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Portable Sensors for Hydrogen Analysis

Yu. A. Dobrovol'skii[a], L. S. Leonova[a], A. E. Ukshe[a], A. V. Levchenko[a], A. M. Baranov[b], and A. A. Vasil'ev[c]

[a] Institute of Problems of Chemical Physics, Russian Academy of Sciences,
prosp. Akad. Semenova 1, 142432 Chernogolovka, Moscow oblast, Russia
tel: +007(496)5221657
fax: +007(496)5155420
e-mail: dobr@icp.ac.ru
[b] MATI Tsiolkovskii Russian State Technical University
[c] Kurchartovskii Institute Russian Research Center

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Abstract—Presently available methods for the determination of hydrogen in the gas phase are analyzed. Various procedures for the detection of hydrogen both at pre-explosion and at very low (less than 50 ppm) concentrations by means of thermocatalytic, semiconductor, amperometric, and potentiometric electrochemical sensors are considered.

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INTRODUCTION

Progress of hydrogen power engineering suggests extending application field of hydrogen. Domestic use of hydrogen brings to the fore fire and explosion safety problems. Even customary natural gas causes accidents with its inflammation and explosion. Hydrogen, while being ecologically attractive, is even more dangerous in operation. Mixtures of hydrogen with oxygen are highly explosive at hydrogen concentrations ranging from 4 to 75%. Hydrogen is odorless and colorless, it cannot be doped with mercaptanes, like natural gas, since sulfur-containing compounds are strong catalytic poisons for electrode materials in fuel cells (FC). In this connection development of devices for trace analysis of hydrogen is an urgent problem.

Hydrogen sensors can also be used to detect inflammation. Hydrogen is already released at the stage of smoldering in the course of pyrolysis of wood, paper, plastics, and other hydrocarbon materials. Therewith, its concentration, even at a considerable distance from the inflammation site, can reach 10–100 ppm (the background hydrogen level in air is about 0,5 ppm). Moreover, hydrogen diffuses at a high rate and penetrates outside of even closed rooms, and the ability to detect low concentrations of hydrogen can aid in preventing fire long before it develops.

Commercially available hydrogen leak detectors are unsuitable for routine use as testers for fuel cells and fire safety systems because of their large size and high cost. New sensors are required, with a minimum power consumption and capable of operating at room temperatures. The sensors should be compact, low-cost, and readily integrable into chips and printed circuit boards.

The present review is devoted to compact hydrogen sensors [1].

A sensor is a structure capable of responding to a change in a value to be measured by changing its electrophysical, optic, mechanic, and other properties. A sensor most commonly consists of a layer selectively sensitive to a component to be detected, which generates a signal proportional to the component concentration, and a signal converter. Depending on the sensor parameter changed and the principle of operation of the response converter, several types of gas sensors can be recognized (Fig. 1).

The general requirements for sensors of any type are high sensitivity, selectivity, short response time, durability, small size, and low cost.

At present catalytic, semiconductor, and electrochemical hydrogen sensors have enjoyed the widest application.

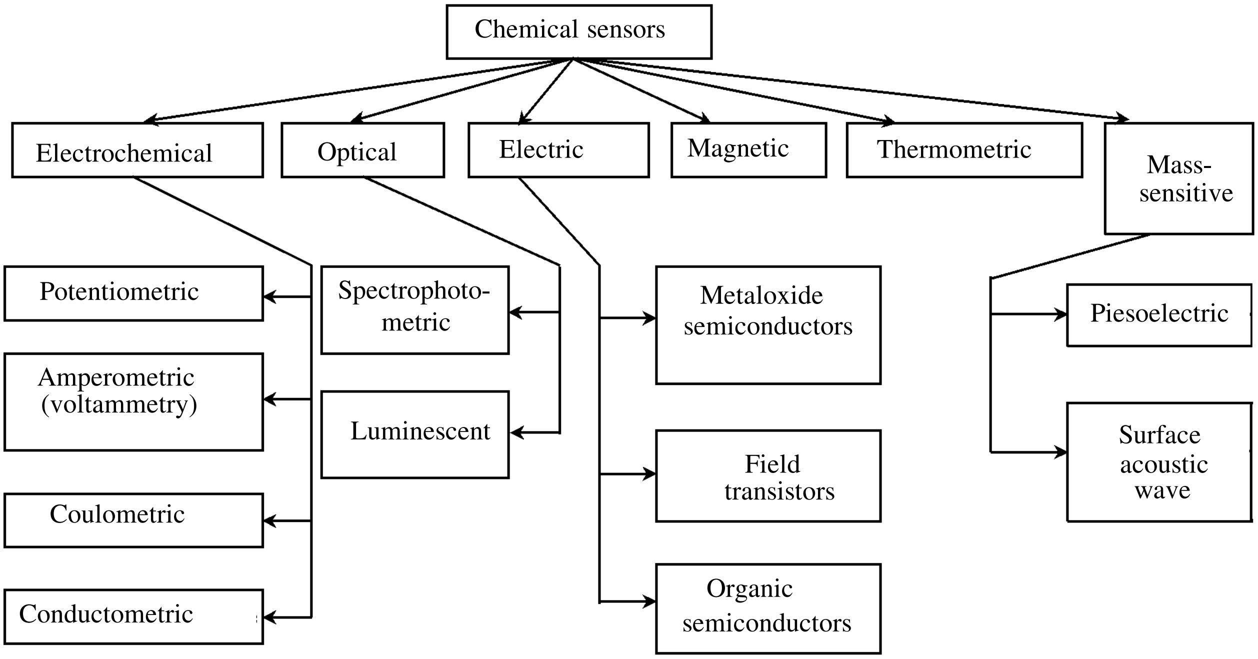

Fig. 1. Classification of gas sensors [2, 3].

