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ORIGINAL PAPER

New advanced in situ carbon monoxide sensor for the process application

P. Shuk · E. Bailey · J. Zosel · U. Guth

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Abstract Mixed potential solid electrolyte CO sensors with sensing electrodes based on composite with various semiconducting oxides were extensively studied in the temperature range 500–650 °C for sensitivity, stability and cross-sensitivity besides CO to other combustion components like CO_2, H_2O, O_2, and SO_2. The highest CO sensitivity was found for the CO sensor with composite electrode based on Au/Ga_2O_3 showing also good reproducibility and stability in hazardous combustion environment. CO sensor response behavior in non equilibrated oxygen containing gas mixtures is mainly determined by the catalytic activity of the measuring electrode and depends strongly on preparation and measuring conditions. Mixed oxides based on doped chromites show only a little sensitivity to CO. CO sensor based on Au/Ga_2O_3 composite electrodes was showing good CO selectivity in the presence of other combustion gas species and finally was tested in combustion environment at power plant.

Keywords Solid electrolyte · Stabilized zirconia · Electrochemical gas sensor · Mixed potential · CO sensor

Introduction

There is a continuous need to detect and control pollutant gases, i.e., carbon monoxide, CO, and nitric oxides, NO_x and control the combustion efficiency in fuel burning chambers. Sensors are critical elements for combustion control and/or monitoring and their integration in combustion systems is extensively explored [1]. A number of studies have been done on chemical gas sensors based on semiconducting oxides used now worldwide for combustible gas detecting [2–4]. This type of sensor known as the Taguchi sensor employs a solid-state device made of sintered n-type metallic oxide (iron, zinc, and tin families), but poor selectivity and insufficient long-term stability have been the major difficulty of these semiconducting sensors application in the process.

For the extractive combustion analyzers, an advanced calorimetric CO sensor was recently developed using resistivity-type detector (RTD) and utilizing combustible reaction heat on the catalyst film over RTD [5]. The catalyst was selected and merged with RTD, so CO in the gas phase was selectively oxidized on the catalyst film cover over RTD. Oxidation reaction occurs between combustible specie and oxygen with defined heat release depending on combustible concentration. Calorimetric CO sensor can measure CO concentration down to ppm level with detection limit ~10 ppm CO. But, this type of sensor would be not especially suitable for the in situ application because of the flow variation and temperature vulnerability in the process affecting catalytic combustion reaction.

First introduced by Sandler [6] and Fleming [7], mixed potential sensor with zirconia solid electrolyte and two different activity electrodes was proposed for detecting combustible gases. The presence of CO or any other combustible specie could affect the well-known zirconia oxygen sensor signal in either of two ways. Combustible specie may reduce the local O_2 concentration at the electrode

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P. Shuk (✉) · E. Bailey
Rosemount Analytical Inc., Emerson Process Management,
6565 Davis Industrial Parkway,
Solon, OH, 44139, USA
e-mail: Pavel.Shuk@Emerson.com

J. Zosel · U. Guth
Kurt-Schwabe-Institute for Measuring and Sensor Technology,
Kurt-Schwabe-Str., Meinsberg,
04720 Ziegra-Knobelsdorf, Germany

surface because of combustion reaction $\left(CO + ½\, O_2 = CO_2\right)$ and/or will be involved in electrochemical process:

$$½\, O2(g) + V_O^{\bullet\bullet} + 2e^- \rightleftharpoons O_O(YSZ) \quad (1)$$

$$CO(g) + O_O(YSZ) \rightleftharpoons CO_2(g) + V_O^{\bullet\bullet}(YSZ) + 2e^- \quad (2)$$

$$½ O_2(g) + CO(g) \rightleftharpoons CO_2(g), \quad (3)$$

where $V_O^{\bullet\bullet}$ is oxygen vacancy and O_O (YSZ) is oxygen ion, O^{2-}.

The competing reactions of oxygen reduction and CO oxidation will establish mixed potential depending on CO concentration:

$$U_{\text{mix}} = U_0 - A \ln(\varphi_{CO} + \varphi_0) \quad (4)$$

where U_0, A and φ_0 are constants.

