Electrochemical detection of simple alkanes by utilizing a solid-state zirconia-based gas sensor

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Abstract

Solid-state gas sensors composed of complex oxide electrolytes offer great potential for analyzing various atmospheres at high temperatures. While relatively simple gas mixtures (H_2O+N_2, O_2+N_2) have been successfully studied by means of ZrO_2-based sensors, the precise detection of more complex compounds represents a challenging task. In this work, we present our findings regarding the analysis of lower alkanes (CH_4, C_2H_6, and C_3H_8) mixed with nitrogen as an inert gas, utilizing an amperometric ZrO_2-based sensor. This sensor, serving as an electrochemical cell with a diffusion barrier, was tested at 500–600 °C to measure the limiting current, which depends on the gas composition and can be further used as a basis for calibration curves. In addition, the diffusion coefficients of the specified gas mixtures were successfully found and compared with references, confirming the applicability of the fabricated sensor for studying diffusion processes in wide concentration and temperature ranges.

1. Introduction

Complex oxide electrolytes based on zirconia are widely used in many fields of science and technology. One of the promising fields of ZrO_2-containing materials application is analytical chemistry. For example, potentiometric solid-state sensors have been successfully used to monitor the exhaust gases of various heat units and vehicles [1–4]; moreover, they can be used to measure the oxygen activity in metal melts [5] and to detect some gases in the environments (NH_3 [6], NO_2 [7], H_2S [8]). Based on the concept of potential reading, such types of sensors operate efficiently for detecting low oxygen contents in gases/melts compared to reference conditions (an electrode in air or oxygen atmospheres). To detect a relatively high concentration of the analyzed components, the so-called amperometric-type sensors can be employed. In detail, the ZrO_2-based amperometric sensors have recently been used for measuring the contents of O_2, H_2, CO_2 and H_2O in inert gases [9–13]. The reading parameter of such sensors is a limiting current, representing an electrical equivalent of the concentration and diffusion parameters of the analyzed gas media.

The amperometric sensors allow the analysis of more complex gases, which may contain lower alkanes (CH_4, C_2H_6, and C_3H_8), not only in terms of gas composition, but also in terms of diffusion coefficients. At present, there are no reliable methods or appropriate techniques for measuring the diffusion coefficients of gases due to the complexity of the equipment and the methodological difficulties, although these coefficients are widely used in the calculation of combustion processes, in chemical kinetics; in addition, the diffusion coefficients are included in many dimensionless criteria for heat and mass transfer. The knowledge of the binary diffusion coefficients for combustible gases is necessary when calculating the processes of transport and regasification of natural gases.

In the present work, we develop a new high-temperature YSZ-based sensor for the analysis of CH_4+N_2, $C_2H_6+N_2$, and $C_3H_8+N_2$ gas mixtures and the determination of their binary diffusion coefficients.
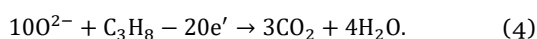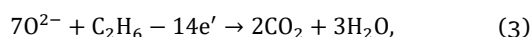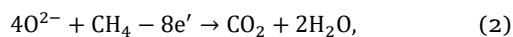
2. Experimental part

2.1. Operation principles

The working principle of the fabricated amperometric sensor is shown in Figure 1. This sensor consists of two plates made of YSZ (0.91ZrO₂ + 0.09Y₂O₃) electrolyte glued together by a high-temperature glass sealant. Each plate has a cavity, in which a capillary was placed as a diffusion barrier. The capillary is a ceramic tube with an inner diameter of 265 μm and a length of 20 mm. The cavity has a depth of 0.5 mm and an area of approximately 60 mm². Platinum electrodes with wire current leads were organized on opposite surfaces of one solid electrolyte plate.

During all the measurements, the electrochemical cell is in the flow of the analyzed gas, while the latter diffuses through the capillary into its internal cavity. There is no free oxygen in the analyzed gas, and oxygen is formed as a result of the dissociation of moisture present in the analyzed gas:

$$H_2O + 2e' \rightarrow H_2 + O^{2-}. \tag{1}$$
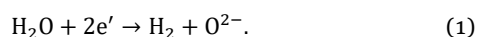
The oxygen produced by the dissociation of water vapor must be pumped into the cavity of the cell. To provide such a pumping, it is necessary to apply a minus from a DC source to the outer electrode of the cell, and a plus to the inner electrode, respectively. Alkane oxidation then takes place at the inner electrode according to the following overall reactions:

