Electrochemical Materials and Technologies

ARTICLE

eISSN: 2949-0561

Cite this: Electrochem. Mater. Technol. 3 (2024) 20243026

Stability and reproducibility of solid electrolyte amperometry sensors at the analysis of hydrogen in nitrogen-containing gas mixtures

Anatoly Kalyakin [a], Alexander Volkov [a]*, Maxim Gorshkov [a]

Received: 9 November 2023
Accepted: 13 December 2023
Published online: 12 January 2024

DOI: 10.15826/elmattech.2024.3.026

This paper illustrates the results of long-term tests on the stability of the output signal of the solid electrolyte amperometry sensor when measuring the hydrogen concentration in the $H_2 + N_2$ gaseous mixture. The obtained experimental data verify the stability and reproducibility of the sensor output signal for hydrogen concentration measurements in the nitrogen-containing gaseous mixture during > 8000 h of operation. The output signal drift, i.e., the limiting current value, was insignificant, less than ± 5 %. The sensor operation was performed at 3 temperature shifts with different time intervals; these changes did not have any impact either on the sensor integrity or on its operation. The structure of the solid electrolyte sensor, intermediate solid electrolyte / electrode layer and electrodes did not undergo any significant changes during operation. The dynamic characteristics of the sensor, the response time in particular, remained stable during the operation.

keywords: hydrogen, solid electrolyte, sensor, stability, limiting current, response time

1. Introduction

Solid electrolytes with oxygen-ionic conductivity are widely used in sensors to analyze the content of free oxygen in the gas media and metallic melts [1–9]. The majority of published research on solid electrolyte sensors is devoted to the study of such sensors with the mixed potential based on oxygen-conducting solid electrolytes with single gas space [10–15]. When detecting the gas, for instance hydrogen in various gas media, the occurring processes result in the deviation of the concentration dependence from the Nernst dependence. This effect may be caused either by the occurrence of several simultaneous potential determining processes or by the accumulation of the process products on the three-phase boundary or by slow adsorption on the three-phase boundary.

a: Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg 620066, Russian Federation

* Corresponding author: a.volkov@ihte.ru

The dependence of the generated EMF on the concentration of the inflammable compound in the analyzed gas of such sensors is described by the following equation:

$$E = E_0 + k \cdot \ln[H_2], \quad (1)$$

where k is an empirically derived constant.

The value of the appeared mixed potential is determined mainly by a number of factors including the concentration and composition of the analyzed gas media, the material of the measuring electrode and operation temperature.

Potentiometric sensors based on solid electrolytes of the YSZ composition are the most widely known. These sensors, based on the solid electrolytes with the unipolar oxygen conductivity, proved to be efficient in the heat engineering, metallurgy, chemistry and motor industry. They are characterized by ability to determine wide oxygen concentration range, rapid operation, simplicity of the construction and simple processing of the obtained electrical signal, i.e., EMF, to the hydrogen

concentration. The serious drawback of potentiometric sensors is that an etalon gas with known and stable oxygen concentration is required for accurate sensor operation. This fact makes the application of the sensor more complicated, as in some cases a separate etalon gas supply is hindered [16–22].

Recently solid electrolyte amperometric sensors with diffusion barrier aimed at the analysis of oxygen, hydrogen and moisture concentrations in inert and oxidizing gas media have been actively analyzed in a published literature [23–29]. These sensors are typically composed of YSZ solid electrolytes. The data on the most promising amperometric sensors design, composition of electrolytes, electrode materials, the most appropriate operating temperatures for the data analysis and etc. are accumulated in the obtained results of the published works [30–35]. The major part of the research is devoted to the determination of the hydrogen content in gas mixtures.

Among the vast published literature data, we would like to elucidate the results on the evaluation and practical usage of amperometic sensors based on solid electrolytes with proton conductivity by Katahira et al. [36]. The authors developed and tested complex sensors composed of two electrochemical cells: hydrogen pump and potentiometric sensor based on the $SrCe_{0.95}Yb_{0.05}O_3$ electrolyte. Development of amperometric sensors design and detailed analysis of their characteristics are illustrated in papers by Yajima et al. [37, 38].