The developed mixed potential depends mostly on kinetic factors and is a strong function of the electrodes electrochemical and catalytic activity as well as morphology. Various metals and metal oxides were investigated in sensitive electrodes in non-Nernstian CO sensors [8–16].

It is well established that gold is the most promising sensitive electrode because of its low catalytic activity for the combustion and chemical stability in hazardous chemicals environment. Unfortunately, Au electrode would recrystallize and coarsen at the temperatures over 500 °C changing electrode–electrolyte–gas triple phase boundary and sensitivity of the sensor [13]. Gold composite materials based on TiO_2 [17] and Nb_2O_5 [18] showed more promises, but their catalytic activity for the chemical combustion of carbon monoxide and hydrocarbons was well too high. Recently, it was shown that Au composites with 20–30% gallium oxide (Ga_2O_3) are the most promising electrode materials for the potentiometric hydrocarbon sensors based on their high sensitivity and long-term stability in hydrocarbons environment [19, 20].

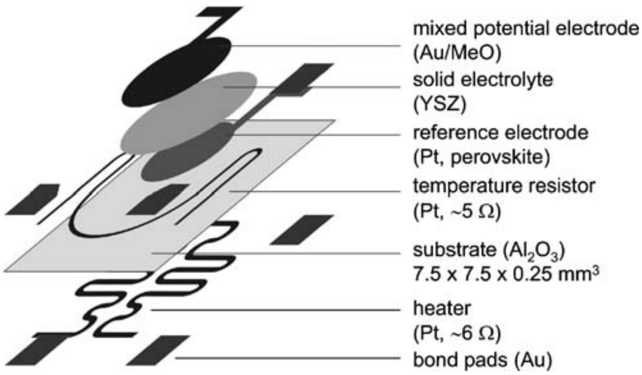


Fig. 1 Schematic view of CO sensor sandwich structure

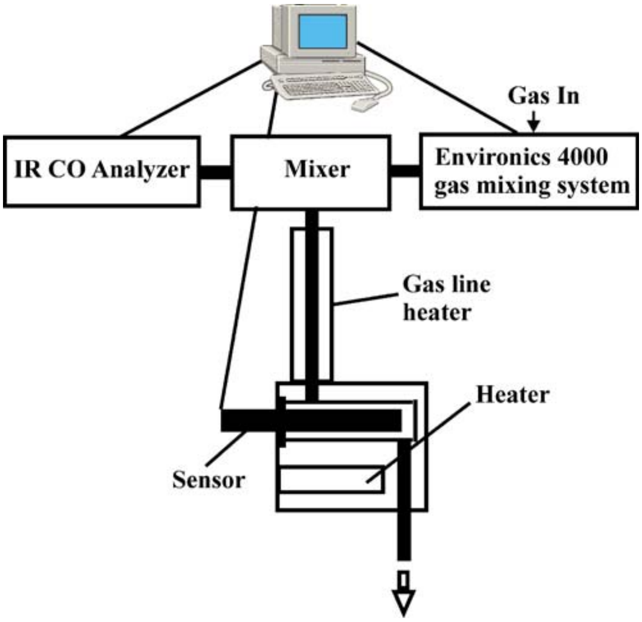


Fig. 2 Sensor test setup

In this study, we examine different composite electrodes in the mixed potential in situ CO sensor for the process application.

Experimental

Heater, temperature resistor, and the reference electrode were prepared from commercially available Pt paste (ESL, USA) and fired at 1,400 °C for ~1 h. Zirconia solid electrolyte paste was made from yttria stabilized zirconia powder (YSZ, TOSOH) with organic binder, and thick YSZ films were made using screen printing with final firing at 1,200 °C for 1 h. The commercially available metal oxide powder (Koch Light Laboratories, UK) was ground in ethanol to adjust the particle size between 1–5 µm. The dried powders were mixed in small portion steps with commercially available Au paste (Heraeus, Germany) giving final composite paste with ~20 mass-% metal oxide content. These electrode films as well as the bond pads where fired at 980 °C for 1 h. The amount of 20 mass-% Ga_2O_3 was found to be an optimum with respect to the percolation limit (around 30%) and the optimum effect on the mixed potential value. Strontium-doped lanthanium gallium chromites were prepared by a solid-state reaction at 1400 °C for 20 h. The sintered materials were ground in ethanol over 8 h, characterized as powders, and mixed with an organic binder for manufacturing of pastes for screen printing.