THERMOCATALYTIC SENSORS

Thermocatalytic sensors are widely used for measuring fairly high concentrations of hydrogen in air (0.1–10 vol%). These sensors measure the combustion heat of a flammable gas to be detected, which is proportional to its concentration. A platinum–palladium catalyst applied on fine alimuna is used [4]. A catalytic sensor comprises two heaters, and the catalyst is applied on one of them. The second heater is insensitive to the composition of the gas medium and serves to generate the reference signal. The analyzed gas is oxidized on the catalytic layer, the energy that releases changes the heater resistance, thus forming a primary sensor signal. The minimal operating temperature of such sensors is 450°C, which adversely affects the sensitivity of the determination. The response time may attain 20 s [5].

Up to now platinum spiral heaters have been used in most thermocatalytic sensors. The diameter of the platinum spiral in best sensors was 10 μm, power consumption 120 mW.

The principal drawback of thermocatalytic sensors of this type is complexity in fabrication, which limits their application field. These limitations are overcome by using thin-film heaters on a membrane of silicon oxide (nitride), aluminum oxide, or their combination.

In a multilayer membrane comprising alternating silicon oxide and silicon nitride layers, the layer voltages have opposite signs that can be compensated for by a certain combination of the layers. As a result, a membrane several mm^2 in surface area and 1–2 μm in thickness can be obtained.

There are four technologies for fabrication of low-power sensors. (1) Chips on the basis of silicon technology and thin dielectric silicon oxide/nitride membranes. (2) Sensors on the basis of hanging miniature silicon elements. (3) Sensors with thin silicon dioxide membranes and a platform, fabricated by the "silicon-on-isolator" technology. (4) Sensors with a porous (silicon, alumina) low-heat-capacity membrane as support and isolator.

The choice between the technologies is mostly determined by the tendency to minimize power consumption but preserve reasonable cost and fabrication burden.

Such device can be exemplified by a construction described in [6]. The membrane is fabricated by consecutive chemical vapor deposition of silicon oxide, silicon nitride, and silicon oxide layers, the heater is of polycrystalline silicon, and its contacts are platinum. Therewith, the contacts are located in the hot zone. This chip is disadvantageous in that it has a nonoptimal heater/membrane size ratio, which results in an unreasonable power gain (to about 60 mW). Furthermore, a polycrystalline silicon heater is unstable at high operating temperatures. Its yearly resistance drift is about 30–50%.

The best material for heaters operating at 400–500°C is platinum which is tolerant to oxidation under these conditions. The main problem consists in platinum adhesion to membrane material. Most commonly, for better adhesion of the platinum layer to membrane some intermediate sub-layers, for example, platinum, are used. However, the platinum film can flake away due to oxidation of the titanium adhesive layer. Gas-sensitive layers formed at a higher temperature (up to 900°C) tend to flake away faster. This makes unsuitable group technologies for fabrication of thermocatalytic sensors and welding for making leading-out wires for sensors with adhesive layers. With tantalum layers, similar adhesion problems arise. These layers, too, are oxidized near 500°C, as a result of which the platinum coating flakes away from the silicon oxide surface.

One of the best, in terms of power consumption, is a thermocatalytic sensor described in [7]. The sensor works at 500°C and consumes about 20 mW (Fig. 2).

Qui et al. [8, 9] suggested a modified termocatalytic sensor. To measure the concentration of hydrogen, the referees made used of the thermoemf effect. As a result, the sensor temperature could be lowered to 100°C and the catalyst selectivity could be increased. The sensor features a linear dependence of thermal emf on hydrogen concentration [8].

SEMICONDUCTOR SENSORS

Semiconductor sensors operate by changing electrophysical parameters in response to chemisorption or redox reactions of a gas to be detected. Such sensors can be divided into two big groups: metal oxide sensors and metal–dielectric–semiconductor (MDS) or metal–semiconductor structures [10].

Metal Oxide Resistance Sensors

In a general case, such detector comprises an oxide semiconductor sensitive layer, for example, SiO_2, applied to a dielectric support [11]. Metal oxide semiconductor sensors operate by changing resistance of the gas-sensitive layer in response to chemisorption or oxidation of donor gases (various flammable gases: hydrogen, methane, propane, gasoline vapors; CO, ammonia, hydrogen sulfide, etc.) or electron acceptors (ozone, nitrogen oxides, fluorine) [12, 13]. The processes that occur change irreversibly the concentration of current carriers in the semiconductor and the conductivity of the sensitive layer by decreasing the potential barrier (Fig. 3) [14, 15]. The sensitivity threshold of metal oxide semiconductor sensors with respect to hydrogen is about 1 ppm.