Due to the growing interest towards amperometric sensors with diffusion barriers, our research group evaluated the long-term operation stability of the output signal of the sensor based on the proton solid electrolyte of the $CaZr_{0.9}Sc_{0.1}O_{3-\delta}$ composition to determine the hydrogen concentration in its mixture with nitrogen.

2. Experimental

2.1. Samples preparation

In the present paper an amperometric sensor with a diffusion barrier, i.e. an electrochemical cell made on the basis of the proton-conducting solid electrolyte of the $CaZr_{0.9}Sc_{0.1}O_{3-\delta}$ composition, was studied. The sensor schematic and appearance are presented in Figures 1 and 2. It is made of two solid electrolyte plates of 25 mm length, 12 mm width, and 1 mm thickness. One of the plates is concave. The depth of the concave is 0.5 mm and diameter is 6 mm. Porous platinum electrodes with a platinum wire current lead of 0.1 mm in diameter are applied to the opposite surfaces of the solid electrolyte concaved plate. A ceramic capillary of 257 μm inner diameter and 20 mm length was located between the

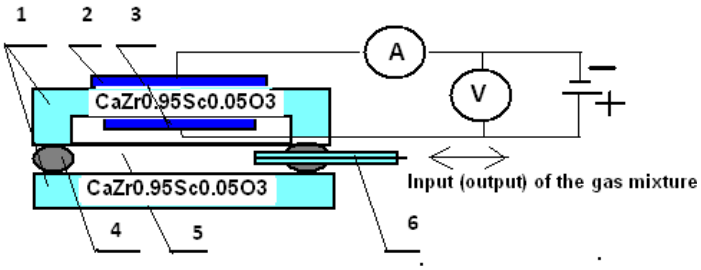

Figure 1 Sensor schematic. 1 – solid electrolyte plates, 2 – outer electrode, 3 – inner electrode, 4 – glassy hermetic, 5 – cavity, 6 – capillary, A – amperemeter, V – voltmeter.

Figure 2 General view of the sensor before the tests (the sensor appearance after 8000 h tests remained unchanged).

electrolyte plates. The plates were glued by a thermo-resistant glass. To provide a constant voltage on the electrochemical cell we used a GPS-18500 source of a constant current; the value of current passed through the cell was measured by a GDM-8246 type multimeter. We used H_2 (2 %) + nitrogen as a test gas mixture.

Constant current voltage was applied to the sensor electrodes with different polarity to provide pumping hydrogen from the sensor inner cavity to the analyzed gas flow. Via the sensor capillary the analyzed gas mixture input and the output nitrogen from the cavity exchanged. When a definite value of the input voltage was reached these processes became equilibrium. This is testified by the appearance of the limiting current. The value of the limiting current allows calculating the amount of hydrogen in the analyzed gas according to Equation (2).

$$I_{L(H_2+N_2)} = \left(\frac{2F \cdot D_{t(H_2+N_2)} \cdot S \cdot P}{R \cdot T \cdot L}\right) \cdot X_{H_2}, \quad (2)$$

where $2F$ is the amount of electricity necessary for the transfer of one mole of hydrogen; P is the total pressure of the analyzed gas; D is the diffusion coefficient of hydrogen in nitrogen; S and L denote the cross section

area and length of the capillary diffusion channel; R is the gas constant; T is the absolute temperature; X_{H_2} is the hydrogen concentration (volume fractions).

2.2. Experiment procedures

The electrochemical sensor, illustrated in Figure 1, was placed into a tube furnace with a nichrome heater. The volume of the tube furnace was 0.65 l. The temperatures in the furnace were maintained with the accuracy of ± 3 °C using a thermoregulator TP 703 Varta (Laboratory of ceramics Ltd., Moscow, Russia). The analyzed gas mixture was blown through the inner furnace area; the gas consumption was 20 ml/min. The gas mixture of the set composition (H_2 (2 %) + nitrogen) was additionally purified from moisture and admixtures (zeolite). Gas batching was performed using the F-201C-33-V type gas consumption regulator. The sensor operated in the pulse mode, i.e., during the whole experimental period there were four cooling-heating cycles to verify the sensor thermal resistance.