Figure 1 shows the structure of typical CO sensor including YSZ film sandwiched between platinum and Au-composite electrodes on alumina substrate used for the CO-sensor response tests.

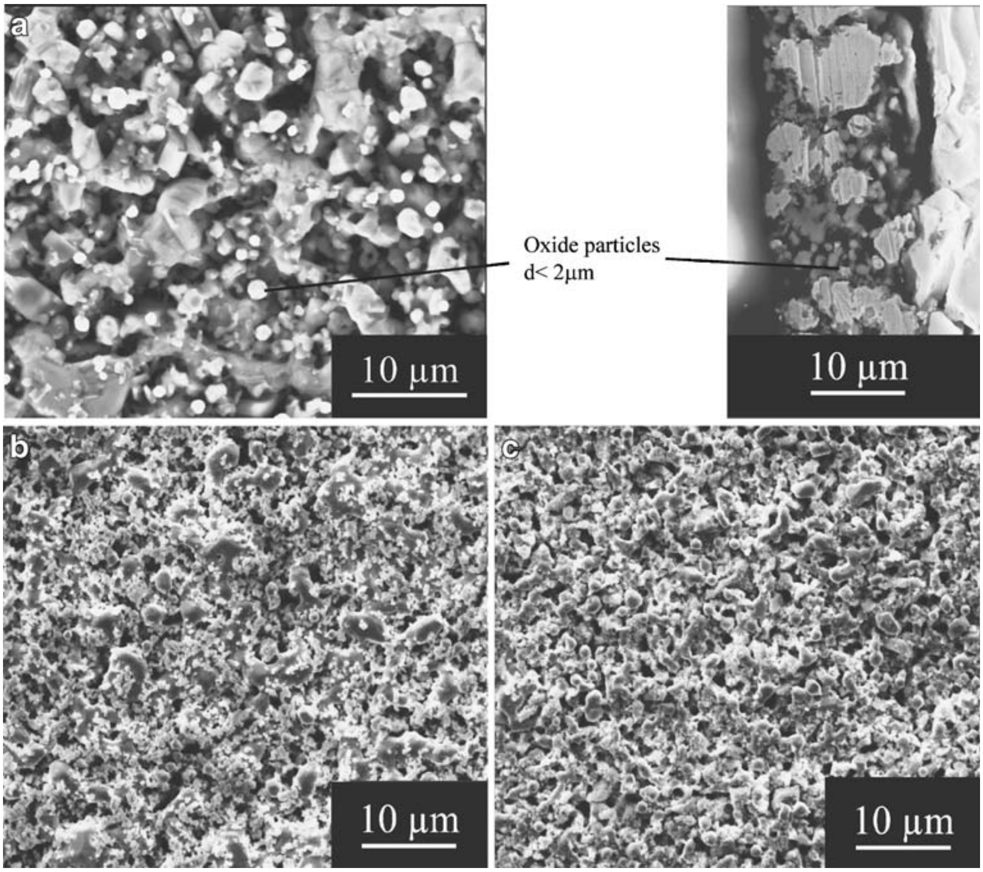


Fig. 3 SEM micrograph of Au/metal oxide composite electrodes: **a** Au/Ga_2O_3 **b** Au/Nb_2O_5 **c** Au/CeO_2

The microstructure of sintered electrode films was studied using scanning electron microscope (SEM, Model DSM 940A Carl Zeiss Inc., Germany) equipped with energy dispersive spectroscopy system (Link ISIS Oxford Instruments Microanalysis Group, UK) for semiquantitative analysis.

