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Electrocatalytic effects in gas sensors based on low-temperature superprotonics

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Abstract

The behavior of low-temperature hydrogen sensors based on the PbO_2/heteropoly compound/Pt electrochemical cells, where heteropoly compound is $H_4SiW_{12}O_{40}{\cdot}nH_2O$ or $Me_xH_{3-x}PW_{12}O_{40}{\cdot}nH_2O$ (Me = Li, Na, K, Rb, NH_4, $x = 0, 2, 3$), in H_2–Ar and H_2–air atmospheres was studied. All heteropoly compounds studied were shown to be electrocatalytically active in reactions involving hydrogen. The dependences of the emf of the sensors with different electrolytes on the hydrogen concentration (calculated relatively to the standard hydrogen potential in inert media or to the air potential in oxygen-containing media) are identical for all the electrolytes used. The rate of emf relaxation of the sensors upon the impulse admission of hydrogen depends, on the contrary, on both the anion nature (increases in the series from compounds of 12-silicotungstic acid to 12-phosphotungstic acid compounds) and the cation nature, increasing with an increase in the cation size in the series of alkaline metal cations.

Based on our studies, we proposed the electrochemical solid-state sensor, which can determine hydrogen concentrations from 10^{-2} to 5 vol.% in inert gases and air without maintaining constant temperature and hydrostatic regimes in the temperature interval from −60 to +60 °C.

Keywords: Hydrogen sensors; Heteropoly compounds; Potential relaxation; Solid electrolytes

1. Introduction

Electrochemical cells using solid electrolytes (superionics) are usually used for hydrogen detection under standard conditions [1–14]. The detection can often be carried out without heating and maintaining constant temperature and hydrostatic regimes. Antimonic acid, Nafion, other organic and hybrid polymers, hydrated Nasicon, heteropoly compounds, and many other superprotonics are used as H^+-SE in these cells. The Ag/Ag^+ electrodes (Ag, Ag_2SO_4; Ag, AgCl); transition metal hydrides, for example, TiH_2; hydrated oxides, for example, NiO, PbO_2; were proposed as RE. Analysis in [4] has shown that the system

$$PbO_2(NH_4)_2HPW_{12}O_{40} \cdot nH_2O/Pt, O_2, H_2 \quad (1)$$

gives a fast and high-sensitive response to a change in the hydrogen content in both an inert gas and oxygen-containing media.

The purpose of this work is to study the influence of the composition of the solid electrolytes based on heteropoly compounds on the characteristics of potentiometric H_2 sensors similar to (1).

1.1. Procedure of measurements

Phosphotungstic ($H_3PW_{12}O_{40}{\cdot}nH_2O$) and silicotungstic ($H_4SiW_{12}O_{40}{\cdot}nH_2O$) acids, $M_3PW_{12}O_{40}{\cdot}nH_2O$ and $MH_2PW_{12}O_{40}{\cdot}nH_2O$ salts, where M = H^+, (NH_4^+), Li^+, K^+, Na^+, and Cs^+, were used as starting substances. The dependence of the emf of the sensors on the hydrogen concentration in inert (Ar) and oxygen-containing (air) media and emf relaxation of the sensors upon an impulse change in the hydrogen concentration in the medium under consideration were studied.

The cell

$$PbO_2/H^+\text{-SE}/Pt, H_2, \text{air or Ar} \quad (2)$$

was used in the work, where PbO_2 is a reference electrode, and the Pt sponge is a sensitive electrode, whose design is presented in Fig. 1. The sensor was prepared by molding of

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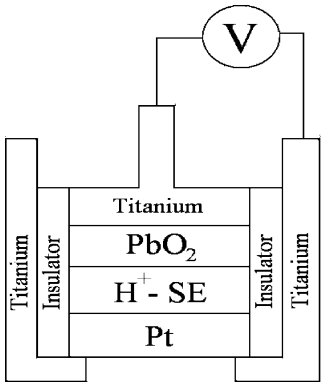

Fig. 1. Design of the electrochemical cell used as a hydrogen sensor.

two electrodes onto the solid electrolyte followed by storage of the cell above a constant humidity of ~50 rel.%. The prepared pellet was placed in a cylindrical shell of an insulating material in a titanium body. Measurements detected the potential difference between the titanium body, which was in direct contact with the platinum electrode, and a titanium current contact jaw connecting with the reference electrode (lead dioxide).