3. Results and discussion

When the sensor was heated to 500 °C, the constant current voltage was applied to the electrodes. As the applied voltage increased, the current passing through the sensor solid electrolyte plate increased. When a definite value of the applied voltage was reached, the current reached the desired value and stabilized; this current value was considered to be the limiting current. At each hydrogen concentration in the analyzed gas mixture and under otherwise equal conditions including diffusion barrier parameters, temperature, gaseous mixture component composition, and pressure, the limiting current was constant. Figure 3 illustrates voltammetry characteristics of the sensor during the determination of the hydrogen content at the temperatures of 500 and 550 °C. It is seen that the limiting current appears at the voltage of about 1 V. The measured limiting currents of the sensor, observed for gas mixtures containing from 0 to 4 % of hydrogen, allowed obtaining a linear dependence of the limiting current on hydrogen, presented in Figure 4.

Apart from the sensor characteristics illustrated in Figures 3 and 4, we recorded dynamic characteristics of the sensor before resource and stability tests (Figure 5). The time of the sensor reaction and sensor signal of 90 % of the nominal value were determined. The time of the sensor initial response varied from 3 to 5 seconds, and the time of the sensor signal output of the 90 % nominal value was from 70 to 100 seconds (these values were obtained using the transport delay).

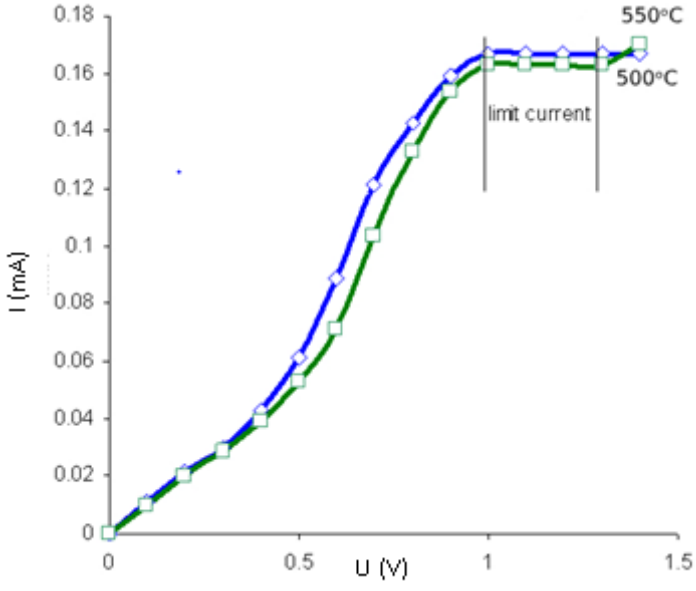

Figure 3 Dependence of the sensor current on the applied voltage. Hydrogen concentration in the gas mixture was 1.4 %.

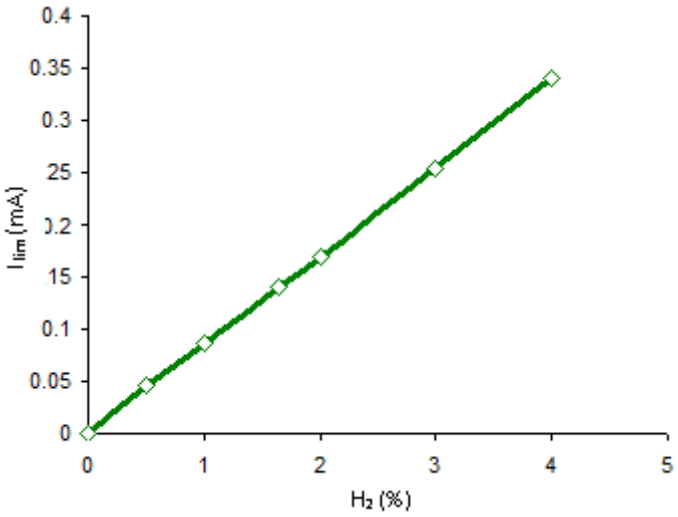

Figure 4 Dependence of the sensor limiting current on the hydrogen concentration.

