Electrochemical Materials and Technologies

LETTER

Electrochemical Materials and Technologies

eISSN: 2949-0561

Cite this: Electrochem. Mater. Technol. 2 (2023) 20232019

Sensor for operational control of oxygen and combustible gases concentration in waste gases of thermal units

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Received: 14 August 2023
Accepted: 22 September 2023
Published online: 3 October 2023

DOI: 10.15826/elmattech.2023.2.019

A new sensor has been developed for continuous monitoring of oxygen and combustible gases content in the waste gases of thermal units. The target application of the sensor is its installation in shunt pipes of thermal units, directly into the waste gas flow. The sensor is characterized by one reference gas electrode and three measuring electrodes applied on the surface of a solid electrolyte tube made of a zirconia electrolyte (e.g., 8YSZ). The reference gas electrode and one of the measuring electrodes were made of silver, the second measuring electrode was made of platinum, the third measuring electrode was made of a mixture of zinc oxide (95 wt %) and lanthanum-strontium manganite (5 wt %). The oxygen content in the gas mixture was determined by the well-known potentiometric method in accordance with the Nernst equation, i.e. an Ag|8YSZ|Ag electrochemical cell was used. To determine the products of incomplete combustion of fuel, the method of mixed potential between Pt- and Zn-based electrodes was used; the obtained potential value was determined by the difference in the oxidation rate of carbon monoxide as the main component of unburned fuels, on different materials of measuring electrodes. The experimental results of the sensor for the determination of carbon monoxide, hydrogen, and methane in a gas mixture are presented.

keywords: gas sensors, combustible gases, electrochemical analysis, solid state electrolytes, mixed potential

1. Introduction

The control of combustion processes in metallurgical and cement furnaces, as well as in boiler units of thermal power plants is an important issue, since the selection of optimization mode of fuel combustion requires data on oxygen concentration and products content for incomplete combustion of fuels in the exhaust gases in real time [1–3].

Typical furnaces and boiler units use various fuels with different calorific values, resulting in exhaust gases of different compositions. The optimum fuel/air ratio varies depending on the fuel used. Coal, gas, or oil are the most common fuels used in stove burners. For optimum combustion, oxygen excess and fuel must be minimized [3–5].

For the purpose of operative control over the content of O_2 and fuel residues in waste gases, the most promising are solid-state electrolyte sensors [6–8], because they are sufficiently reliable and stable to withstand severe process conditions, and demonstrate a fast response at the same time. Usually, solid-state potentiometric-type oxygen sensors based on the Nernst principle are used for these applications [9–12]. But there is no similar reliable sensor for simultaneous monitoring of fuel residues in gases.

Electrochemical cells based on yttria-stabilized zirconia (YSZ) are widely used in solid oxide fuel cells, oxygen pumps, oxygen generators, and gas sensors [13–15]. To analyze gas media, the classical electrochemical oxygen sensor is traditionally used, which has the form of a solid electrolyte tube with electrodes on its inner and outer surfaces [16].

A number of analytical methods can be used to control the combustible gas content in the waste gas

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stream of thermal units, which are unburned fuel residues. These methods include:

– Chemical methods, which are based either on sequential selective absorption of gas mixture components by different absorbers or on combustion of gases with subsequent analysis of oxidized products;

– Physical methods, which are based on the measurement of any physical quantity, which is in a regular dependence on the gas composition.

In turn, the physical methods of analyzing combustible gases include:

– Thermoconductometric [17]. The method is based on the comparison of relative thermal conductivity of gases. When analyzing a multi-component mixture, it is possible to determine the concentration of only one component, and the thermal conductivity of the remaining components should be approximately the same. This method is applicable to determine primarily hydrogen in combustion products, and when determining one of these components, the other two should be removed from the gas mixture.

– Thermochemical [18]. This method is applicable to the analysis of combustible gases (CO, CH_4, H_2). It uses the thermal effect of the combustion reaction of these components. By burning CO, H_2, and CH_4 at different temperatures, it is possible to analyze them separately;

– Optical [19]. The method is based on the different ability of gases to absorb infrared or ultraviolet rays, comparison of refractive indices of the analyzed gas and gas of known concentration, spectral measurements;

– Sorption [20]. The method provides for the determination of adsorption or desorption of the analyzed component of gas mixtures. The most common type of this analysis is a chromatographic method based on adsorption of the components of a complex gas mixture and then the sequential separation of individual components.

