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Features of behavior of solid-state CO_2 sensors at low temperatures

Abstract The dependence of the impedance of low-temperature sensors for carbon dioxide based on the solid-state electrochemical cells $Na_{0.5}WO_3/Na_5Gd-Si_4O_{12}/SnO_2(Sb_2O_4)$ on the concentration of carbon dioxide in the air was studied. The reversible change in the sensor resistance was shown to be due to adsorption processes at intergrain boundaries of the solid electrolyte. The composition of the products of the electrochemical processes occurring in the sensors was established.

Keywords Carbon dioxide · Sensor · Solid electrolyte

Introduction

The first experiments on the detection of CO_2 in gases using solid electrolytes were carried out on carbonate electrolytes with conductivity using alkaline and alkali-earth metal cations [1]. Electrolytes of the β-alumina and NASICON type with a high ion conductivity at low temperatures were used further to decrease the working temperature of these sensors [2]. This made it possible to decrease the working temperature to 400 K. The accumulation of dielectric products and the blocking of the working electrode/electrolyte interfaces appeared to be the limiting processes. The modern state of development of sensors for CO_2 working at elevated temperatures is reviewed in Ref. [3].

In Refs. [4, 5, 6] we reported that the potential of the sodium-conducting solid electrolyte/metal oxide interface was reversible and changed selectively with a change of CO_2 concentration in the air under the following conditions: 250–315 K, moisture content 15–75 rel%). The authors of Refs. [7, 8] proposed that reversibility in the proposed systems was determined by the possibility of removal of the reaction products over the boundaries of the electrolyte and electrode grains. It was shown that the electrochemical solid-state cell

$$Na_{0.5}WO_3/Na_5GdSi_4O_{12}/SnO_2(Sb_2O_4) \qquad (1)$$

is suitable for the low-temperature detection of CO_2.

The dependence of the sensor electromotive force (emf) upon CO_2 concentration in the air is described by the Nernst equation for one-electron processes.

The authors of Ref. [9] confirmed the main results of Refs. [5, 6]. Recently it has been shown that the introduction of an auxiliary layer consisting of sodium hydrocarbonates or hydrophosphates at the interface between the working electrode and solid electrolyte stabilizes the work of sensors for CO_2 at room temperature [10].

This work was aimed at studying products of potential-determining processes in low-temperature sensors for CO_2 based on the electrochemical cell (Eq. 1).

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Experimental

The emf of the electrochemical cells was measured by a Shch-300 high-ohmic voltmeter connected to a cell through a U-5-11 amplifier (the input resistance was 10 GΩ). Frequency functions of resistances were measured in the range from 10 Hz to 500 kHz using a VM-507 impedance meter.

The composition of the products formed during the work of a sensor was determined by a linear heating of the sensor or its individual elements in a vacuum along with simultaneous mass spectrometric analysis of the gas-phase composition. The heating rate of the samples was varied from 0.1 to 50 K/min. The dependence of the amount of the evolved gas on the heating time

(thermal decomposition spectrum) was detected. An MI-1201 mass spectrometer was used for the determination of the gas-phase composition during thermal decomposition.
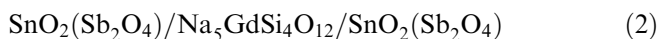
Sodium–tungsten oxide bronze $Na_{0.5}WO_3$ was prepared by the reduction of $Na_2W_4O_{13}$ with hydrogen at 900 K. $Na_5GdSi_4O_{12}$ was synthesized according to the procedure described in Ref. [11]. Solid solutions based on tin dioxide were obtained by the calcination of the hydroxides precipitated in common.

Results and discussion

Parameters of electrochemical cells

The emf of the cell (Eq. 1) changes stepwise with a stepwise change of the CO_2 concentration in the gas phase. The time of establishment of the stationary emf (τ_{90}) decreases with an increase in the CO_2 concentration (Fig. 1). The concentration dependence of the emf is described by the Nernst equation for a one-electron process in the temperature interval from 250 to 315 K and humidity variations from 15 to 85 rel% (Fig. 2).