The schematic diagram of the sensor test setup is shown in Fig. 2. CO sensor was packaged with diffuser cap to

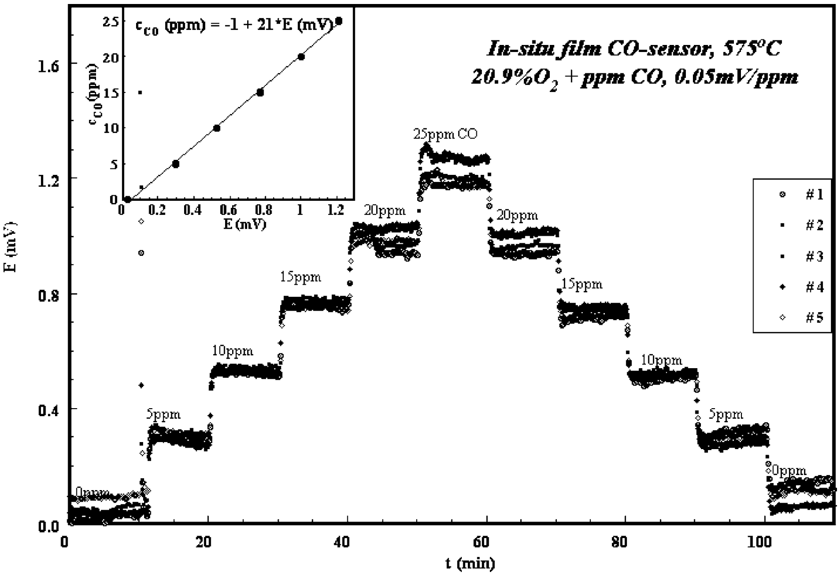
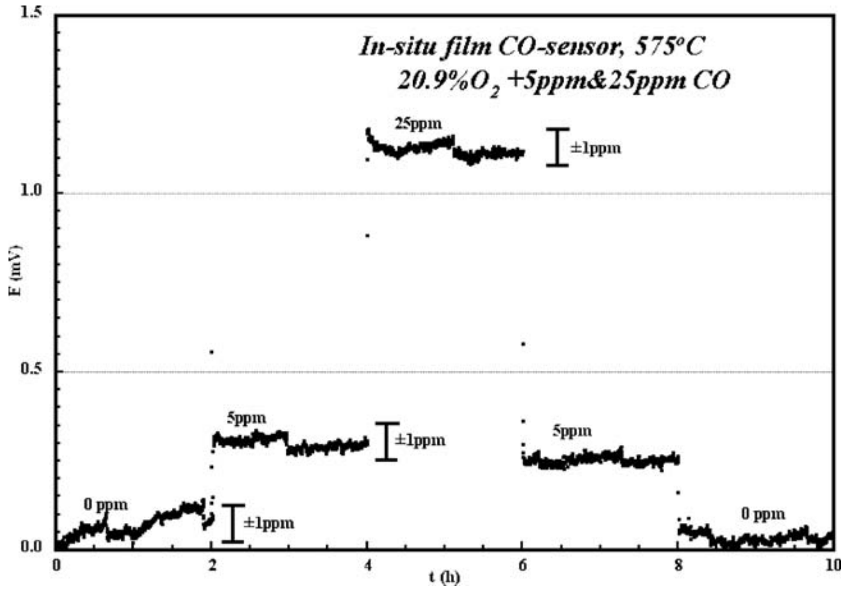


Fig. 4 Typical $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor response to 5 ppm CO stepwise change in an air at 575°C

Fig. 5 $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor response stability at 0, 5, and 25 ppm CO at 575 °C



reduce gas flow and temperature effect. Test gas mixtures were prepared using Environics 4000 mixing system (Environics, Inc., CT, USA) and CO concentration was controlled by the IR-type Rosemount 880A CO Analyzer (Rosemount Analytical, Inc., CA, USA). The gas flow rate was kept constant 30 L/h. Gas line outside the sensor package was heated to ~130 °C to prevent moisture condensation. The gas concentration was varied between 0 and 1,000 ppm for CO, 0 and 5,000 ppm for SO_2, 0% and 20% CO_2, and 1% and 5% O_2 using purified nitrogen as a balance gas. Initial response and all stability tests were done using balanced air with varied humidity to evaluate humidity effect on CO sensor sensitivity. Data acquisition system from National Instruments including signal conditioning module (SCXI-1000 + SCXI-1102 card), and the plug-in DAQ card (AT-MIO-16 XE-50) was used for the sensor data collection.