$$4O^{2-} + CH_4 - 8e' \rightarrow CO_2 + 2H_2O, \tag{2}$$

$$7O^{2-} + C_2H_6 - 14e' \rightarrow 2CO_2 + 3H_2O, \tag{3}$$

$$10O^{2-} + C_3H_8 - 20e' \rightarrow 3CO_2 + 4H_2O. \tag{4}$$

When working with mixtures of CH₄+N₂, C₂H₆+N₂, and C₃H₈+N₂, the oxygen pumping current into the sensor cavity ranged from several microamperes to tens of microamperes. As the voltage applied to the cell increases, the current increases and then stabilizes, reaching a certain value corresponding to the as-called limiting current. Its values, as shown by the results of this study, are proportional to the concentration of methane, ethane, or propane in the analyzed gases. The appearance of the limiting current is due to the reaction between the hydrocarbons and oxygen ions on the inner surface of the zirconium electrolyte. It is important to note that the flow of the analyzed combustible gas entering the cavity of the electrochemical cell is limited by the diffusion barrier (capillary), which governs the limiting current value. Therefore, the measured limiting current is a function of the concentration of the measured hydrocarbon in the analyzed gaseous medium, temperature and geometrical parameters of the diffusion barrier according to the following equation [13]:

$$I_{\lim} = \frac{n \cdot F \cdot P \cdot D \cdot S}{R \cdot T \cdot L} \ln\left(1 - c_{C_xH_y}\right), \tag{5}$$

where n in the electron numbers required for full oxidation of 1 mole of alkane, F is the Faraday's constant, P is the total pressure of the analyzed gas (P = 1 atm), D is the binary diffusion coefficient of N₂ and alkane mixture, S and L are the cross-section area and length of the capillary, R is the universal gas constant, T is the absolute temperature, $c_{C_xH_y}$ is the volume concentration of alkane in nitrogen.

At the relatively low concentration values, the $\ln\left(1 - c_{C_xH_y}\right)$ term is equal to $c_{C_xH_y}$. In turn, the D values depend on the standard conditions as follows [14]:

$$D = D_0 \left(\frac{T}{T_0}\right)^n \left(\frac{P}{P_0}\right), \tag{6}$$

where T_0 and P_0 are the standard parameters.

Considering equations (5) and (6) together, one can see that the standard diffusion coefficients can be found, if the limiting current values are known.

2.2. Characterization of the sensor

The fabricated sensor was placed in an oven and heated to the desired temperature (500, 550 or 600 °C). Then the analyzed gas mixtures (CH₄+N₂, C₂H₆+N₂, or C₃H₈+N₂) were fed to the sensor followed by equilibration of this system for 1 h. These gas mixtures were prepared by adding a portion of hydrocarbons into the nitrogen flow by F-201C-33-V gas flow meters. The DC voltage (GPS-18500 INSTEK) was applied to the electrodes to provide electrochemical pumping of oxygen.

3. Results and Discussion

The as-fabricated sensor was first tested with the CH₄+N₂ gas mixtures. Its typical volt-ampere dependences at different gas compositions are presented in Figure 2a. Three clearly distinguished regions appear at these dependences with a gradual increase in the applied voltage: current growth (I region), a wide range of constant current values (II region) followed by further current growth (III region). In the I region, the applied voltage causes oxygen pumping from the external to inner electrode, where the methane oxidation reaction occurs (equation (1)).
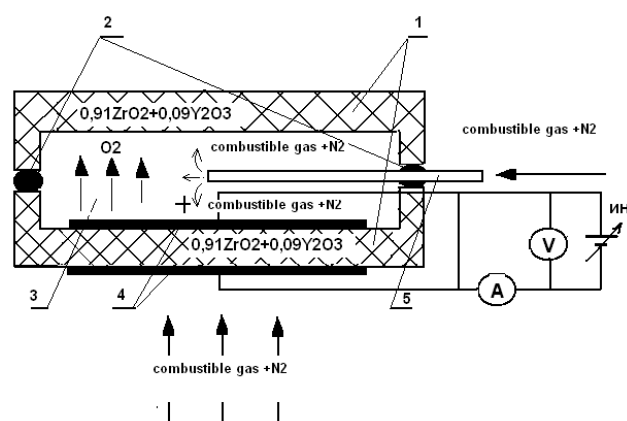