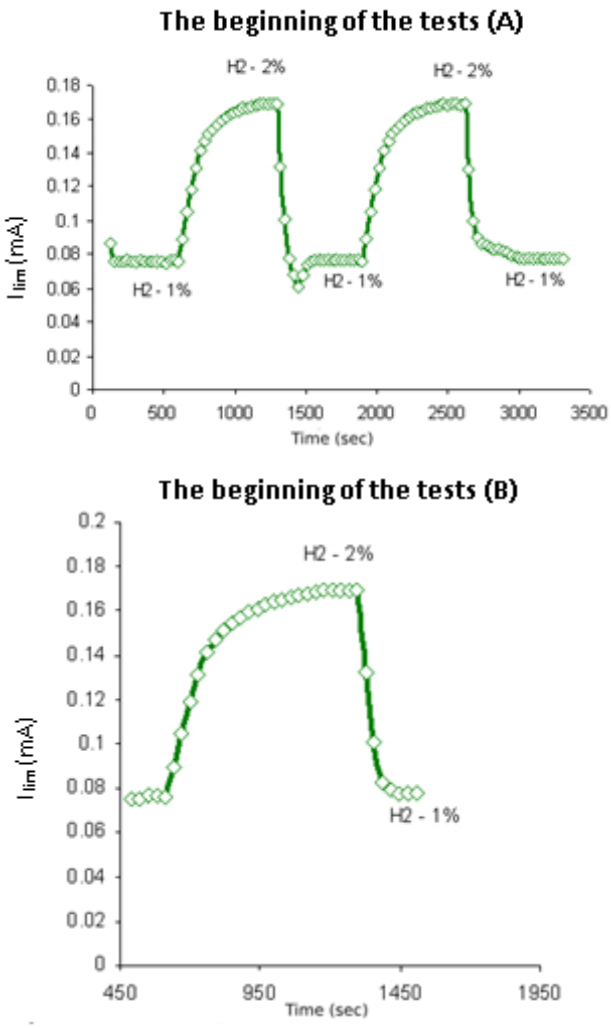

Figure 5 Dependence of the sensor dynamic characteristics on the hydrogen concentration change at the beginning of the tests.

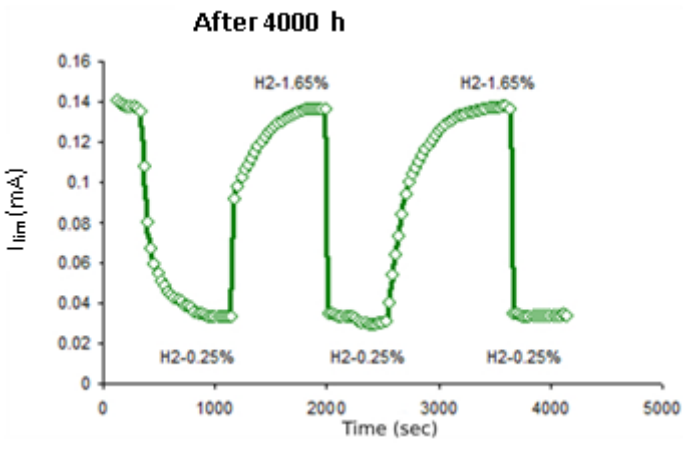

Figure 6 Dependences of the sensor dynamic characteristics on the hydrogen concentrations in nitrogen after the 4000-hour operation.

The dynamic characteristics of the sensor were evaluated after 4-thousand-hour operation and after 8 thousand hours (Figures 6 and 7). Figure 8 illustrates the dependence of the sensor limiting current changes on the hydrogen concentration in air during 8000 hours. During the tests, there were 3 heating-cooling cycles of the different time length. These thermal changes did not cause any destruction, decompression, or fault in the reproducibility of the sensor measurements.

Figures 6, 7 and 8 illustrate that the sensor dynamic characteristics remain almost stable during the whole test period. These figures verify good reproducibility of the sensor results. The deviations of the limiting current values during the tests were ± 5 % of the average value.

The sensor demonstrated a stable operation and well-reproducible results. The absolute hydrogen measurement error ranged from 0 to 4 % and was ± 0.3, which is satisfactory for hydrogen analyzers, based on different measuring modes. For instance, the hydrogen analyzer in gases HY-OPTIMA by the Artvik Company (Almaty, Kazakhstan) is based on the analysis of the regularities of hydrogen dissolution in metals and has an absolute measurement error of ± 3 mA. The amperometric hydrogen analyzer in the inert gas EHDV-G produced by FSUE 'NII NPO "Luch" (Podolsk, Russia) is based on liquid electrolyte and has a measurement error of ± 15 %.