2. Results and discussion

2.1. Influence of the nature of the electrolyte anion and environment composition on the characteristics of the sensor

The plots of the emf of sensors (2) with heteropoly acids as solid electrolytes versus hydrogen concentration in air-less and air atmospheres are presented in Fig. 2. In the absence of oxygen at 20 °C, the concentration dependence of the emf for cell (2) with phosphotungstic acid is described by the Nernst equation

$$E = (1.545 \pm 0.002) - (0.028 \pm 0.002)\log[H_2] \quad (3)$$

These values correspond to hydrogen oxidation at the working electrode

$$H_2 - 2e^- \rightarrow 2H^+ \quad (4)$$

Simultaneously, lead dioxide is reduced at the reference electrode

$$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O \quad (5)$$

The oxygen and hydrogen content in the analyzed medium has no effect on the potential of this electrode (1.4–1.6 V) but it depends on the nature of the solid electrolyte, because the proton activity differs in electrolytes different in nature. The concentration dependence of the emf recalculated to the standard hydrogen electrode (by subtraction of the emf of the sensor at a hydrogen pressure of 1 atm from the measured emf values of the same sensor) are described by the Nernst equation for a two-electron process for all sensors studied (the theoretical value of the pre-logarithmic factor for $t = 25\,^{\circ}C$ is $2.303RT/2F = 0.0293$). Phosphomolybdic acid turned out to be absolutely inappropriate for operating in the composition of cells (2), because its chemical reduction with molecular hydrogen results in the appearance of a very high fraction of electron conductivity, and the emf of the cell changes irreversibly upon reduction.

In the presence of oxygen, the concentration dependence of the emf is non-Nernst (Fig. 2). Similar concentration plots of the emf are characteristic of several potential-determining processes simultaneously occurring at the electrode. For example, in the case of a hydrogen sensor, we can assume

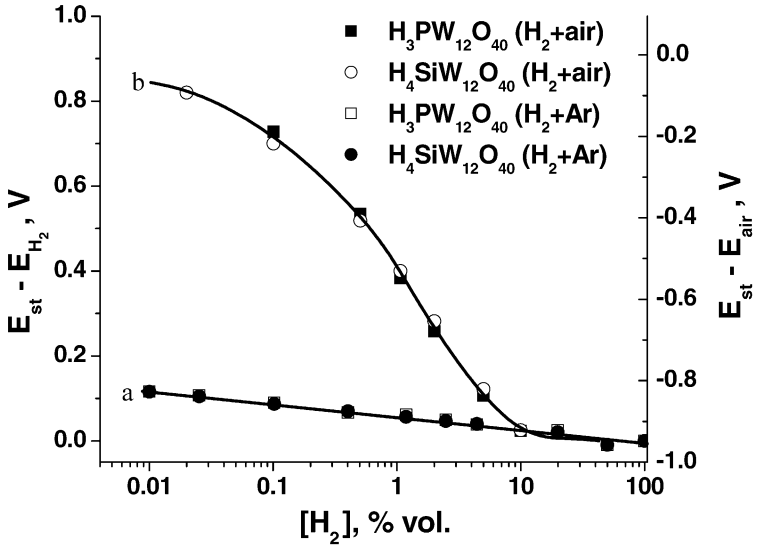

Fig. 2. Plots of the potentials of the platinum electrodes in cells (2) with $H_4SiW_{12}O_{40}{\cdot}nH_2O$ and $H_3PW_{12}O_{40}{\cdot}nH_2O$ vs. hydrogen concentration in inert (a) and oxygen-containing (b) media recalculated to the standard hydrogen potential (left scale) and air potential (right scale). $t = 25\,^{\circ}C$, relative humidity = 52%.