However, both chemical and known physical methods of analysis are quite labor-intensive and require complex equipment. And their main disadvantage is the fact that sampling, sample delivery, sample preparation and analysis operations are required for the analysis. Although the optimal option is continuous analysis of the gas mixture in real time. In order to realize the optimal option, the electrochemical method using mixed potential is the most promising [21]. The use of this method allows creating a rather miniature sensor working directly in the flow of the analyzed gas, for example, in a shunt tube. A lot of research has been carried out in this direction, various combinations of measuring electrodes have been considered, both for the selective analysis of combustible gases and for the analysis of individual gases.

The operation principle of solid-state potentiometric sensors is well known. Usually, a YSZ-based solid electrolyte tube is used. Platinum electrodes are applied on the opposite surfaces of such a tube. One of the electrodes is supplied with a reference gas with known oxygen content (usually air), and the other electrode is fed with the analyzed gas. When analyzing gas mixtures containing oxygen and an inert gas, the electrochemical circuit of the sensor is as follows:

$$O_2(p'O_2), Me' \left| O^{2-} \right| Me'', O_2(p''O_2), \quad (1)$$

where $p'O_2$ and $p''O_2$ are the oxygen partial pressures at the reference and measuring electrodes. Usually, platinum is used as the material for the reference and measuring electrodes. When analyzing gas mixtures containing oxygen and combustible gases such as CO, H_2, and CH_4, the electrochemical circuit of the sensor is as follows:

$$O_2(p'O_2) + \mathrm{red}(p_{red}), Me' \left| O^{2-} \right| Me'', O_2(p''O_2), \quad (2)$$

where p_{red} is the partial pressure of combustible gas, red = CO or H_2.

On the measuring electrode, the following electrochemical reactions occur:

$$1/2O_2 + 2e' \rightleftarrows O^{2-}, \quad (3)$$

$$\mathrm{red} + O^{2-} \rightleftarrows \mathrm{ox} + 2e'. \quad (4)$$

The simultaneous occurrence of reactions (3) and (4) causes the appearance of the so-called mixed potential. The mixed potential differs from the equilibrium potential due to the delayed chemical reactions. The reaction kinetics are highly dependent on the type of electrode material and its structure. For example, the potential at the measuring electrode made of some oxides differs significantly from the potential at the Pt-electrodes, which is a good catalyst [22]. In the works [23, 24], it was noted that such parameters of electrochemical sensors as sensitivity, selectivity, and stability of measurements are conditioned by the mechanism of mixed potential and peculiarities (nature) of the measuring electrode materials. Low sensitivity and reproducibility, as well as slow dynamics of response to combustible gas at temperatures below 700 °C and unsatisfactory temporal stability of mixed potential sensors remain serious problems [25, 26] preventing their widespread use.

The purpose of this work is to study the capability of the sensor for the simultaneous measurement of oxygen and carbon monoxide contents in the analyzed gas

mixtures. If there is enough information on the determination of oxygen content in various gas mixtures by solid-state potentiometric sensors, there is little information on the study of the response of various oxide electrodes to the content of combustible gases in the oxygen-containing gas mixtures, especially at temperatures from 500 to 550 °C.

2. Experimental part

Silver was chosen as a material for the reference electrode and one of the measuring electrodes of the sensor. This allows the operating temperature for oxygen analysis to be reduced to 500–550 °C. Taking into account the fact that even at these temperatures silver can evaporate and affect the normal operation of other measuring electrodes due to condensation of silver vapor on them, the silver measuring electrode was coated with a solid electrolyte slurry. This coating prevented the transfer of silver vapor to the other electrodes and had virtually no effect on the measurement dynamics. Regarding two other electrodes of the sensor, the following compositions were used: one measuring electrode was made of Pt, while the second electrode was performed from a mixture of ZnO (95 wt %) and $La_{0.6}Sr_{0.4}MnO_{3-\delta}$ (5 wt%). The choice of Pt and ZnO as measuring electrode materials was based on the results of previous work [27]. The addition of lanthanum-strontium manganite to the zinc oxide was found to improve adhesion of the ZnO electrode to the surface of the YSZ electrolyte tube.

The experiments were carried out over a temperature range of 500–550 °C. The concentration of oxygen in the analyzed gas mixtures was between 0.2 and 4 vol %, while the content of combustible gases in the analyzed oxygen-containing gas mixtures varied from 10 to 2000 ppm.