In order to study the processes in CO_2 sensors, the impedance of the symmetrical cells

$$SnO_2(Sb_2O_4)/Na_5GdSi_4O_{12}/SnO_2(Sb_2O_4) \qquad (2)$$

$$Na_{0.5}WO_3/Na_5GdSi_4O_{12}/Na_{0.5}WO_3 \qquad (3)$$

in the air in the presence of different amounts of CO_2 was investigated.

The impedance hodographs of both the symmetrical (Eqs. 2, 3) and nonsymmetrical (Eq. 1) cells are like. The typical shape of the hodographs is presented in Fig. 3. They are represented by two arcs, whose centres are considerably dropped relative to the real axis. The total resistance of the sensor (the low-frequency cutoff in the real axis) changes reversibly with changing the CO_2 concentration. The plot of this resistance versus the thickness of the solid electrolyte is linear and indicates the absence of a noticeable contribution of the electrode impedance to the total resistance (Fig. 4). In addition,
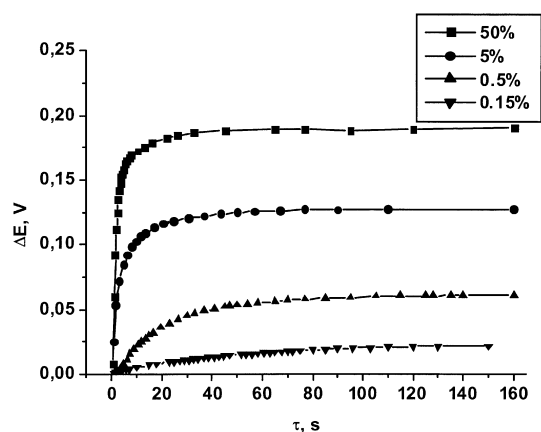

Fig. 2 The electromotive force (*emf*) dependence of the cells $Na_{0.5}WO_3/Na^+$-solid electrolyte/$SnO_2(Sb_2O_4)$ on CO_2 concentration in air. 294 K, 52% relative humidity

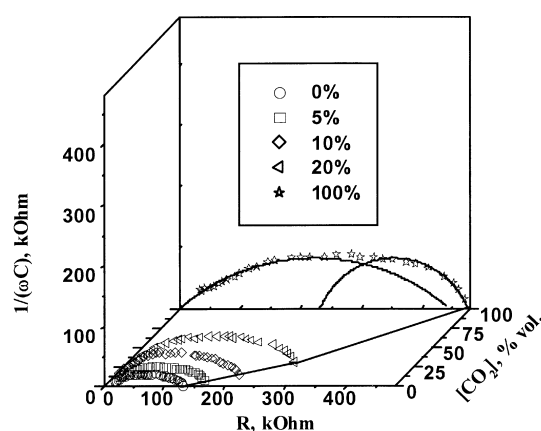**Fig. 3** Evolution of impedance hodographs of the cell (Eq. 1) for increases of CO_2 concentration in air. 294 K, 52% relative humidity

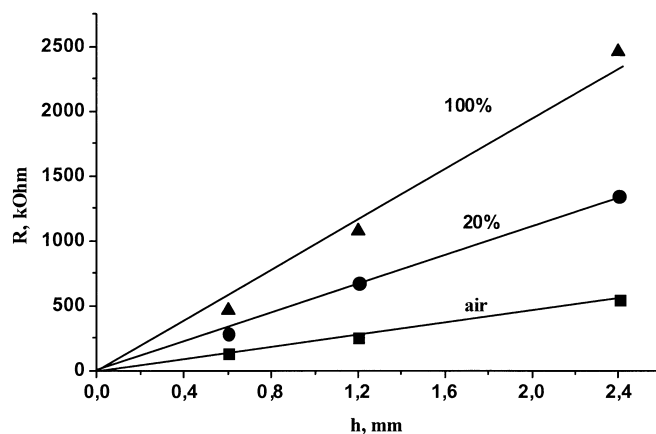**Fig. 1** Potential relaxation for changes in CO_2 concentration in air. 294 K, 52% relative humidity

Fig. 4 Dependence of the total resistance of the cell (Eq. 1) on the solid electrolyte thickness at various CO_2 concentrations in air. 294 K, 52% relative humidity

the volume resistance of the ceramic electrolyte is much lower (about 300Ω cm at 298 K) than the observed resistances, which indicates that both arcs characterize the intergrain conductivity of the solid electrolyte.