Figure 1 Principle scheme of operating the fabricated gas sensor: 1 is the electrolyte discs, 2 is the high-temperature glass sealant, 3 is the cavity, 4 is the platinum electrodes, and 5 is the capillary.
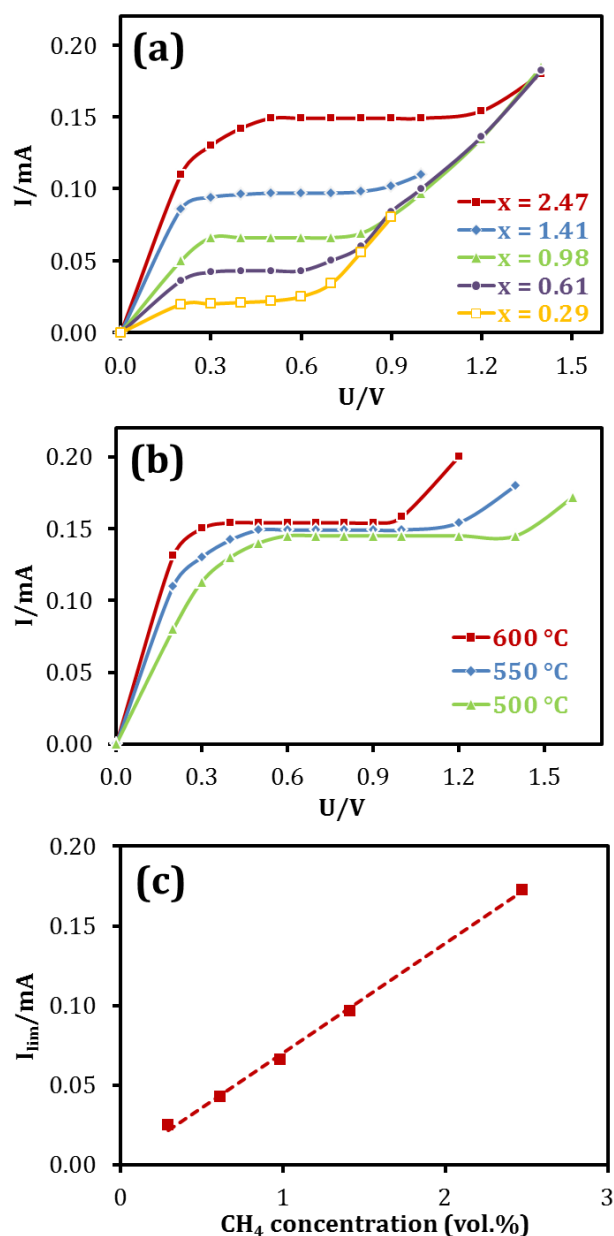
Figure 2 Electrochemical response of the sensor operated in x vol.% CH_4 + (1–x) vol.% N_2 gas mixtures: (a) volt-ampere dependences at 550 °C and various methane concentration; (b) volt-ampere dependences at various temperature and x = 2.47; (c) calibration curve at 550 °C.

An amount of methane is sufficiently high compared to the oxygen equivalent flow expressed in the current term; as a result, the current rises with increasing the applied voltage. When all the methane molecules in the sensor's cavity (including those supplied through the capillary) are electrochemically oxidized, the current values stabilize and do not change with a further increase of the applied voltage, II region. This region corresponds to the realization of the limiting current. Finally, when the applied voltage exceeds a certain value, the current increases again (III region) due to the possible appearance of electronic conductivity [15]. Considering the effects of gas composition, it can be seen that the limiting current region increases with its range and in absolute current values, indicating that more oxygen ions should be pumped to oxidize more methane molecules.

Figure 2b shows similar volt-ampere dependencies obtained for a given gas composition at various temperatures. The limiting current range is virtually unchanged with heating (~about 0.6 V), but the limiting current value increases at the same time. The latter can be explained by improved diffusion of methane molecules into the sensor's cavity. Therefore, a higher oxygen-ion flux is required to oxidize these molecules. The concentration dependence of the limiting current is close to a linear form (Figure 2c), which allows these data to be used for the analysis of real CH_4+N_2 gas mixtures with unknown concentrations of the components. Similar characteristics were obtained for C_2H_6+N_2 and C_3H_8+N_2 mixtures in the temperature range of 500–600 °C (Figure 3). In general, the electrochemical characteristics have similar trends discussed for the CH_4+N_2 gas mixtures, with some distinctive points. First, the limiting current values considerably decrease in a series of CH_4–C_2H_6–C_3H_8 (at close concentrations and the same temperatures), indicating that heavy molecules diffuse more slowly through the capillary. Second, the concentration range of the limiting current narrows as the molecular weight of the alkane increases, which limits the analytical capabilities of the sensor.