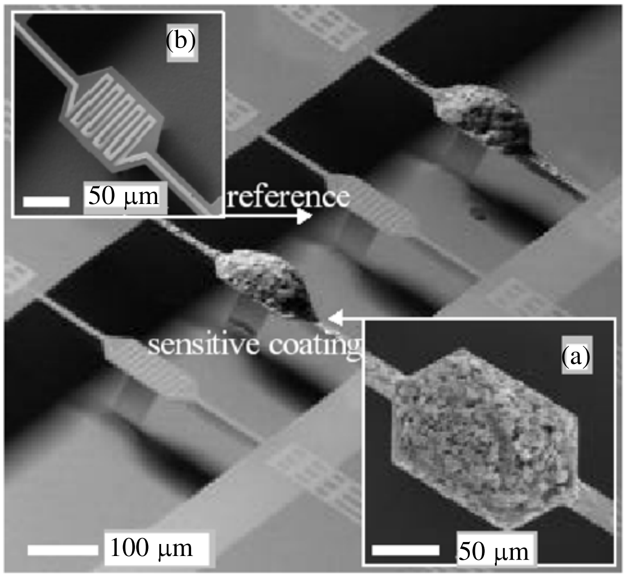

Fig. 2. Thermocatalytic sensor with platinum heaters on silicon oxide membranes: (a) working element with a catalytic coating and (b) reference element.

When hydrogen is detected, the first stage of the process involves chemisorption with simultaneous ionization:

$$H_2 \rightleftarrows H_2^+ + e^-.$$

The conductor conductivity is proportional to the square root of the hydrogen concentration in the gas phase:

$$\sigma \sim \sqrt{[H_2]}\ . \qquad (1)$$

The second stage involves the reaction of protons with adsorbed oxygen to form water. Therewith, the concentration dependence is described by the following empirical relation:

$$\frac{\Lambda\sigma}{\sigma_0} \sim p^{\alpha}. \qquad (2)$$

Here σ_0 is the conductivity of the material in the absence of hydrogen; p, partial pressure of gas; and α, coefficient varying from 0.25 to 1.

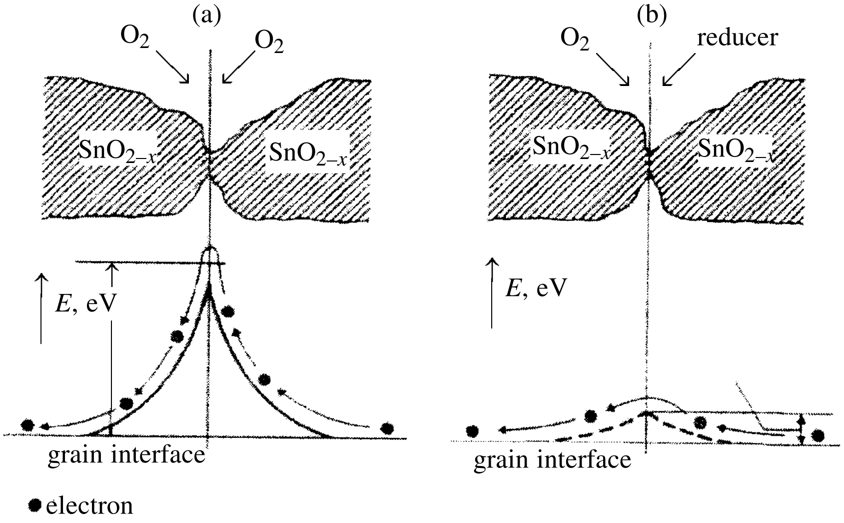

Fig. 3. Formation of a potential barrier on the SnO_2 grain interface in air (a) on heating and (b) in the presence of reducers.

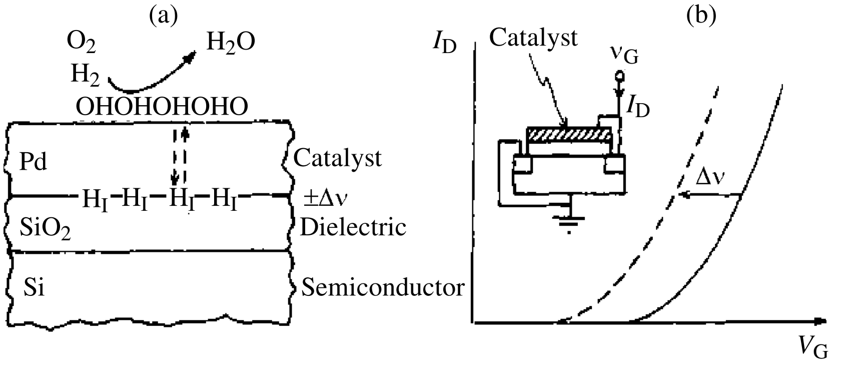

Fig. 4. Metal–dielectric–semiconductor transistor: (a) structure and (b) current–voltage characteristics [4].

For the sensor operation speed to be about a few second, the surface chemical reactions should be fairly fast. Therefore, the sensor is heated above 250°C for detection of alcohol vapors or hydrogen and to 500°C with methane.

Fine metal oxides (SnO_2, ZnO, In_2O_3, etc.) with a specific surface area of about 50 $m^2 g^{-1}$ are used as sensitive semiconductor layers. These materials are sufficiently stable at operating temperatures. Nanosized catalysts are applied to the surface of semiconductor materials surface and provide selectivity of surface oxidation reactions and enhance selectivity of semiconductor sensors [16]. In an oxygen medium (in air), the response and make-up times of such sensors are a few seconds, whereas in an inert atmosphere, a few minutes. Detailed analysis of the response times is given in [17].

The selectivity of the sensors can be improved by means of physical silicon oxide filters applied to the surface of a metal oxide sensitive layer [18]. Hydrogen sensors of this type are among the most widespread, since they are fairly easy to produce. They are produced by a number of companies, and the most known of them is Figaro.