Results and discussion

SEM image of Au-based composite electrode films indicates relatively porous microstructure with 1–2 μm oxide particles homogeneously distributed in the Au bulk structure (Fig. 3).

Initially response and stability evaluation was performed on CO sensors with Pt and $(Au)_{0.8}(Ga_2O_3)_{0.2}$ composite comb structure electrodes on the zirconia substrate. CO

Fig. 6 $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor long-term stability at 0 ppm CO

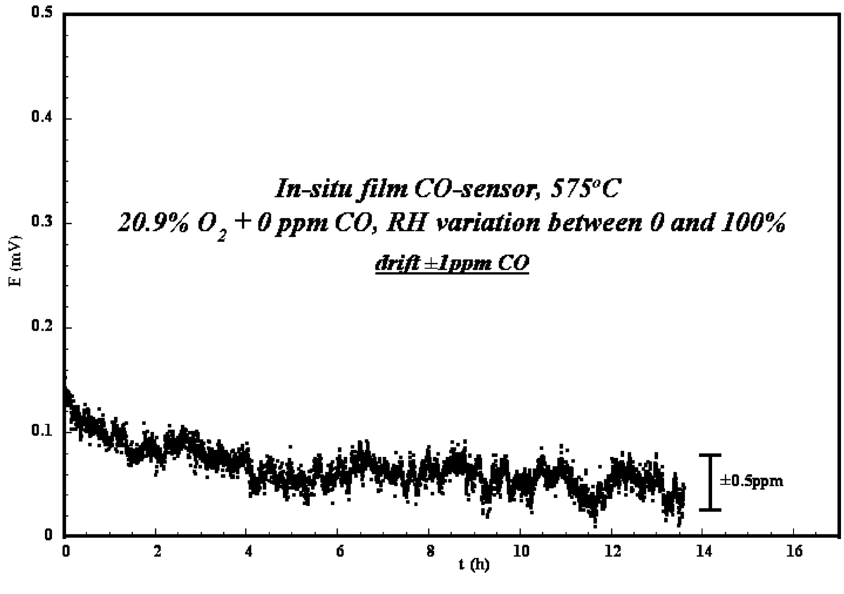
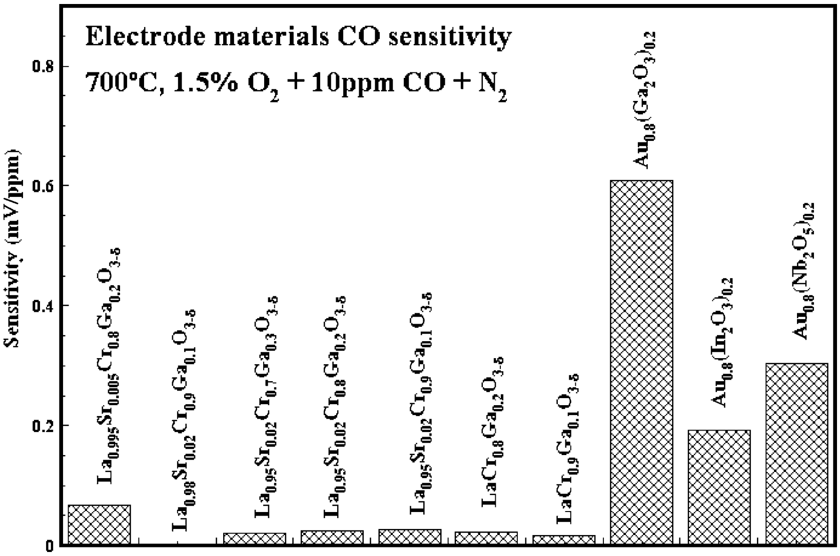


Fig. 7 Sandwich structure CO sensors sensitivity comparison at 550 °C



sensor based on Au/Ga_2O_3 composite was showing CO sensitivity limit ~5 ppm and stable, reproducible response to 5 ppm stepwise CO concentration change in the range of 0 to 25 ppm CO. CO sensor response was still reproducible after months of repeatable tests (Fig. 4). The response stability was within ±1 ppm range at 0, 5, and 25 ppm CO, and sensitivity was ~50 μV/ppm (Fig. 5). All these tests were performed using balanced air with varied humidity and were showing a little bit or none effect of humidity on CO sensor sensitivity. Long-term stability test at 0 ppm CO and relative humidity variation between 0% and 100% was showing none cross-sensitivity to H_2O (Fig. 6).