Nevertheless, an important advantage of the fabricated sensor is the ability to determine the binary diffusion coefficients from the measured limiting current values (even if they are not high) according to equations (5) and (6). Table 1 lists the experimentally obtained diffusion coefficient values for methane in nitrogen for three temperatures and their comparison with reference data.

As can be seen from Table 1, the experimentally obtained D values for methane in nitrogen have some discrepancies with the reference data obtained by other methods. This may be due to the fact that the reference data do not take the CH_4 concentration into account, since in most cases, the D values were obtained for mixtures with a parity concentration of the components, usually 50% to 50%. In addition, available reference data are often presented for several temperatures, typically 0 and 25 °C, and had to be recalculated for elevated temperatures according to equation (6). The experimental data show that the D values depend not only on the temperature, but also on the component concentrations (especially, methane), and this dependence is quite complex.

Table 2 presents similar D data measured and compared for the C_2H_6+N_2 gas mixtures. There is an acceptable agreement between the measured D values and reference data. However, the reference D values are somewhat higher than the experimental data for the entire temperature range and the considered ethane concentrations. This may be due to the different features of the experimental techniques used in the literature and in this work.

Finally, Table 3 lists the experimental results for the propane – nitrogen gas mixtures. The comparison of the experimental and reference values shows that they are in the best agreement with each other.
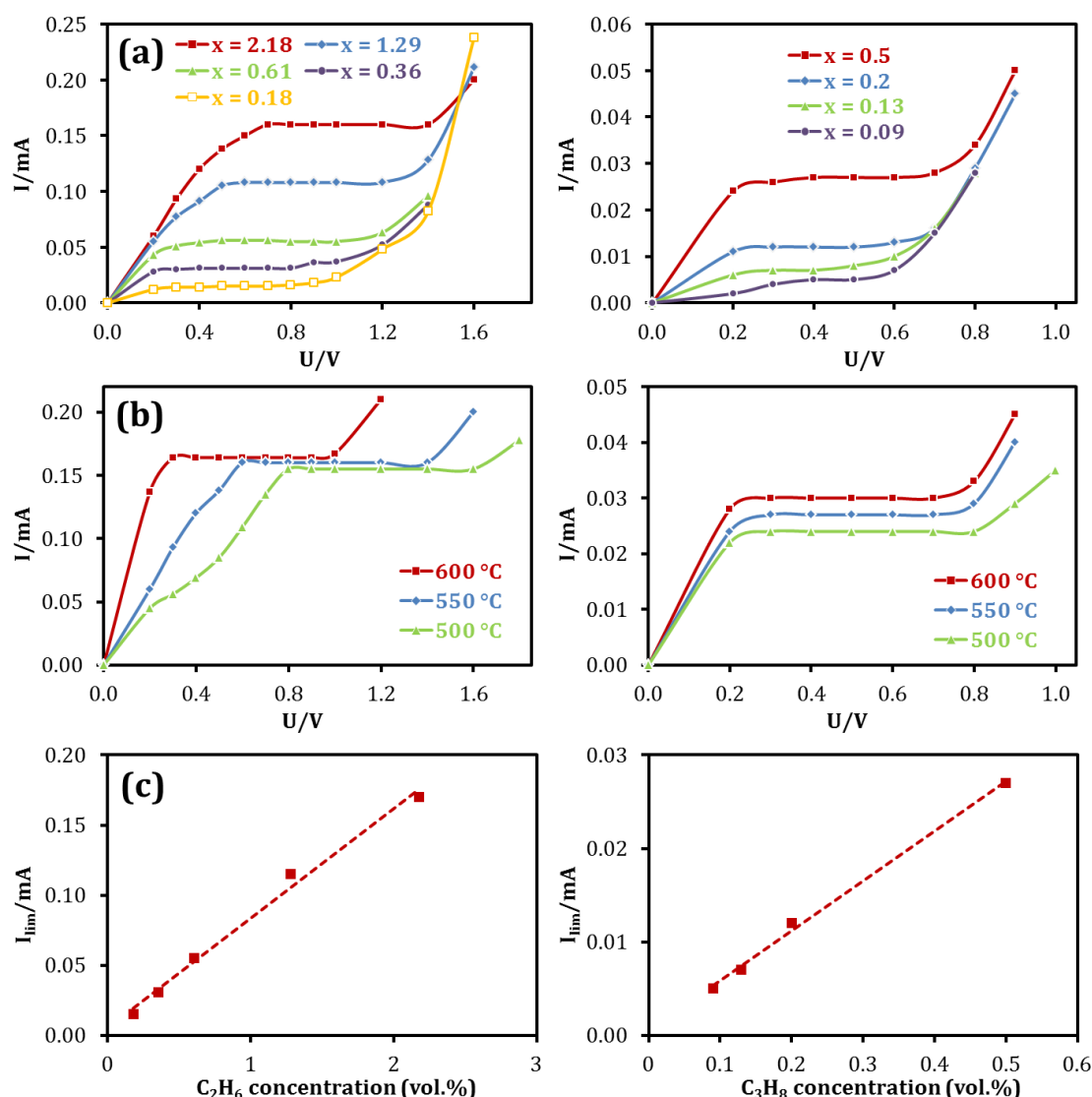
Figure 3 Electrochemical response of the sensor operated in x vol.% C_2H_6 + (1–x) vol.% N_2 gas mixtures (left column) and x vol.% C_3H_8 + (1–x) vol.% N_2 gas mixtures (right column): (a) volt-ampere dependences at 550 °C and various methane concentration; (b) volt-ampere dependences at various temperature and x = 2.47; (c) calibration curve at 550 °C.

