Multiple gas detection by dynamic electrochemical methods

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Summary:

Multiple redox gas detection such as carbon monoxide, nitrogen monoxide and oxygen by solid electrolyte gas sensors (SESs), operated in a dynamic detection regime, is reported. To this aim, an oxygen-pumping SES was used in cyclic voltammetry mode at different operational conditions and gas concentrations. The obtained results demonstrate the possibility of selective detection of CO and NO in nitrogen gas flow with one device.

Keywords: Yttria-stabilized zirconia (YSZ), carbon monoxide, nitrogen oxide, cyclic voltammetry, solid electrolyte sensor (SES)

Motivation

One common source of toxic gas exposure is the incomplete combustion of fuels in combustion engines. Exhaust gases usually contain mixtures of redox-active gases, for example CO and NO. In order to detect such redox active gases selectively and simultaneously, electrochemical sensors operated in dynamic mode can be applied. The advantage of dynamic measurements is the utilization of different electrode reaction kinetics, which are not visible in static mode of operation with signals corresponding to the total equilibrium between the gases [1, 2].

In the presented work, a Pt/YSZ/Pt-based solid electrolyte gas sensor is used for multiple redox-active gas detection by means of dynamic electrochemical measurements for the example of cyclic voltammetry in combination with static open circuit potential measurements in the gas outflow.

Experimental setup

The set-up described in [3] was modified to establish and detect NO, CO, and O_2 concentrations in nitrogen gas flow (see Figure 1). The total flow rate and the analyte concentrations were regulated by mass flow controllers. In contrast to this control, the O_2 concentrations were established by means of constant polarization of SES 1. All dynamic electrochemical measure-
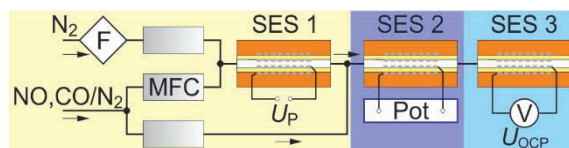

Fig. 1. Experimental setup. MFC – mass flow controller, SES – solid electrolyte sensor, Pot – electrochemical measuring system, F – triple filter.

ments were carried out in SES 2 at different experimental settings. SES 3 was used to measure open circuit potentials in the outlet gas.

Results

The curves given in Figure 2 show cyclic voltammograms (CVs) recorded at SES 2 at 700 °C in dry gas flow with a mixture of different concentrations of CO and NO and at $c(O_2) = 65$ ppmv in N_2. The gas concentrations have been changed from 150 to 0 ppmv of each gas in the mixture. For each concentration, CVs with three cycles were recorded. For NO detection every second cycle was taken, while the CO peak of the first cycle was taken for peak quantification.

Curves in Figure 2A were measured at a scan rate 1000 mV/s, while this parameter was optimized for NO gas detection in previous work [4]. As the NO gas concentration increases, the NO-related peak also increases (see inset in Fig. 2A), showing cross-selectivity to CO gas in the concentration range between 0 and 150 ppmv.
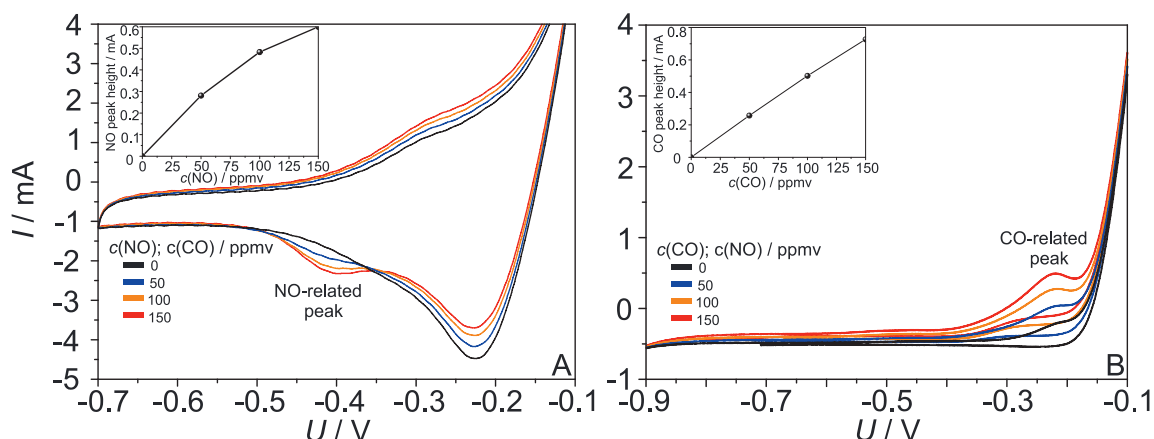
Fig. 2. Cyclic voltammograms in the gas mixture of NO and CO gases diluted in nitrogen at (A) 1000 mV/s scan rate and (B) at 20 mV/s scan rate. Sensor temperature T = 700 °C; flow rate = 20 sccm; $c(O_2)$ =65 ppmv.