Since the changes in the resistances are reversible, and they return to the initial values after removal of CO_2 from the gas phase, we can suppose that they correspond to adsorption processes at the grain boundaries. Similar adsorption is the necessary stage during CO_2 detection, which is indicated by the investigations of the sensors with different solid electrolyte. The sensor with NAS-ICON ($Na_3Zr_2Si_2PO_{12}$) as a solid electrolyte, whose resistance depends on CO_2 concentration very weakly, has a nonlinear concentration dependence of the emf and low sensitivity (Fig. 2). The use of $Na_3Sc_2(PO_4)_3$, whose resistance is independent of the CO_2 concentration, results in the absence of the potentiometric response at a change in the CO_2 concentration. Probably, at this stage, as follows from the results of quantum-chemical calculations [12], carbonate and hydrocarbonate ions are formed involving water and oxygen molecules adsorbed on the surface according to the equations

$$CO_2 + O^{2-} = CO_3^{2-} \tag{4}$$

$$CO_2 + H_2O = HCO_3^- + H^+ \tag{5}$$

In accordance with the reactions the response of the electrochemical cells to the change of CO_2 content is determined by the hydration ability of the solid electrolytes. As shown in Ref. [13], this ability increases in the series $Na_3Sc_2(PO_4)_3 < Na_3Zr_2Si_2PO_{12} < Na_5GdSi_4O_{12}$, which conforms to the different sensitivities of the sensors based on the electrolytes to the change of CO_2 concentration.

Processes resulting in sensor degradation

A slow monotonic change in the parameters is observed during storage in a CO_2-containing atmosphere in parallel with the reversible change in the parameters of the cells (Eq. 1) related to a change in the CO_2 concentration. So, as the sensor works, the sensitivity of the sensor decreases (sensitivity depends on the number of electrons involved in the potential-determining processes), whereas the total resistance increases monotonically (Fig. 5). This indicates that the processes that occur in the potentiometric cell (Eq. 1) are not completely reversible, and the process products are concentrated inside the sensor. This irreversibility is due to the electronic component of the conductivity of the solid electrolyte. However, since this value is low, the total amount of the product that formed is also low. For example, on storing the sensor for 4 months in air plus 0.1% CO_2 at 294 K, its resistance increases more than by 2 orders of magnitude, whereas only 1–2 μg of bound carbon per 100 mg of the sensor is accumulated.
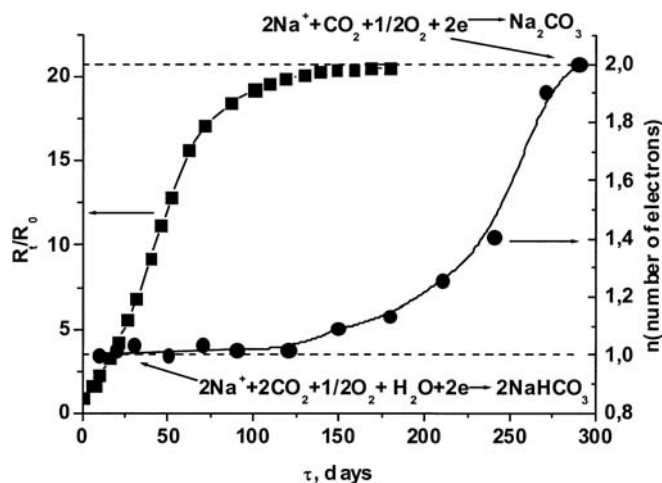

Fig. 5 Dependence of the total resistance (*squares*) and the number of electrons (*circles*) in the potential-determining reaction according to the Nernst equation upon storage time for the sensor under an atmosphere of air plus 0.1% CO_2. 294 K, 52% relative humidity