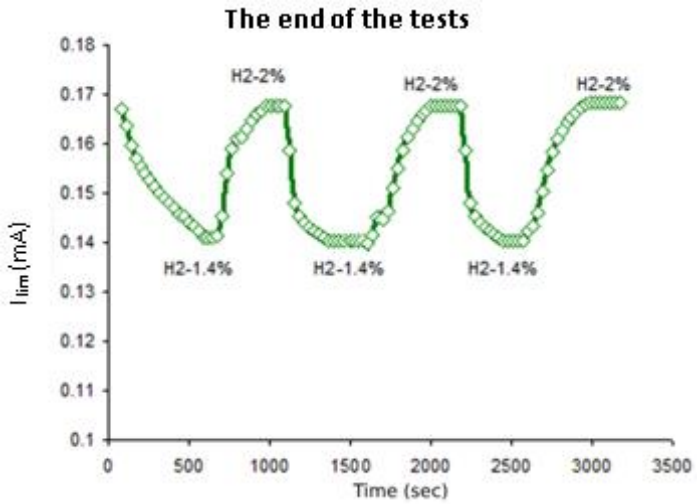

Figure 7 Dependences of the sensor dynamic characteristics on the hydrogen concentrations in nitrogen after the 8000-hour operation.

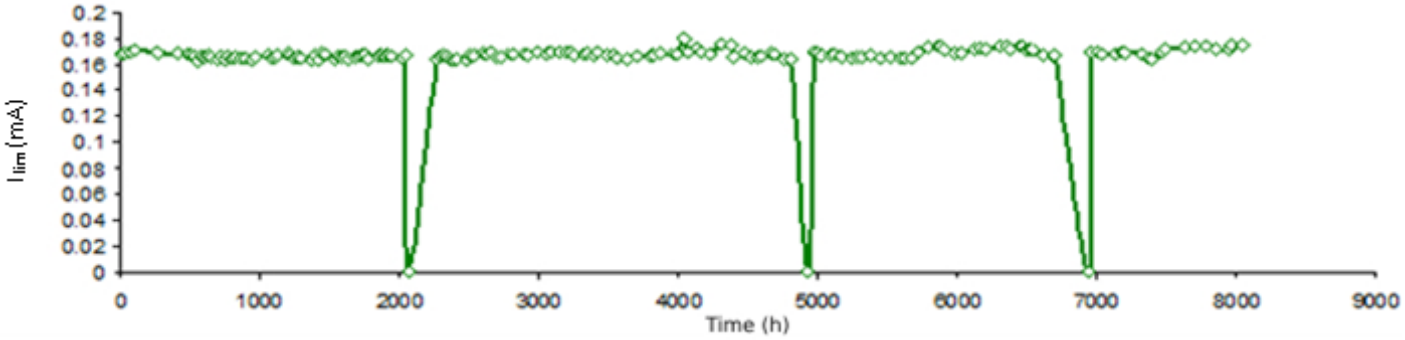

Figure 8 Changes in the sensor limiting current during the tests.

4. Conclusions

The stability of the amperometric solid electrolyte $CaZr_{0.9}Sc_{0.1}O_{3-\sigma}$ sensor with the diffusion barrier has been studied for measuring the concentration of hydrogen in the hydrogen-nitrogen gas mixture during 8000 hours. The sensor demonstrated stable operation and good data reproducibility. The performed 3 heating-cooling cycles did not cause any faults in the sensor operation. The sensor characteristics were found to be promising for its practical implementation.

Supplementary materials

No supplementary materials are available.

Funding

The present research was performed within the budget plan of the Institute of High Temperature Electrochemistry.

Acknowledgments

None.

Author contributions

Anatoly Kalyakin: Data curation; Formal Analysis; Investigation; Methodology.

Alexander Volkov: Investigation; Validation; Data curation; Methodology; Resources; Supervision; Writing – Original draft; Writing – Review & Editing.

Maxim Gorshkov: Investigation; Software; Visualization.

Conflict of interest

The authors declare no conflict of interest.

Additional information

Anatoly Kalyakin, https://orcid.org/0000-0002-8816-4303;

Alexander Volkov, https://orcid.org/0000-0002-5184-986X;

Maxim Gorshkov, https://orcid.org/0000-0002-8123-7223.