Curves in Figure 2B have been recorded at 20 mV/s scan rate, in order to detect carbon monoxide in presence of oxygen and nitrogen monoxide. Linear concentration dependency was observed for the detected CO-related peak in the concentration range between 0 and 150 ppmv.

Monitoring of the open circuit potential U_{OCP} in the outlet gas during measurements and pauses between experiments is plotted in Figure 3 as a temporal course. The baseline shift due to gas concentration changes can be clearly seen on the curves as well as the changes of U_{OCP} during each cycle of cyclic voltammograms. During taking the voltammograms at 1000 mV/s scan rate, the potential was changed to more positive values, illustrating an increase of oxygen concentration during NO detection. In contrast to that, very negative potentials, e.g. reducing conditions have been reached for CO detection at cyclic voltammograms at 20 mV/s.

References

[1] X. Zhang, H. Kohler, M. Schwotzer, Y. Wu, U. Guth, Mixed-potential gas sensor with layered Au,Pt-YSZ electrode: Investigating the sensing mechanism with steady state and dynamic electrochemical methods, *Sensors and Actuators B: Chemical* 252, 554-560 (2017); doi: 10.1016/j.snb.2017.05.168

[2] T. Ritter, J. Lattus, G. Hagen, and R. Moos, Effect of the Heterogeneous Catalytic Activity of Electrodes for Mixed Potential Sensors, *Journal of The Electrochemical Society* 165, B795-B803 (2018); doi: 10.1149/2.0181816jes

[3] A. Ruchets, N. Donker, D. Schönauer-Kamin, R. Moos, J. Zosel, U. Guth, M. Mertig, Selectivity improvement towards hydrogen and oxygen of solid electrolyte sensors by dynamic electrochemical methods, *Sensors and Actuators B: Chemical* 290, 53-58 (2019); doi: 10.1016/j.snb.2019.03.063

[4] A. Ruchets, N. Donker, D. Schönauer-Kamin, R. Moos, J. Zosel, U. Guth, M. Mertig, Cyclic and square-wave voltammetry for selective simultaneous NO and O_2 gas detection by means of solid electrolyte sensors, *Journal of Sensors and Sensor Systems* 9, 355-362 (2020); doi: 10.5194/jsss-9-355-2020
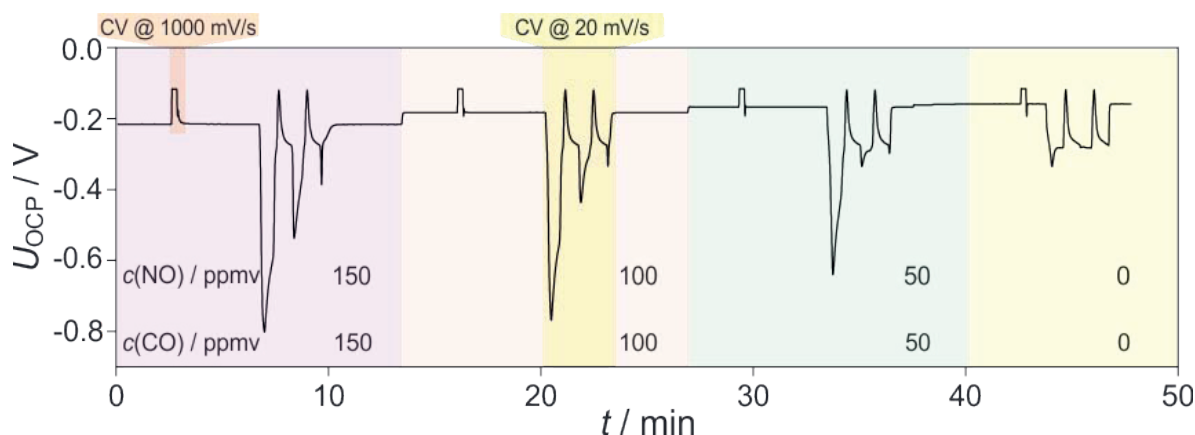
Fig. 3. OCP measurement in the outlet gas flow with SES 3.