MDS Structures

Structures of this type can be divided into MDS structures as such, MDS transistors, and metal–semiconductor structures (Schottki diodes). Figure 4 presents a typical design of a sensor on the basis of an MDS transistor.

The principle of gas detection with an MDS transistor consists of hydrogen adsorption on the surface of a gate (most commonly, platinum or palladium), dissociation of molecules and diffusion of hydrogen atoms inside the gate to the metal–dielectric interface. As a result, an additional electric field arises, which changes the zone diagram of the MDS transistor.

At a zero gate potential ($V_G = 0$), the current between the input and output is lacking ($I_D = 0$), since one of the *p–n* transitions is always locked. If the gate potential differs from zero ($V_G \neq 0$), a conducting channel appears between the input and output, and the current I_D is generally given by the equation $I_D \sim K(V_G - V_T)U_D$, where U_D is the input–output potential difference and V_T, threshold voltage (at $V_G < V_T$, $I_D = 0$). The threshold potential V_T is linearly related to the metal gate work function. Thus, the gate is a sensitive element, and gas absorption on its surface changes the surface charge on the metal–dielectric interface and, as a result, gate potential (V_G), and this potential change is proportional to the quantity of adsorbed gas.

Lundstrom et al. [19, 20] showed that the potential change (ΔV) of a palladium-gated MDS transistor, induces by formation of a double electric layer in the presence of hydrogen can be described by empirical relation (3):

$$\frac{\Delta V}{\Delta V_{\max}} = \frac{\sqrt{P_{H_2}/P_0}}{1 + \sqrt{P_{H_2}/P_0}}, \qquad (3)$$

where $\Delta V_{\max} \approx 750–1000$ mV is the maximum potential change due to integral charge (depends on the nature of metal and dielectric); P_0, maximum hydrogen concentration (~130 ppm); and P_{H_2}, hydrogen concentration in air.

Sensors of this group offer important advantages of the high sensitivity, good reproducibility, and lowcost microelectronics technology. The disadvantages are the low selectivity and fairly high operating temperatures (>100°C).

Schottki diodes are used as semiconductor structures for detecting low hydrogen concentrations. These structures comprise platinum and palladium applied to a monocrystalline silicon or silicon carbide. Hydrogen response of Schottki diodes is associated with the generation of charge on the metal/silicon interface, which affects the diode current.

Another example is provided by a PbS/Si semiconductor heterojunction [21]. In this case, hydrogen response, too, is associated with a change in the concentration of charge carriers in the PbS layer upon dissociative dissolution of hydrogen. Hydrogen selectivity of such crystalline systems is due to diffusion limitations for transport of more complex molecules in the heterotransition region. An interesting example is a Pd/TiO_2/*n*-Si diode structure [22] which exhibits an anomalously high hydrogen response at romm temperature: The resistance of this system changes 50 times for 4 ppm and five orders of magnitude for 10 000 ppm H_2 with respect to a hydrogen-free atmosphere. The signal is considered to be mostly contributed by the TiO_2 layer.

Table 1. Comparative characteristics of amperometric and potentiometric sensors

Amperometric	Potentiometric
Presence of mass transfer and, as a result, low durability	Lack of mass transfer and high durability
Narrow concentration range (1 order)	Wide concentration range (3–4 orders)
High precision	Medium precision
High power consumption	Low power consumption
Signal depends on the electrode/electrolyte interface surface area	Signal is independent of geometric parameters

ELECTROCHEMICAL SENSORS

Electrochemical sensors generally include two electrodes intervened by a solid electrolyte layer. The electrode signal goes to a converter. In terms of the measurement mode, electrochemical sensors are classed with amperometric that measure current generated when a preset potential difference is applied to the electrodes and potentiometric that measure cell potential at zero current. Comparative characteristics of amperometric and potentiometric sensors [23] are presented in Table 1.

Amperometric Sensors

The principle of operation is based on the fact that if a certain potential corresponding to oxidation or reduction of an analyte is applied to the cell, the cell current is proportional to the concentration of the analyte. As a result, such sensors are more precise and have narrower detection ranges than potentiometric. Amperometric sensors (conductometric, current) are of limited use because of the low durability.

The selectivity of amperometric sensors is defined by the nature of the electrode surface material and by the potential of reactions involving the analyte. Both electrodes are most commonly the same, and electrode/ionic conductor interface should be reversible. Only one of the electrodes contacts with the atmosphere.

Potentiometric Sensors

Potentiometric gas sensors respond to a change in the potential difference between the working and

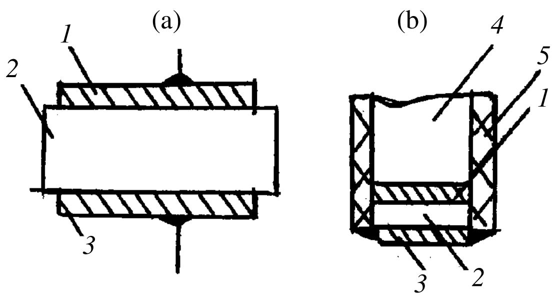

Fig. 5. Scheme of a potentiometric sensor with a (a) solid and (b) gas reference electrode: (*1*) reference electrode, (*2*) solid electrolyte, (*3*) sensitive electrode, (*4*) reference gas, and (*5*) housing.

reference electrodes. A conceptual sketch of a solid state sensor is given in Fig. 5.