The measuring electrode with the Au/Ga_2O_3 composite in CO-containing gases is the negative electrode against a Pt-reference (oxygen) electrode as expected from the mixed potential theory. Huge improvement in CO sensitivity was observed in sensors by switching from comb sensor structure to Pt/zirconia/Au-Ga_2O_3 sandwich structure on alumina substrate presented in Fig. 1. It is probably related to the significant increase in reaction surface and triple boundary interface (gas–electrode–zirconia electrolyte) area increase by switching from comb electrodes on zirconia substrate to sandwich-type CO sensor with microfilm of zirconia.

Fig. 8 $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor response temperature dependence

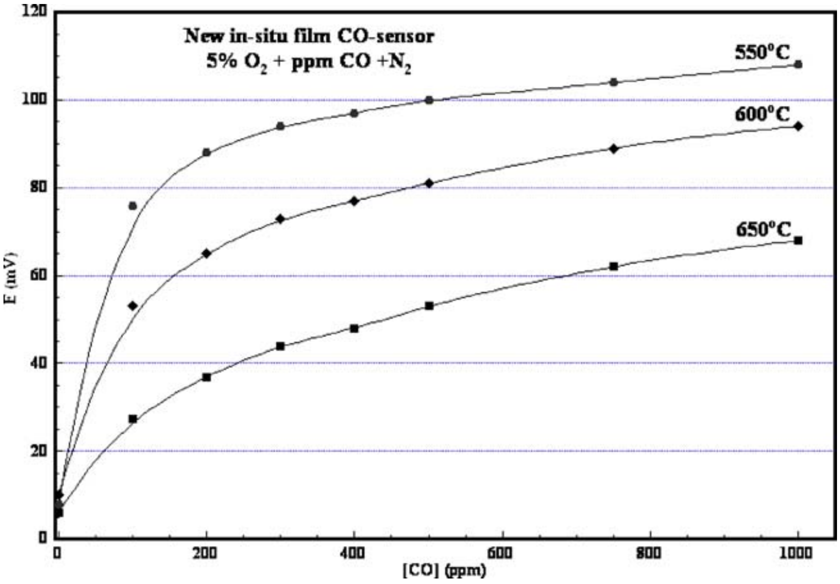
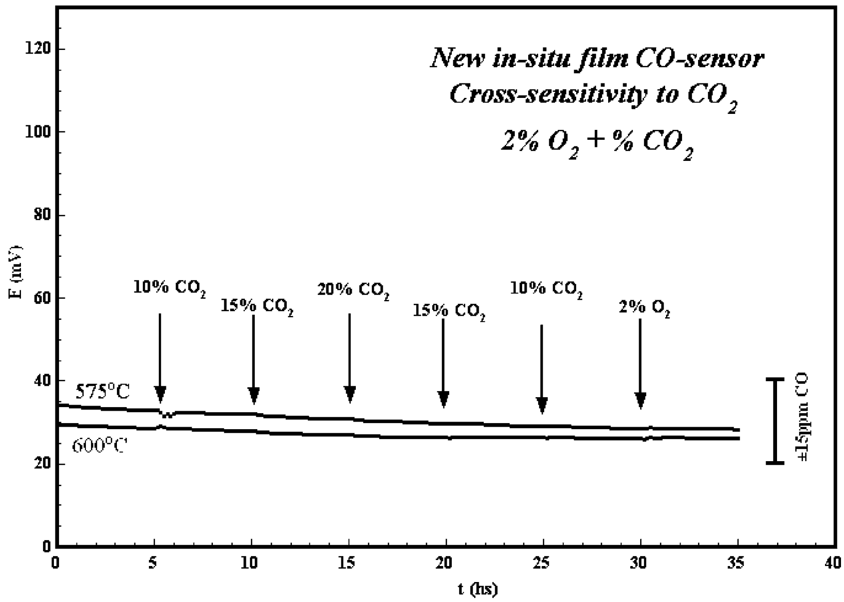
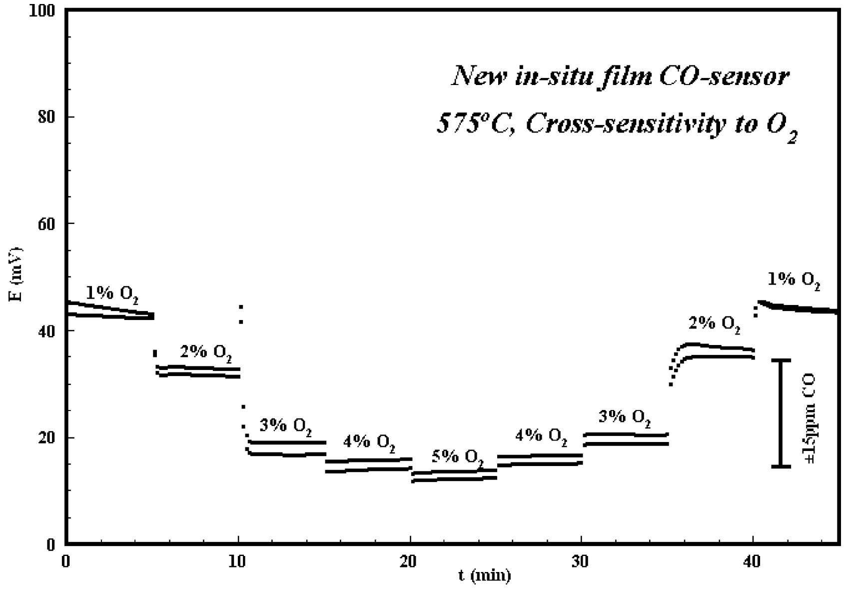