References

1. Okamoto H, Obayashi H, Kudo T, Carbon monoxide gas sensor made of stabilized zirconia, Solid State Ion., **1(3–4)** (1980) 319–326. https://doi.org/10.1016/0167-2738(80)90012-0

2. Zheng Y, Wang J, Yu B, Zhang W, et al., A review of high temperature co-electrolysis of H_2O and CO_2 to produce sustainable fuels using solid oxide electrolysis cells (SOECs): advanced materials and technology, Chem. Soc. Rev., **46** (2017) 1427–1463. https://doi.org/10.1039/C6CS00403B

3. Fadeev GI, Kalyakin AS, Somov SI, Electrode potentials of electrochemical cells with oxide-conducting solid electrolyte in chemically nonequilibrium gas mixtures, Russ. J. Electrochem., **45** (2009) 429–433. https://doi.org/10.1134/S1023193509040119

4. Volkov A, Neimin A, Sosnovsky V, Study of durability of the solid electrolyte electrochemical sensors with etalon electrodes of the Me-Me_xO_y type at measuring of the oxygen concentration of the gaseous media (Issledovaniye dolgovechnosti tverdoelektrolitnykh electrokhimicheskikh datchikov s etalonnymi electrodami tipa Me-Me_xO_y pri izmerenii kislorodsoderzhaniya gazovykh sred), Zavodskaya laboratoriya, **48** (1982) 6–8.

5. Zhuiykov S, Miura N. Solid-state electrochemical gas sensors for emission control. In book: Sorrell CC, Sugihara S, Nowotny J (eds) Materials for energy conversion devices. Woodhead Publishing: Cambridge; 2005. 303–335 pp. https://doi.org/10.1533/9781845690915.2.303

6. Park CO, Fergus JW, Miura N, Park J, Choi A, Solid-state electrochemical gas sensors, Ionics, **15** (2009) 261–284. https://doi.org/10.1007/s11581-008-0300-6

7. Kalyakin A, Demin A, Gorbova E, Volkov A, Tsiakaras A, Sensor Based on a Solid Oxide Electrolyte for Measuring the Water Vapor and Hydrogen Content in Air, Catalysts, **12(12)** (2022) 1558. https://doi.org/10.3390/catal12121558

8. Shuk P, Bailey E, Guth U, Zirconia Oxygen Sensor for the Process Application: State-of-the-Art, Sens. Transducers, **90** (2008) 174–184. https://doi.org/10.1007/s11581-008-0274-4

9. Liu T, Jin H, Li L, Yu J, A novel method for preparing dense diffusion barrier limiting current oxygen sensor, J. Am. Ceram. Soc., **101(4)** (2018) 1537–1543. https://doi.org/10.1111/jace.15302

10. Sekhar PK, Brosha EL, Mukundan R, Nelson MA, et al., Development and testing of a miniaturized hydrogen safety sensor prototype, Sens. Actuators B: Chem., **148(2)** (2010) 469–477. https://doi.org/10.1016/j.snb.2010.05.031

11. Flege E, Vonau C, Guth U, Characterization of Pt,O_2|YSZ electrodes for lambda probes and their ageing in humid atmosphere, Technisches Messen, **84(10)** (2017) 635–643. https://doi.org/10.1515/teme-2016-0079

12. Lalauze R, Visconte E, Montanaro L, Pijolat C, A new type of mixed potential sensor using a thick film of beta alumina, Sens. Actuators B: Chem., **13(1–3)** (1993) 241–243. https://doi.org/10.1016/0925-4005(93)85371-G

13. Guillet N, Lalauze R, Pijolat C, Oxygen and carbon monoxide role on the electrical response of a non-Nernstian potentiometric gas sensor; proposition of a model, Sens. Actuators B: Chem., **98(2–3)** (2004) 130–139. https://doi.org/10.1016/j.snb.2003.10.001

14. Driesner O, Gumprecht F, Guth U, In situ measurements of O_2 and CO eq. in cement kilns, J. Sens. Sens. Syst., **6(2)** (2017) 327–330. https://doi.org/10.5194/jsss-6-327-2017

15. Chevallier L, Di Bartolomeo E, Grilli ML, Mainas M, et al., Non-Nernstian planar sensors based on YSZ with a Nb_2O_5 electrode, Sens. Actuators B: Chem., **129(2)** (2008) 591–598. https://doi.org/10.1016/j.snb.2007.09.037