Table 1 Measured and reference binary diffusion coefficients (D) for the x vol.% CH_4 + (1-x) vol.% N_2 gas mixtures.

Temperature (°C)	D (cm² s⁻¹) x = 0.29	D (cm² s⁻¹) x = 0.61	D (cm² s⁻¹) x = 0.98	D (cm² s⁻¹) x = 1.41	D (cm² s⁻¹) x = 2.47	D (cm² s⁻¹) [16]	D (cm² s⁻¹) [17]
500	1.8	1.8	1.78	1.77	1.6	1.22	1.32
550	1.3	1.4	1.8	1.9	1.7	1.35	1.48
600	2.2	2.1	2.05	1.7	1.8	1.50	1.66

Table 2 Measured and reference binary diffusion coefficients (D) for the x vol.% C_2H_6 + (1–x) vol.% N_2 gas mixtures.

Temperature (°C)	D (cm² s⁻¹) x = 0.18	D (cm² s⁻¹) x = 0.36	D (cm² s⁻¹) x = 0.60	D (cm² s⁻¹) x = 1.28	D (cm² s⁻¹) x = 2.18	D (cm² s⁻¹) [17]
500	0.64	0.65	0.69	0.63	0.55	0.76
550	0.68	0.69	0.74	0.67	0.59	0.85
600	0.72	0.73	0.78	0.71	0.62	0.93

Table 3 Measured binary diffusion coefficients (D) for the x vol.% C_3H_8 + (1–x) vol.% N_2 gas mixtures.

Temperature (°C)	D (cm² s⁻¹) x = 0.09	D (cm² s⁻¹) x = 0.13	D (cm² s⁻¹) x = 0.20	D (cm² s⁻¹) x = 0.51	D (cm² s⁻¹) [17]
500	0.52	0.49	0.59	0.50	0.55
550	0.62	0.61	0.67	0.60	0.61
600	0.72	0.72	0.73	0.71	0.67

4. Limitations

As can be seen from the experimental data (Figures 2 and 3), the fabricated sensor shows good operability at low concentrations of alkanes in nitrogen. The higher hydrocarbon contents will provide the higher limiting current. However, a longer response time is required in this case. At the lower concentrations of hydrocarbons, a limiting current region is expected to be very weak, which does not allow the formation of the calibration curves.

5. Conclusions

This work reports on the possibility of using an amperometric sensor with a diffusion barrier to determine the concentration and binary diffusion coefficients of some light alkanes in nitrogen at elevated temperatures (500–600 ºC). We have experimentally obtained the values of the diffusion coefficients for CH_4+N_2, $C_2H_6+N_2$, and $C_3H_8+N_2$ gas mixtures. Our values are in good agreement with those reported in published data.

● Supplementary materials

No supplementary materials are available.

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● Author contributions

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● Conflict of interest

The authors declare no conflict of interest.

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