Fig. 9 $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor cross sensitivity to CO_2



The previous investigations of oxide electrodes based on gallium-doped lanthanum chromites $La_{1-x}Ga_yCr_{1-y}O_{3-\delta}$ well known as a new oxygen ion conducting solid electrolyte family showed remarkable sensitivity of these electrodes to the hydrocarbons [16, 21]. Detailed investigations of gallium-doped chromite-sensitive electrodes show, however, none or little CO sensitivity. Figure 7 summarized CO sensitivity of different gallium-doped chromites and individual oxides. The highest sensitivity was established for CO sensor with Au–Ga_2O_3 composite sensitive electrode. At lower concentration (<50 ppm), CO sensitivity was as high as 0.6 mV/ppm dropping down to 0.1 mV/ppm at 1,000 ppm. CO sensor mV signal dependence on the concentration was logarithmic and sensor signal was highly depending on the application temperature. Temperature increase by 100 °C was reducing 90% sensor response time (t_{90}) from ~25–30 s at 550 °C down to ~15–20 s at 650 °C but also sensor sensitivity was dropping by the factor of two (Fig. 8). CO sensor evaluation in dry CO_2 mixtures and saturated with moisture at 25 °C did not show any or little cross-sensitivity to moisture and none cross-sensitivity to CO_2 in a wide concentration range (Fig. 9). The cross-

Fig. 10 $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor cross sensitivity to O_2 at 575 °C



sensitivity to O_2 was found to be in the range of ±15 ppm CO by the typical for the combustion control oxygen concentration variation between 2% and 5% O_2 (Fig. 10). After exposure to 1,000 ppm SO_2 CO sensor sensitivity increased by 50%, but response was stable and reproducible (Fig. 11).

CO sensor prototype was packaged using hardware from Rosemount Oxygen Analyzer OXT 4000 with slightly modified software and installed at coal-fired power plant boiler. CO concentration in the combustion process was mostly under 100 ppm with several 150–250 ppm spikes related to the not perfect air–fuel mixing and not complete combustion. Ongoing long term O_2–CO evaluation at power plant in Ohio shows definite trends in CO concentration increasing with O_2 concentration reduction and vice versa (Fig. 12). Independent CO-concentration measurements were done in the coal fired power plant process environment by Bacharach Portable Combustion Analyzer PCA 65 (Bacharach Inc., PA, USA) confirming our CO-sensor measurements value within accuracy range. CO-sensor evaluation in coal-fired power plant environment was performed for 10 months and is still ongoing.