The reference electrode functions here, like in any other electrochemical system, to maintain a stable potential jump on the interface with the electrolyte, independent of the composition of the gas phase. A classical reference electrode in liquid and solid state cells is a hydrogen electrode, but it is unsuitable for sensors. Hydrogen–oxide, calomel, and silver chloride electrodes have received wide use in solution chemistry. The potential of the working electrode, by contrast, should depend on the concentration of an electroactive component of the gas phase. Potentiometric systems have attracted considerable attention [3] due to the following advantages:

(1) Potentiometric sensors convert the energy of a chemical reaction into an electric signal (potential difference) and, therefore, no external power source is needed.

(2) The magnitude of the electric signal is independent of sensor size, which creates prerequisites for miniaturization.

(3) The signal is linearly related to the log concentration of the analyzed gas, which allows measurements in a wide concentration range.

(4) Potentiometric sensors function reversibly, and measurement of the electrode potential does not disturb the electrode–electrolyte equilibrium.

One of the main problems associated with these sensors is that the steady-state potential of the working electrode and the time of its stabilization depend on the composition of the solid electrolyte. Most characteristics of electrochemical sensors are determined by the composition of the solid electrolyte, as well as its electrocatalytic properties and working temperature range. Table 2 lists the available published data on solid electrolytes and certain characteristics of hydrogen sensors.

Basic principles of highly selective and reliable detection of various gases have been described in [50, 51]. A known example is an oxygen sensor on the basis of zirconium oxide stabilized with yttrium oxide, which is widely used in motor industry.

Electrochemical hydrogen sensors are based on proton and oxygen conductors. The very problem of electrochemical detection of hydrogen can be divided into two parts: detection in an inert atmosphere and in the presence of oxygen. In the first case, the behavior of the sensor in the presence of hydrogen is described by the Nernst equation; therewith, in the case of proton conductors, the working electrode process involves proton formation. With oxygen conductors, water is formed. The concentration dependence of emf is described by the Nernst equation:

$$E = E_0 - \frac{RT}{2F} \ln [H_2],$$

where R is the universal gas constant; T, absolute temperature; and F, Faraday's constant.

Side processes attendant on the detection of hydrogen in air result in that the concentration dependence deviates from Nernstian. Such deviations are explained by a number of reasons. Among them, concurrent occurrence of several potential-determining processes, accumulation of products, and retarded adsorption on three-phase interfaces. Most commonly such deviations are associated with the presence of oxygen, specifically oxygen discharge or hydrogen oxidation on the working electrode surface. In this case, the concentration dependence of emf can be nonlinear but is frequently described by a logarithmic function:

$$E = E_0 + k\ln [H_2],$$

where k is an empirical constant.

A typical example of a detector on the basis of oxygen conductors is provided by a potentiometric sensor comprising a tube of stabilized zirconium dioxide, in which stability of the gas reference electrode is maintained by blowing air inside the tube [25, 52]. The working electrode was ZnO; therewith, the process that occurs on the ZrO_2/ZnO/H_2 three-phase interface involves water formation complicated with oxygen discharge. As a result, the concentration dependence deviates from Nernstian, and the slope is 100 mV at a 10-fold concentration change.

The above sensor works at 600°C, exhibits good response to H_2 in mixtures with NO, NO_2, CH_4, CO_2, and H_2O, and its emf varies linearly with log hydrogen concentrations in the range 450–600°C (Fig. 6).

Table 2. Characteristics of solid electrolyte hydrogen sensors

Solid electrolyte	Concentration range, vol%	Working temperature, °C	Reference
Sensors on the basis of proton conductors			
$H_4SiW_{12}O_{40}\cdot nH_2O$ or $Me_xH_{3-x}PW_{12}O_{40}\cdot nH_2O$	0.01–10	–60–60	[24–26]
Nafion	0.005–0.15 0.056–1.15	10–90	[27–30]
PBI (polybenzimidazoles)		100–250	[31, 32]
Nasicon with Na^+ substituted by H^+	0.01–100	0–50	[33]
$Sb_2O_5\cdot 4H_2O$	0.001–0.5	0–50	[34–36]
$Zr(HPO_4)_2\cdot nH_2O$	0.001–0.1	10–200	[37, 38]
Na-β-Al_2O_3 with Na^+ substituted by H^+	0.01–1	150–200	[39]
$Sb_2O_5\cdot 4H_2O$ + polyvinyl alcohol	0.005–1	10–50	[40]
Polyvinyl alcohol–H_3PO_4	0.0005–0.005	0–40	[41]
$Sb_2O_5\cdot H_3PO_4$	0.001–0.2	0–50	[42]
$H_2Ti_3O_7$	0.01–1	400–700	[43]
$P_2O_5 . SiO_2$ glass	0.1–4	–30–50	[44]
$CsHSO_4$ composites	0.015–1	100–200	[45]
Sensors on the basis of oxygen conductors			
YSZ (ZrO_2, stabilized by yttrium)	0.002–0.1	400–800	[46–48]
$BaZr_{0.4}Ce_{0.4}In_{0.2}O_3$	0.02–1	300–700	[49]

The principal drawbacks of such sensors include high working temperatures and a gas reference electrode. The first drawback makes this sensor unusable in air because of the possible hydrogen inflammation and the second much complicates its design. In this connection most researcher's emphasis is given to potentiometric sensors with solid proton electrolytes whose use makes it possible to lower the working temperatures to ambient and to get rid of a gas reference electrode.