The fabricated sensor represents a tube made of the YSZ electrolyte with four potential electrodes: two Ag electrodes formed on the opposite sides of the tube and two (Pt- and ZnO-based) electrode rings formed onto the inner tube surface, as it is shown in Figure 1.

For the testing of the sensor, it was first placed in a quartz tube with a diameter of 30 mm, which was also a tube furnace with a nichrome heater. The operating temperatures were maintained with an accuracy of ± 3 °C using a TP 703 temperature controller (Varta, Russia). The interior of the quartz tube was fed by a gas mixture, the composition of which was adjusted by mixing air, nitrogen, and combustible gases using a F-201C-FAC-33-V gas flowmeters (Bronkhorst, Germany).

Gas mixtures with known component concentrations (purchased from a manufacturer of technical gases) were used as analyzed atmospheres: $O_2 + N_2$, $CO + N_2$, $H_2 + N_2$, and $CH_4 + N_2$. The total flow rate of the gas mixtures was 60 ml/min. Steady-state electrode potential measurements were performed using a B7-77 digital voltmeter (MNIPI, Russia). The accuracy of voltage measurement was 0.5 mV. Measurements were made after 30 min of holding the sensor at constant temperature.

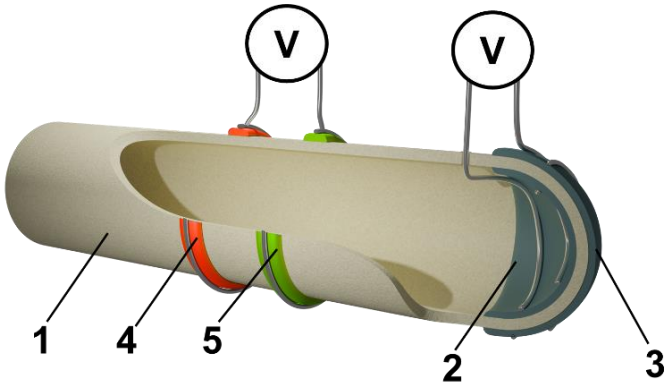

Figure 1 A scheme of the fabricated sensor allowing the joint measurements of Nernst and mixed potentials: 1 – YSZ tube, 2 – reference Ag electrode, 3 – measuring Ag electrode, 4 – measuring Pt electrode, 5 – measuring ZnO-based electrode.

3. Results and discussion

At the preliminary stage, the influence of the oxygen content on the mixed potential value between the measuring Pt- and ZnO-based electrodes was determined in the presence of a constant concentration of carbon monoxide in the analyzed $O_2 + CO + N_2$ gases. Measurements were carried out in the temperature range at 550 °C. According to Figure 2, the mixed potential value is almost stable and almost does not depend on the oxygen concentration with its variation from 0.15 to 2 vol %, when the CO concentration in these gas mixtures is constant. The slight signal fluctuations observed may be related to the different degrees of combustion over the Pt electrode, which is known to catalyze various conversion processes at elevated temperatures.

Figure 3 shows the changes in the mixed potential value depending on the carbon monoxide concentration in oxygen + carbon monoxide + nitrogen gas mixtures at 500 and 550 °C. As can be seen, there is an almost linear relationship between the mixed potential value and the carbon monoxide concentration, indicating that the sensor is characterized by high sensitivity, which is around 23 mV/1000 ppm CO at 550 °C. The linearity of the sensor response is well maintained in the CO concentration range from 0 to 0.15 vol %. As the CO concentration increases above 0.15 vol %, a slight decrease in response is observed. This can be explained by the fact that the amount of adsorbed carbon monoxide at

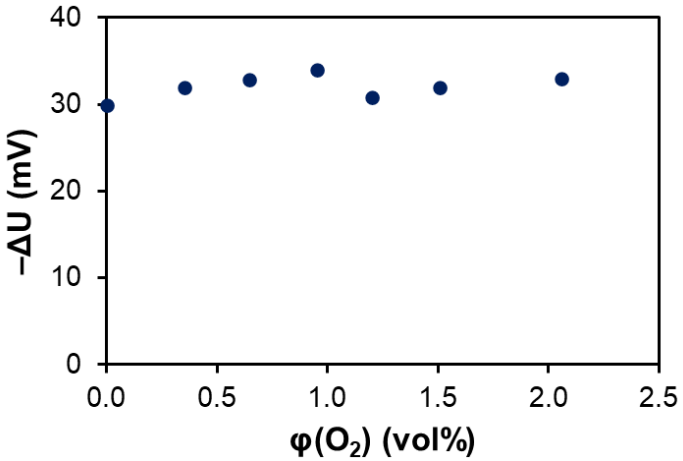

Figure 2 Mixed potential change at 550 °C depending on the oxygen content in O_2 + CO + N_2 gases.