Conclusions

CO sensor based on $Au_{0.8}(Ga_2O_3)_{0.2}$ composite was showing the highest CO sensitivity among studied doped perovskites and individual oxides (~0.6 mV/ppm at 25 ppm CO and ~0.1 mV/ppm at 1,000 ppm CO). Sensor sensitivity limit was found to be ~5 ppm CO. The response stability was in ±1 ppm range at 0, 5, and 25 ppm CO. The cross-sensitivity to O_2 was found to be in the range of ±15 ppm CO by the typical for the combustion control oxygen concentration variation between 2% and 5% O_2. CO sensor based on Au–Ga_2O_3 composite did not show any cross-sensitivity to moisture and CO_2 in a wide concentration range. After exposure to 1,000 ppm SO_2, CO sensor sensitivity increased by 50% but CO response was still stable and reproducible. Ongoing long-term O_2–CO evaluation at coal-fired power plant boiler shows definite trends in CO concentration increasing with O_2 concentration reduction.

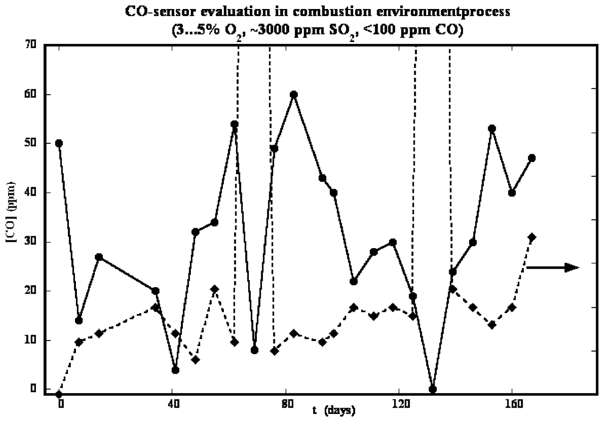


Fig. 12 In situ CO sensor/O_2 sensor evaluation at coal-fired power plant boiler

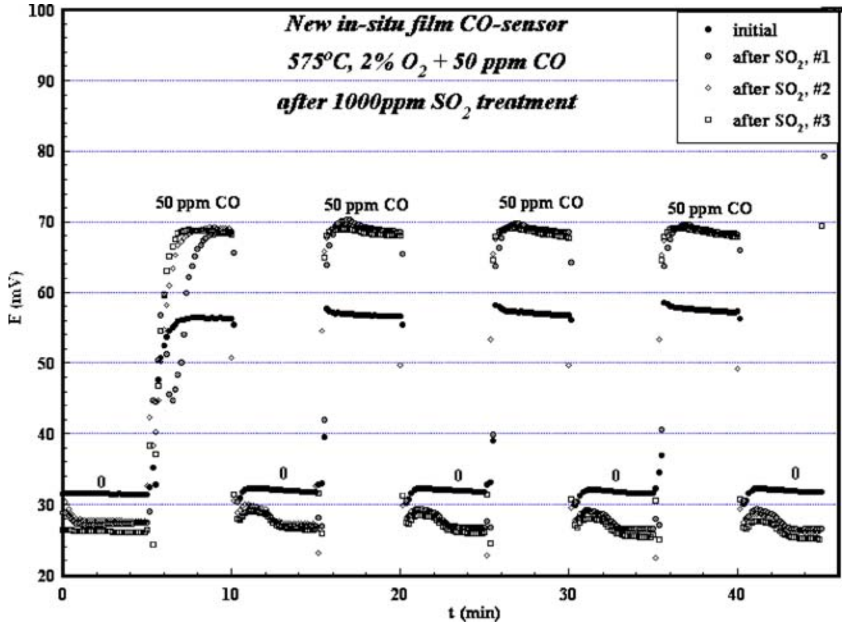


Fig. 11 $Au_{0.8}(Ga_2O_3)_{0.2}$ composite CO sensor response stability after SO_2 treatment at 575 °C

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