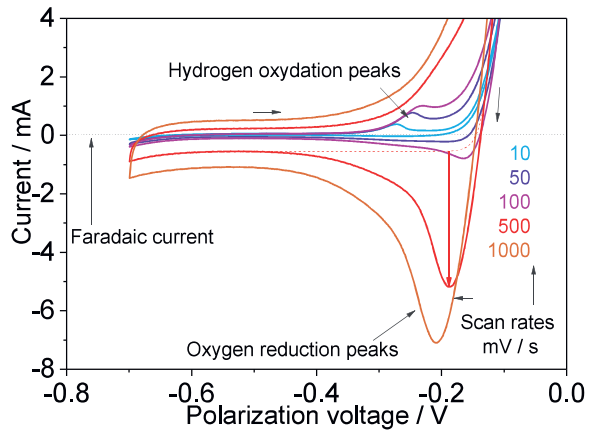


Fig. 5: Cyclic voltammograms CV for different scan rates for SEC 2 at 750 °C for 50 ppm H_2 and 10 ppm O_2 in N_2 .

Fig. 6 shows the measured current of cell 2 of the oxygen exchange measurement (setup see Fig. 3) of a Pt|YSZ|Pt sensor at 400 °C with 10 ppm O_2 . The polarization of the sensor with 1 V seems to result in an uptake of oxygen by the sensor device. One explanation could be the formation of PtO_x on the Pt electrodes. These effects need further investigation.

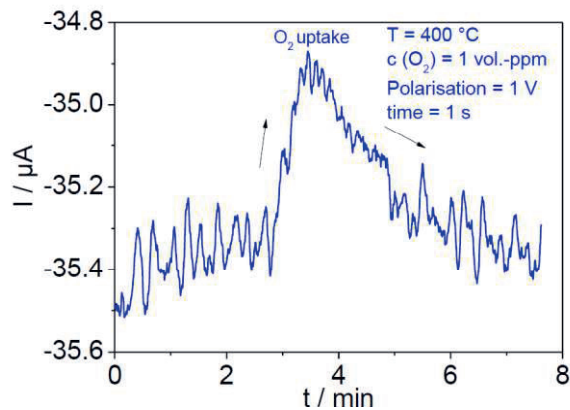


Fig. 6: Measured current at cell 2 for oxygen exchange measurement of Pt|YSZ|Pt sensor at 400 °C and 10 ppm O_2 .

References

- [1] S. Fischer, R. Pohle, B. Farber, R. Proch, J. Kaniuk, M. Fleischer, R. Moos, Method for detection of NO_x in exhaust gased by pulsed discharge measurements using standard zirconia-based lambda sensors, *Sens. Act. B: Chem.* **147** (2010) 780 – 785, doi: 10.1016/j.snb.2010.03.092.
- [2] M. Schelter et al.: Electrolyte sensor for the analysis of gaseous mixtures, *J. Sens. Sens. Syst.* **5** (2016) 319 – 324, doi: 10.5194/jsss-5-319-2016
- [3] J. Zosel, A. Herms, J. Yao, M. Schelter, V. Vashook, U. Guth, M. Mertig, Oxygen solid electrolyte coulometry: Chances, challenges and new approaches, Proceedings of International Meeting on Chemical Sensors IMCS July 2018, Vienna, Austria.