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Electrochemical processes of H₂S detection in air and solution

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Abstract An electrochemical cell of potentiometric type Na_{0.5}WO₃ (reference electrode)/Na⁺-solid electrolyte/PbS (working electrode) capable of rapid and selective changing of the electromotive force value owing to H₂S concentration variations in gas surroundings has been investigated at 295 ± 1 K and a relative humidity of 52%. The sensitivity of this cell was 130 mV/decade at a H₂S concentration within the range 13–130 ppm. Sodium-conducting solid electrolytes of Na₃Zr₂Si₂PO₁₂ and Na₅GdSi₄O₁₂ compositions were used as the Na⁺ solid electrolyte. Such a cell can be used for analysis of H₂S containing water solutions when the reference electrode and the Na⁺ solid electrolyte are thoroughly isolated from the surroundings.

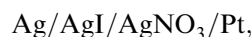
Keywords Hydrogen sulphide sensor · Solid-state electrochemical cell

Introduction

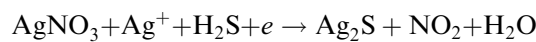
The development of sensors for discovering low concentrations of H₂S in gaseous and liquid phases is an important scientific and practical problem. The sources of H₂S entering the surroundings have natural (biogenic and geochemical) and technogenic nature (those connected with human activity).

Owing to the importance of H₂S detection for ecological and technological control, considerable attention has been focussed on the elaboration of H₂S sensors lately [1, 2, 3, 4, 5, 6, 7]. The investigations are being

carried out in the area of electrochemical and semiconducting sensors. Let us consider a few examples of electrochemical sensor creations. The Japanese researchers [1] described a galvanic solid-state sensor for H₂S monitoring on the basis of the electrochemical chain

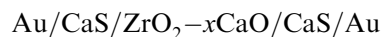


which can determine H₂S at low concentrations up to 0.0005 ppm with a response time of 5–15 min at 377 K. Since the electrochemical reaction



is accompanied by Ag₂S production, the efficiency of this sensor at H₂S concentrations up to 100 ppm does not exceed 50 h of continuous operation.

High-temperature H₂S detectors based on the electrochemical chains

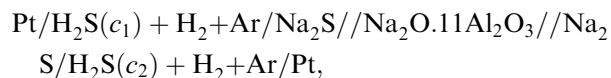


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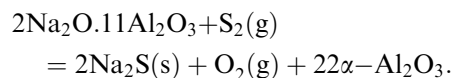


proved to be nondurable and to have low selectivity at 873–973 K [2, 3].

The sensors of type



where c_1 is the H₂S concentration and c_2 is the H₂S concentration in the reference electrode, in a H₂S-containing atmosphere at 873 K showed high instability, which was explained by Na₂S auxiliary layer formation on the surface of Na-β-alumina caused by interaction with sulphur vapours at high temperature [4, 5]:



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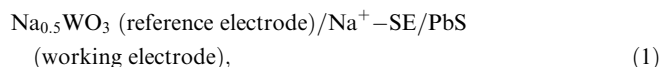
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To exclude the electromotive force (emf) drift, the authors suggested, firstly, to keep the sensors in H₂S surroundings for 2 weeks after their production to form a stable Na₂S phase performing the role of an auxiliary layer and, secondly, to use a two-phase solid electrolyte: Na-β-alumina + α-Al₂O₃.

The low-temperature H₂S sensor based on a solid electrolyte was described in Refs. [6, 7]. The present work is concerned with a solid-state sensor capable of selective and rapid determination of H₂S concentration at ambient temperatures in both gas and liquid phases.

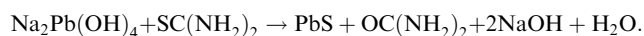
Experimental

The sensor studied was an electrochemical cell of a potentiometric type:



where Na⁺-SE is a solid electrolyte with an unipolar Na⁺ ion conductivity. Na₃Zr₂Si₂PO₁₂ ("true" NASICON), Na₅GdSi₄O₁₂ and Na₃Sc₂(PO₄)₃ were used as a Na⁺-SE. Investigation showed that the sensors on the basis of sodium-scandium phosphate are inert to the presence of H₂S in air and water solutions. The sensors with NASICON as a solid electrolyte showed high stability and sensitivity in water solutions and sensors based on sodium-gadolinium phosphate were less stable in water solutions but more sensitive to H₂S concentration changes in air.