Efficiency of sensors on the basis of proton conductors depends on whether optimal electrodes and electrolytes are chosen. In a hydrogen sensor, an oxygen process can also occur on the working electrode in air; therewith, the potential of this process is determined by ionization of hydrogen and oxygen, as well as by the oxidation degree of the electrode [53].

The sensors feature an electrochemical equilibrium with mobile protons of the solid electrolyte (SEL), i.e. the exchange current on the SEL/electrode interface should be high enough for stable equilibrium. Therewith, the interface potential should be independent of the composition of the medium. We can mention four types of materials that meet this requirement [54, 55]: transition metal hydrides PdH_x, TiH_x, or ZrH_x; hydrogen bronzes H_xMoO_3 and H_xWO_3; hydrated metal oxides PbO_2 and MnO_2; and Ag, AgI, and Ag, Ag_2SO_4 electrodes.

The main drawback of hydrides is gradual hydrogen release, which results in potential drift. Hydrogen bronzes like H_xWO_3 are oxidized when stored in air:

$$H_{0.35}WO_3 + 0.0875O_2 \longrightarrow 0.175H_2O + WO_3.$$

The electrode potential of PbO_2 in solid proton electrolytes can be associated with the follwing electrode reaction:

$$H_2O(H^+\text{-SEL}) \rightleftarrows O(PbO_2) + 2H^+(H^+\text{-SEL}) + 2\bar{e}\ (PbO_2).$$

Parenthesized are phases accommodating the corresponding particle, and H^+-SEL stands for proton

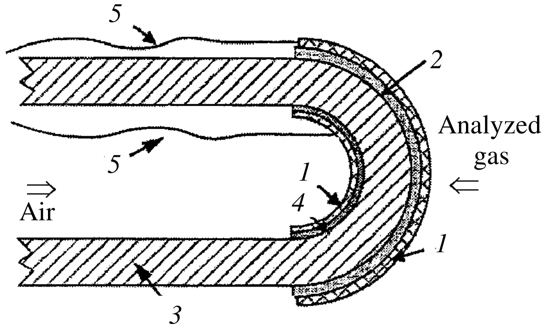

Fig. 6. Scheme of an YSZ hydrogen sensor: (*1*) Pt gauze, (*2*) ZnO layer, (*3*) ZrO_2-coated tube, (*4*) Pt paste, and (*5*) Pt wire.

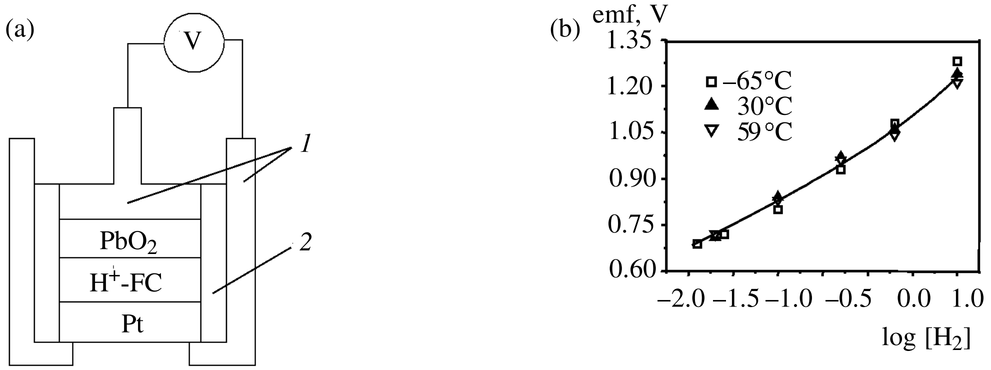

Fig. 7. Sensor on the basis of heteropolycompounds: (a) scheme and (b) characteristic at various temperatures. (*1*) Titanium plates and (*2*) dielectric.

electrolyte. The electrode potential is given by the formula:

$$E_{\mathrm{PbO_2}} = E^0_{\mathrm{PbO_2}} - \frac{RT}{2F}\ln\,[\mathrm{Pb}^{2+}] + \frac{RT}{F}\ln\,[\mathrm{H}^+] + \frac{RT}{F}\ln\,[\mathrm{H_2O}].$$

The silver sulfate electrode probably features the following electrochemical equilibrium:

$$\mathrm{Ag_2SO_4} + \mathrm{H}^+ + \bar{e} \rightleftarrows \mathrm{Ag} + \alpha\text{-}\mathrm{AgHSO_4}.$$

or

$$3\mathrm{Ag_2SO_4} + 4\mathrm{H}^+\ 4\bar{e} \rightleftarrows 4\mathrm{Ag} + \mathrm{Ag_2SO_4}\cdot 2\mathrm{H_2SO_4}.$$

Since silver hydrosulfates form separate phases, the potential of the silver sulfate electrode is described by the following equation:

$$E_{\mathrm{Ag,\,Ag_2SO_4}} = E^0_{\mathrm{Ag,\,Ag_2SO_4}} + \frac{RT}{F}\ln\,[\mathrm{H_2}].$$

There has also been research into detectors on the basis of proton conductors with a gas reference electrode and $\mathrm{CaZr_{0.9}In_{0.1}O_{3-\alpha}}$ membranes [26]. These sensors showed a close-to-linear concentration dependence of emf (in log coordinates) in the working temperature range 500–900°C.