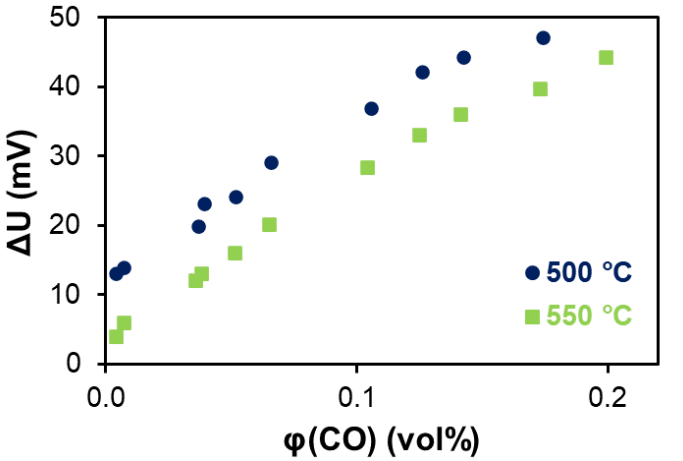

Figure 3 Mixed potential value between Pt- and ZnO-based electrodes depending on the carbon monoxide content in O_2 + CO + N_2 gases.

the electrode-electrolyte interface reaches a certain saturation level for a given temperature.

The Pt/ZnO electrode pair is not selective for carbon monoxide solely. It is more collective for the whole group of combustible components that may be present in the exhaust gases of thermal units. In addition to CO, hydrogen and methane may also be present. The effect of the cross-sensitivity of the sensor towards H_2 and CH_4 is shown in Figure 4.

Figure 4a shows that the mixed potential value of the sensor increases with increasing hydrogen in gas mixtures. However, the sensitivity to hydrogen at 550 °C is negligible, reaching only 2.2 mV/1000 ppm. The weak response of hydrogen is caused by its low autoignition temperature (560 °C); when a platinum electrode is used, this temperature can be even lower. Although the sensor signals for CO and H_2 are generally incomparable in magnitude, taking into account that the sensor is designed to control combustible gases in the aggregate, we end up with a total signal for these two gases. The same occurs for the presence of methane in the exhaust gases. The dependence of the mixed potential of the sensor on the methane content in the analyzed gas is shown in Figure 4b. The corresponding dependence at 550 °C is nearly linear in the methane range from 0 to 2000 rpm, while at 500 °C the linearity range is weakened up to 1500 rpm followed by a sign of stabilization. The magnitude of the response is larger than that of hydrogen but smaller than that of carbon monoxide. Because methane is less reactive than carbon monoxide, its absolute response values are lower. The presence of methane, as well as hydrogen, will increase the total signal of the sensor, increasing its efficiency.

The measured dynamic characteristics of the sensor (Figure 5) show good signal reproducibility and short response time. But even at 550 °C, the dynamics can generally be considered satisfactory. The time to reach 90% of a nominal signal is quite significant and is about one minute.