We analysed the gas phase during linear heating of the sensor to establish the composition of the products formed. The thermal decomposition spectrum of the sensor is presented in Fig. 6. Water, CO_2, and traces of CO were found in the composition of the gas phase. Comparison of the spectra obtained with the spectrum of the decomposition of individual substances allows us to distinguish the spectral regions responsible for the decomposition of sodium carbonate and hydrocarbonate. The peak corresponding to the evolution of CO and CO_2 can be attributed either to the decomposition of sodium acetate or to traces of organic contamination. It is impossible to assign this peak more exactly because its intensity is low.
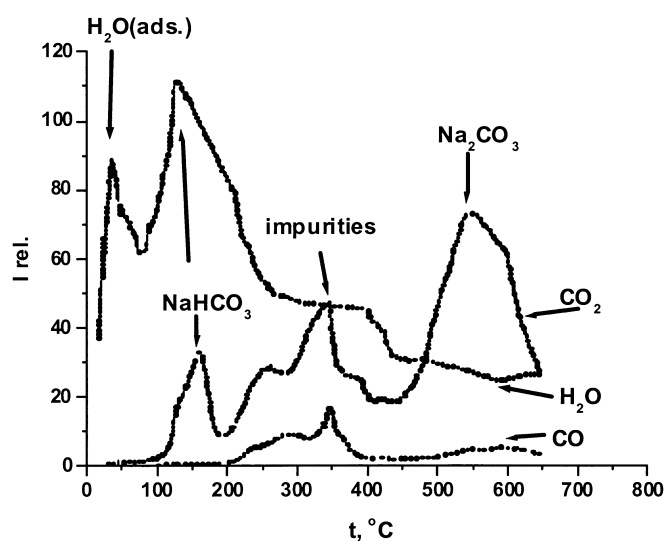

Fig. 6 Thermal desorption spectra of H_2O, CO_2 and CO after storing the cell (Eq. 1) for 6 months under an atmosphere of air plus 0.1% CO_2. 294 K, 52% relative humidity

As for sodium carbonate, its amount calculated from the thermal decomposition peak is greater than that corresponding to the decomposition of hydrocarbonate, indicating that Na_2CO_3 is also formed directly during electrochemical processes. The relative content of the carbonate increases with storage of the sensor.
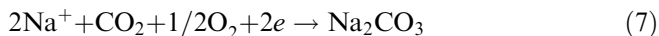
A special thermal decomposition spectrum analysis of the working electrode and the solid electrolyte shows that the sodium hydrocarbonate that formed is not localized at the electrode/electrolyte interface but is uniformly distributed over the whole volume of the electrode material and electrolyte. This indicates the possibility of diffusion over intergrain boundaries of the working electrode and the electrolyte.

The content of sodium carbonate in the solid electrolyte is much higher than that in the electrode; however, the largest portion is still concentrated at the interface of two phases, thus gradually blocking it.

Thus, the main process that determines the behaviour of the sensors is the following:

$$2Na^+ + 2CO_2 + H_2O + 1/2O_2 + 2e \rightarrow 2NaHCO_3 \qquad (6)$$
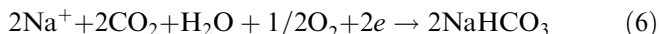
However, as the sensor ages, the process

$$2Na^+ + CO_2 + 1/2O_2 + 2e \rightarrow Na_2CO_3 \qquad (7)$$

gains greater significance.

The process in Eq. (6) can be related to the change in the prelogarithmic coefficient in the Nernst equation with aging of the sensor.

Conclusion

The impedance hodographs can be described by two different processes occurred in the bulk of the cell (Eq. 1). During the detection of CO_2, the cell resistance changes reversibly, which is associated with the intercrystallite adsorption of CO_2.

The parameters of the Nernst equation for the electrochemical sensors $Na_xWO_3/Na_5GdSi_4O_{12}/SnO_2$

(Sb_2O_4), CO_2, air are determined by the formation of sodium hydrocarbonate. The reaction product is not concentrated at the interface but diffuses over intercrystallite boundaries of the electrode and electrolyte, thus providing the reversibility of the potential change.

The change in the parameters of the Nernst equation during prolonged storage of the sensor is related to blocking of the active sites of the sensitive electrode and changes in the mechanism of the potential-determining process (from the formation of sodium hydrocarbonate to the formation of sodium carbonate). Carbonate diffusion from the triphase boundaries is strongly hindered. The accumulation of the product decreases the reversibility and transforms the sensitive electrode into the blocking one.

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