Sensors of two types were studied. The first ones were produced by layer-by-layer pressing of powder samples of both solid electrolyte and electrode materials – sodium tungsten oxide bronze (reference electrode) and PbS (working electrode). The second were prepared on the bases of a Na⁺-SE ceramic sample to the opposite sides of which were pressed the same electrode materials – for measurements in the gas phase, but for measurements in water solutions PbS in the form of a thick film was deposited on one side of the Na⁺-SE ceramic sample according to the reaction



The solid electrolyte and the reference electrode were very carefully isolated using a Teflon cylinder and epoxy resin so that only the working electrode had contact with the surroundings.

During measurements of the emf, the electrochemical cell (Eq. 1) was under thermostatic conditions with a fixed relative humidity, *H*, of 52% created by air bubbled through a saturated solution of Na₂Cr₂O₇. The gas detected was obtained by mixing a certain amount of H₂S with moistened air. Then a vacuumed vessel with the previously installed sensor was filled with this gas mixture. Sulphur in water solution was produced by dissolution of thioacetamide (CH₃-CS-NH₂).

Results and discussion

The emf, *E*, dependence on H₂S concentration in air measured by the sensor with the ceramic ion membrane Na₅GdSi₄O₁₂ at room temperature is shown in Fig. 1. In the H₂S concentration interval of 13–130 ppm the *E*-log*c*(H₂S) dependence is linear and is described by the equation

$$\Delta E = E - E_0 = 131.5 \log c(\text{H}_2\text{S}),$$

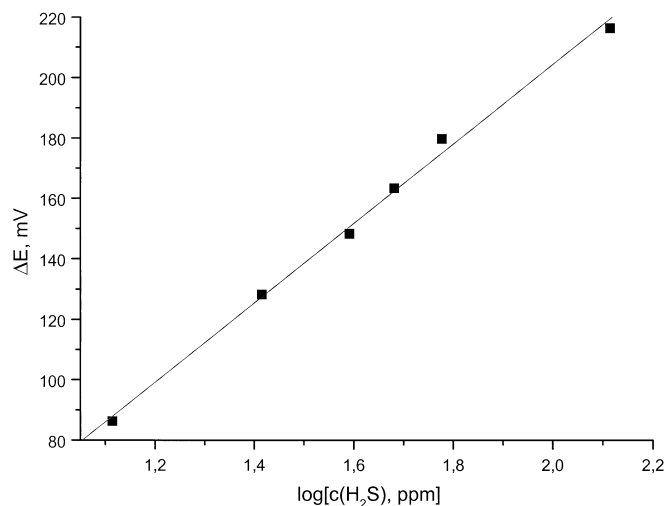


Fig. 1 Dependence of the electromotive force (emf) on H₂S concentration in air

where *E*₀ is emf in the absence of H₂S. A rather high value of the prelogarithmic coefficient may testify to the fact that the stationary potential of the electrochemical cell (Eq. 1) measured in humid air surroundings proves to be the system response to a number of simultaneous electrode reactions. In this case, the mixed potential determined by the kinetic parameters of these reactions is established. The mixed potential with a slope of 140 mV/decade was fixed in the solid-state sensor for H₂ detection in air [8]. The authors explain this phenomena as the sum of two electrode reactions – oxidation of H₂ and reduction of O₂.

The potential relaxation with the pulse concentration change in the gas phase is given in Fig. 2. The response time (*τ*₉₀) varies within the range 5–15 min, decreasing with H₂S concentration increase, whereas the initial rate of the emf change calculated as *dE/dt* at *t*→0 has a linear dependence on H₂S concentration (Fig. 3, line a). Using