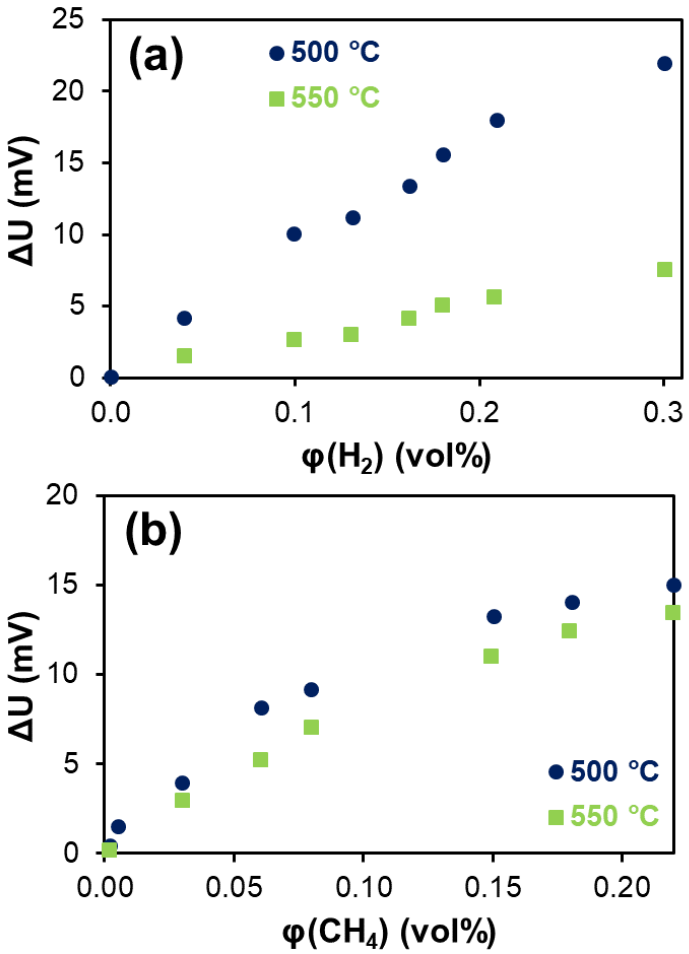

Figure 4 Mixed potential value between Pt- and ZnO-based electrodes depending on (a) the hydrogen content in O_2+H_2+N_2 gases and (b) the methane content in O_2 + CH_4 + N_2 gases.

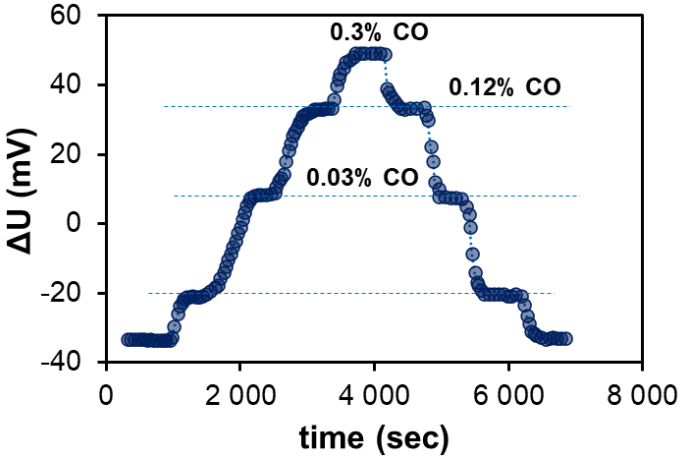

Figure 5 Time dependence of the sensor response towards the CO changes in the analyzed gas mixtures at 550 °C.

According to the recent review [28], a large number of mixed potential sensors have been fabricated for monitoring various gas compounds (NH_3, NO_x, CO, alkanes, H_2S) in the environment. These sensors are able to operate in a wide detection range (from 1 to 2000 ppm) at elevated temperatures (400–1000 °C). Taking CO as an example, the fabricated sensor has good sensitivity and detection range. In addition, this sensor is capable of analyzing not only CO-containing gas mixtures, but also H_2- and CH_4-based gas.

4. Conclusions

The design of an electrochemical sensor for simultaneous measurement of the content of oxygen and products of incomplete fuel combustion in the exhaust gases of thermal units is proposed.

The experimental data of the measurement of the contents of carbon monoxide, hydrogen, and methane in the gas mixtures are obtained.

It is established that the oxygen content of the gas mixtures does not affect the determination of the content of carbon monoxide, hydrogen, and methane when the mixed potential method is used.

The dynamics of the fabricated sensor is studied.

The obtained results allow us to evaluate the use of the mixed potential method as promising for its practical application.

Supplementary materials

No supplementary materials are available.

Funding

This work was prepared within the framework of the budgetary plans of the Institute of High Temperature Electrochemistry (IHTE).

Acknowledgments

None.

Author contributions

Anatoly Kalyakin: Resources; Software; Data curation; Formal Analysis; Investigation.

Alexander Volkov: Conceptualization; Methodology; Validation; Visualization; Writing – original draft; Writing – Review & Editing; Project administration; Supervision.

Conflict of interest

The authors declare no conflict of interest.

Additional information

Web-site of the Laboratory of Electrochemical Devices Based on Solid Oxide Proton Electrolytes (IHTE): https://ihte.ru/?page_id=3787.

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