Bouchet et al. [31] reported a solid state selective cell for hydrogen detection, with a hydrogensubstituted Nasicon as an ionic membrane and silver in contact with a silver-conducting electrolyte ($\mathrm{Ag^+}$–Nasicon) as a reference electrode. This cell shows a Nernstian dependence of emf on hydrogen concentration and works at room temperature.

Ukshe and Leonova [56] considered general principles of operation and characteristics of solid state electrochemical hydrogen sensors with proton solid electrolytes. Hydrogen sensors on the basis of various heteropoly compounds were found to be highly efficient [23]. These sensors are insensitive to carbon monoxide at room temperature, which makes them promising devices. One more feature of such sensors deserves mentioning: The concentration dependence of its emf is temperature-independent (Fig. 7b).

Along with potentiometric hydrogen sensors, amperometric sensors are also being actively studied. Thus, Ramesh et al. [40] described a sensor capable of measuring very low hydrogen concentrations, beginning with 5 ppm. The sensor is highly selective and shows a linear dependence of current on hydrogen concentration (in ppm), which makes it feasible for controlling fire risk situations.

REFERENCES

1. Knauth, P. and Tuller, H.L., *J. Am. Ceram. Soc.,* 2002, vol. 85, p. 1654.
2. Budnikov, G.K., *Soros. Obraz. Zh.,* 1998, no. 3, p. 72.
3. Lundstrom, I., *Sens. Actuators B,* 1996, vol. 35, p. 11.
4. Karpov, E.F. and Basovskii, B.I., *Kontrol' provetrivaniya i degazatsii v ugol'nyh shakhtakh. Spravochnoe* posobie (Control of Ventilation and Degassing in Coal Mines. Reference Book), Moscow: Nedra, 1994.
5. Cattral, R.W., *Chemical Sensors,* Oxford: Oxford Univ. Press, 1997.
6. Fau, P. and Sauvan, M., Abstracts of Papers, *Eurosensors XIV,* Copenhagen, 2000, M2P20.
7. Ducso, Cs., Adam, M., Furjes, P. et al., Abstracts of Papers, *Eurosensors XVI,* Prague, 2000, W1B4.
8. Qiu, F., Shin, W., Matsumiya, M. et al., *Sens. Actuators B,* 2004, vol. 103, p. 252.
9. Qiu, F., Shin, W., Matsumiya, M. et al., *Jpn. J. Appl. Phys.,* 2003, vol. 42, p. 1563.
10. Vasil'ev, R.B., Ryabova, L.I., Rumyantseva, M.N.,

and Gas'kov, A.M., *Usp. Khim.,* 2004, vol. 73, p. 1019.

