

Potential relaxation of the superionic system sensitive to CO₂ concentration

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The recent hard development of all-solid electrochemical gas sensors prompts investigation of relaxation and establishment of potential in all-solid electrochemical circuits of type

working electrode/solid electrolyte/reference electrode under potentiometric conditions. The response of such system to a change in the composition of the environment is the potential difference between the working electrode and reference one. The objective of this work is to investigate the kinetics and mechanism of potential relaxation of the systems sensitive to CO₂ concentration in air.

A known theoretical model of the potential establishment in electrochemical sensors is based on the empirical Fouletir-Seinera-Kleitiz equation [1], received for oxygen electrodes at high temperatures:

$$F(t) = \exp[-(t/\tau)^{1/2}], \text{ or } \ln F(t) = A + B t^{1/2} \quad (1)$$

where $F(t) = (E_t - E_\infty)/(E_o - E_\infty)$ is the reduced time dependence of potential; A and B are empirical constants. As shown in [2], in the case, when the rate of potential establishment is controlled by the rate of a chemical or electrochemical reaction or adsorption, the relaxation is determined by the exchange currents of the respective processes. This can formally be represented as charging of the capacity of an electrical double layer via the Faraday resistance $RF = RT/nFi_o$:

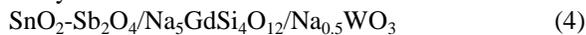
$$F(t) = \exp(-t/R_F C_{dl}) \quad (2)$$

The equation of type (1) can be received only in two cases: under diffusion control [3] and when slow relaxation of the double layer at the electrode/SE interface is the rate-determining process. In the second case diffusion relaxation of type (1) is often observed in region of high frequencies. In frequency coordinates it results to the well-known Warburg impedance:

$$Z_W = W \omega^{-1/2} - j W / \omega^{1/2} \quad (3)$$

that is related to diffusion of minor carriers in solid. The equation of type (2) is realized when relaxation was determined by single process.

We study the relaxation mechanism of potential of sensor system



sensitive to concentration of CO₂ in air by measuring the time response after "chemical pulse" i.e. after fast increasing of CO₂ concentration in environment. CO₂ concentration change was from 0 to correspondent value (0.5 — 50 % vol. of CO₂). However an analysis of potential time dependencies is possible only if relaxation controlled by single process. It is very hard to divide some processes. To time response analysis we convert the experimental time dependencies of potential to frequency complex coordinates by Fourier conversation and then plotted them in the $\text{Re}(F(\omega)) - \text{Im}(F(\omega))$ complex plane. This method proposed in [2].

Relaxation responses to chemical pulse shown in fig.1 (in common coordinates), and in fig.2 (after conversation to frequency response). Based on the fact, that there is single semi-circle observed on this plots, one can conclude, that in contrast to our earlier observation of hydrogen systems [2], the response of CO₂ sensitive systems defined by single relaxation process with time constant 100 - 500 s depending of ending concentration.

Received in this investigation experimental data of relaxation after CO₂ concentration increasing in the system with working electrode of solid solutions SnO₂-Sb₂O₄ allow to expect that the diffusion of CO₂ from gas phase to reaction zone occurs enough quickly and no influent to relaxation processes. The relaxation controlled by chemical reactions. The nature of such reaction discussed in [4].

The critical stage of potential creation process may be an gas adsorbtion at the interface working electrode/SE. The argument for this suggestion is the reversible change of system resistance in atmosphere containing CO₂ (fig.3).

This work is supported by Russian Basic Research Foundation (Projects 00-03-32029a and 01-03-97011a).

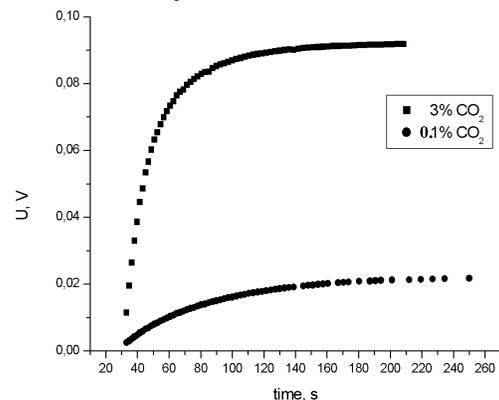


Fig.1. Time response (potential vs time) after chemical pulse from air to CO₂ concentration.

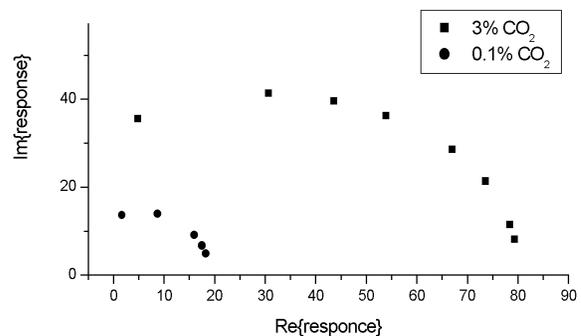


Fig.2. Curves of response to chemical pulse, transformed to frequency plane, in complex coordinates.

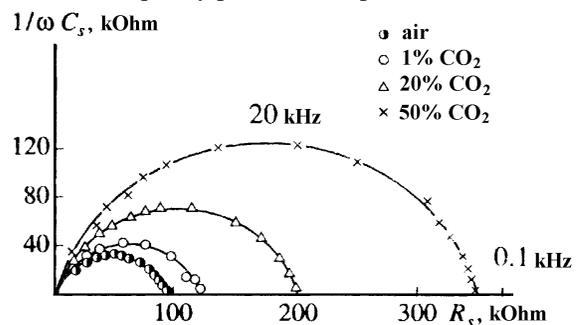


Fig. 3. The impedance hodographs of the system [4] at different concentration of CO₂. The digits near points are the frequencies in kHz.

References

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