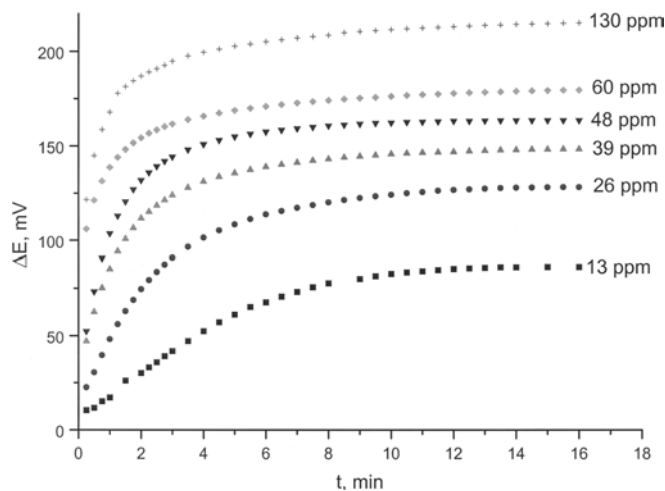


Fig. 2 The potential relaxation at different H₂S concentrations in air

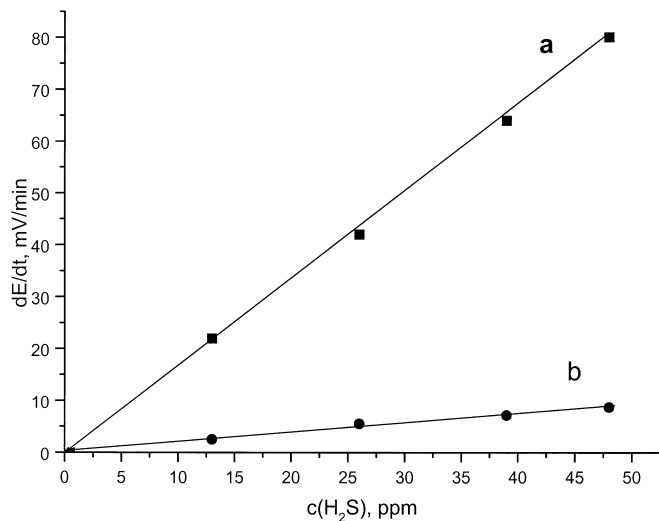


Fig. 3 Dependence of the initial rate of the emf change on H_2S concentration in air (a) and rate of the emf change after H_2S removal from the gas phase (b)

such a dependence allows the process of H_2S concentration determination to be accelerated. For this it is sufficient to know the rate of emf change within 1–2 min after the installation of the sensor into H_2S -containing surroundings. Of interest is the fact that the rate of emf relaxation during H_2S removal from the gas phase has a linear H_2S dependence as well (Fig. 3, line b).

The sensor under review is characterised by high selectivity. The presence of gases such as NH_3 , NO_2 and SO_2 in amounts 10 times higher than the H_2S concentration and 100 times greater amounts of CO , CO_2 and hydrocarbons do not affect the calibration parameters of the electrochemical cell.

The cell (Eq. 1) with the working electrode in the form of a thick PbS film deposited on NASICON ceramic can be used for analysis of H_2S -containing water solutions. The equilibrium potential is set up within 10–15 s. The concentration dependence of the emf (Fig. 4) is described by the linear equation

$$E = 54.3 \log c(HS^- + S^{2-}) + 590,$$

with the prelogarithmic coefficient characterising primarily a one-electron potential-determining reaction. Deviation from the theoretical value can be explained by dissociation of thioacetamide (CH_3CS-NH_2) dissolved in water with S^{2-} and HS^- ion formation.

Conclusions

Solid-state electrochemical cells of the potentiometric type

$Na_{0.5}WO_3$ (reference electrode)/ $Na^+ - SE/PbS$
(working electrode)

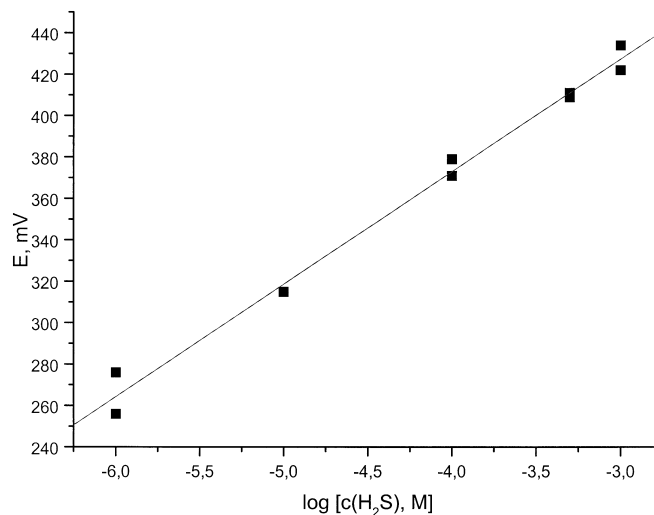


Fig. 4 Dependence of the emf on H_2S concentration in water solutions. The data were obtained with two various sensors

capable of rapid and selective changing of the emf value with H_2S concentration changes in gas surroundings have been developed. The sensitivity of the cell is 130 mV/decade within the H_2S concentration range 13–130 ppm at 295 ± 1 K and a relative humidity of 52%.

The rate of the potential change determined by the initial part of the relaxation curve was discovered to increase linearly with the H_2S concentration increase in air, which can be used for analytical purposes during the express analysis. Thorough isolation of the reference electrode and the solid electrolyte from the surroundings allows this cell to be used for analysis of H_2S -containing water solutions.

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