11. Ryzhikov, A., Shatokhin, A., Putilin, F. et al., *Sens. Actuators B,* 2005, vol. 107, p. 387.
12. Rantala, T., Rantala, T., Vaara, J., and Lantto, V., *Surface Sci.,* 1996, vols. 352–354, p. 77.
13. Zemel, J.N., *Thin Solid Films,* 1988, vol. 163, p. 189.
14. Lundstrom, I., Shivaraman, S., Svensson, C., and Lundkvist, L., *Appl. Phys. Lett.,* 1975, vol. 26, p. 55.
15. Lundstrom, I., *Sens. Actuators,* 1981, p. 403.
16. *Sensors. A Comprehensive Survey,* Goepel, W., Hesse, J., and Zemel, J.N., Eds., Weinheim: VCH, 1991, vol. 2, p. 429.
17. Malyshev, V.V. and Pisliakov, A.V., *Sens. Actuators B,* 2003, vol. 96, p. 413.
18. Weh, T., Fleischer, M., and Meixner, H., *Ibid.,* 2000, vol. 68, p. 146.
19. Lundstrom, I., Shivaraman, M.S., and Svensson, C.M., *J. Appl. Phys.,* 1975, vol. 46, p. 3876.
20. Lundstrom, I., *Sens. Actuators B,* 1996, vols. 35–36, p. 11.
21. Zemel, J.N., Keramati, B., Spivak, C.V., and D'Amico, A., *Ibid.,* 1981, vol. 1. p. 427.
22. Fonash, S.J., Li, Z., and O'Leary, *J. Appl. Phys.,* 1985, vol. 58, p. 4415.
23. Ukshe, E., Leonova, L., and Dobrovolsky, Yu., *Proc. Conf. "Energetika un Ekologija,"* Riga, 1991, p. 165.
24. Treglazov, I., Leonova, L., Dobrovolsky, Yu., Ryabov, A., Vakulenko, A., and Vassiliev, S., *Sens. Actuators B,* 2005, vol. 106, no. 1, p. 164.
25. Miura, N., Lu, G., and Yamazoe, N., *Solid State Ionics,* 2000, vols. 136–137, p. 533.
26. Yajima, T., Koide, K., Takai, H., Fukatsu, N., and Iwahara, H., *Ibid.,* 1995, vol. 79, p. 333.
27. Miura, N., Kato, H., Yamazoe, N., and Seiyama, T., *Proc. Int. Meeting on Chem. Sensors,* Tokyo–Amsterdam: Elsevier, 1983, p. 233.
28. Opekar, F., Langmaier, J., and Samec, Z., *J. Electroanal. Chem.,* 1994, vol. 379, nos. 1↓2, p. 301.
29. Xianbo, Lu, Shouduo, Wu, Li, Wang, and Zhenxi, Su, *Sens. Actuators B,* 2005, vol. 107, no. 2, p. 812.
30. Sakthivel, M. and Weppner, W., *Ibid.,* 2006, vol. 113, no. 2, p. 998.
31. Bouchet, R., Rosini, S., Vitter, G., and Siebert, E., *Ibid.,* 2001, vol. 76, nos. 1–3, p. 610.
32. Rosini, S. and Siebert, E., *Electrochim. Acta,* 2004, vol. 49, no. 4, p. 525.
33. Maffei, N. and Kuriakose, A.K., *Sens. Actuators,* 2004, vol. 98, no. 1, p. 73.
34. Miura, N. and Yamazoe, N., *Chemical Sensor Technology,* Seiyama, T., Ed., Tokyo: Kodansha, 1988, p. 123.
35. Miura, N., Harada, T., and Yamazoe, N., *J. Electrochem. Soc.,* 1989, vol. 136, p. 1215.
36. Miura, N., Lu, G., and Yamazoe, N., *Solid State Ionics,* 1992, vols. 53–56, p. 975.
37. Alberti, G. and Palombari, R., *Ibid., 1989,* vol. 35, p. 153.
38. Hibino, T. and Iwahara, H., *J. Appl. Electrochem.,* 1994, vol. 24, p. 102.
39. Velasko, G., Schnell, J.Ph., and Croset, M., *Sens. Actuators,* 1981–1982, vol. 2, p. 371.
40. Miura, N., Harada, T., Shimizu, Y., and Yamazoe, N., *Ibid.,* 1990, vol. 1, nos. 1–6, p. 125.
41. Ramesh, C., Velayutham, V.G., Murugesan, N. et al., *J. Solid State Electrochem.,* 2003, vol. 7, p. 511.
42. Ponomareva, V.G., Lavrova, G.V., and Hairetdinov, E.F., *Sens. Actuators B,* 1997, vol. 40, no. 2, p. 95.
43. Hyun-Su Kim, Won-Taek Moon, Youn-Ki Jun, and Seong-Hyeon Hong, *Ibid.,* 2006 (in press).
44. Nogami, M., Matsumura, M., and Daiko, Y., *Ibid.,* 2006 (in press).
45. Iwahara, H., Asakura, Y., Katahira, K., and Tanaka, M., *Solid State Ionics,* 2005, vol. 176, nos. 39–40, p. 2979.
46. Lu, G., Miura, N., and Yamazoe, N., *J. Electrochem. Soc.,* 1996, vol. 143, p. L154.
47. Arias de Velasco, A.A., Moseley, P.T., Peat, R., and Pelaez, J.G., *Sens. Actuators B,* 1993, vol. 15, nos. 1–3, p. 55.
48. Martin, L.P., Pham, A.Q., and Glass, R.S., *Corros. Sci.,* 2005, vol. 47, no. 5, p. 1197.
49. Taniguchi, N., Kuroha, T., Nishimura, C., and Iijima, K., *Sens. Actuators B,* 2005, vol. 106, no. 2, p. 784.
50. Kudo, T. and Fueki, K., *Solid State Ionics,* 1990.
51. *Sensors: A Comprehensive* Survey, Gopel, W., Jones, T.A., Kleitz, M., Lundstrom, J., and Seiyama, T., Eds., Weinheim: VCH, 1991, vol. 2.
52. Lu, G., Miura, N., and Yamazoe, N., *Sens. Actuators B,* 1996, vols. 35–36, p. 130.
53. Dobrovol'skii, Yu.A., Leonova, L.S., and Vakulenko, A.M., *Elektrokhimiya,* 1996, vol. 32, p. 475.
54. Kumar, R. and Fray, D., *Sens. Actuators B,* 1988, vol. 15, p. 185.
55. Dubbe, A., *Ibid.,* 2003, vol. 88, p. 138.
56. Ukshe, E.A. and Leonova, L.S., *Elektrokhimiya,* 1992, vol. 28, p. 1427.

Yurii Anatol’evich Dobrovol’skii, Cand. Sc. (Chem.), Head of Laboratory of Solid State Ionics, Institute of Problems of Chemical Physics, Russian Academy of Sciences (IPCP RAS). Scientific areas of focus: chemistry and physics of superionic conductors, solid state proton conduction, chemical sensors, materials for fuel cells.

Lyudmila Sergeevna Leonova, Cand. Sc. (Chem.), Leading Researcher, Laboratory of Solid State Ionics, IPCP RAS. Scientific areas of focus: chemistry and physics of cationic conductors, chemical sensors.

Aleksandr Evgen’evich Ukshe, Cand. Sc.(Phys.–Math.), Senior Researcher, Laboratory of Solid State Ionics, IPCP RAS. Scientific areas of focus: physics of superionic conductors, solid state relaxation, fractal geometry, chemical sensors, materials for fuel cells.

Aleksei Vladimirovich Levchenko, Cand. Sc. (Chem.), Leading Researcher, Laboratory of Solid State Ionics, IPCP RAS. Scientific areas of focus: chemistry and electrochemistry of superionic conductors, surface chemistry, chemical sensors, materials for fuel cells.

Aleksandr Mikhailovich Baranov, Dr. Sc. (Tech.), Prof., Chair of High Radio Electronics Technologies, MATI Tsiolkovskii Russian State Technical University. Scientific areas of focus: ionic plasmic synthesis of catalysts for fuel cells and gas sensors, physics and technology of thin films.

Aleksei Andreevich Vasil’ev, Dr. Sc. (Tech.), Leading Researcher, Kurchartovskii Institut Russian Research Center. Scientific areas of focus: physics and technology of gas sensors.