16. Park CO, Akbar SA, Weppner W, Ceramic electrolytes and electrochemical sensors, J. Mater. Sci., **38** (2003) 4639–4660. https://doi.org/10.1023/A:1027454414224

17. Katahiraa K, Matsumotoa H, Iwaharaa H, Koidea K, Iwamoto T, A solid electrolyte hydrogen sensor with an electrochemically-supplied hydrogen standard, Sens. Actuators B: Chem., **73(2–3)** (2001) 130–134. https://doi.org/10.1016/S0925-4005(00)00672-9

18. Xia ChY, Lu XCh, Yan Y, Wang T, et al., Improved performances of oxygen potentiometric sensor by electrochemical activation, J. Solid State Electrochem., **16** (2012) 2523–2532. https://doi.org/10.1007/s10008-011-1556-8

19. Pasierb P, Rekas M, Solid-state potentiometric gas sensors–current status and future trends, J. Solid State Electrochem., **13** (2009) 3–25. https://doi.org/10.1007/s10008-008-0556-9

20. Möbius H-H, Hartung R, Solid-state potentiometric gas sensors–a supplement, J. Solid State Electrochem., **14** (2010) 669–673. https://doi.org/10.1007/s10008-009-0839-9

21. Pasierb P, Rekas M, Solid-state potentiometric gas sensors–current status and future trends, J. Solid State Electrochem., **13** (2009) 3–25. https://doi.org/10.1007/s10008-008-0556-9

22. Maskell WC, Steele BCH, Solid state potentiometric oxygen gas sensors, J. Appl. Electrochemistry, **16** (1984) 475–489. https://doi.org/10.1007/BF01006843

23. Iwahara H, Uchida H, Ogaki K, Nagato H, Nernstian hydrogen sensor using $BaCeO_3$-based, proton-conducting ceramics operative at 200–900 °C, Journal of the Electrochemical Society, **138** (1991) 295–299. https://doi.org/10.1149/1.2085558

24. Chao Y, Yao S, Buttner WJ, Stetter JR, Amperometric sensor for selective and stable hydrogen measurement, Sens. Actuators B: Chem., **106(2)** (2005) 784–790. https://doi.org/10.1016/j.snb.2004.09.042

25. Lu X, Wu S, Wang L, Su Z, Solid-state amperometric hydrogen sensor based on polymer electrolyte membrane fuel cell, Sens. Actuators B: Chem., **107(2)** (2005) 812–817. https://doi.org/10.1016/j.snb.2004.12.022

26. Tan Y, Tan TC, Sensing behaviour of an amperometric hydrogen sensor, J. Electrochem. Soc., **142** (1995) 1923–1928. https://doi.org/10.1149/1.2044215

27. Sakthivel M, Weppner W, A portable limiting current solid-state electrochemical diffusion hole type hydrogen sensor device for biomass fuel reactors: engineering aspect, Int. J. Hydrogen Energy, **33(2)** (2008) 905–911. https://doi.org/10.1016/j.ijhydene.2007.10.048

28. Kalyakin AS, Volkov AN, Meshcherskikh AN, Dunyushkina LA, Dual chamber YSZ-based sensor for simultaneous measurement of methane and water vapor concentrations in CH_4 + H_2O + N_2 gas mixtures, J. Solid State Electrochem., **26** (2022) 739–747. https://doi.org/10.1007/s10008-022-05116-y

29. Medvedev D. Kalyakin A, Volkov A, Demin A, Tsiakaras P, Electrochemical moisture analysis by combining oxygen- and proton-conducting ceramic electrolytes, Electrochem. commun., **76** (2017) 55–58. https://doi.org/10.1016/j.elecom.2017.01.003

30. Taniguchi N, Kuroha T, Nishimura C, Iijima K, Characteristics of novel $BaZr_{0.4}Ce_{0.4}In_{0.2}O_3$ proton conducting ceramics and their application to hydrogen sensors, Solid State Ion., **176(39–40)** (2005) 2979–2983. https://doi.org/10.1016/j.ssi.2005.09.035

31. Kalyakin AS, Medvedev DA Volkov AN, Electrochemical zirconia-based sensor for measuring hydrogen diffusion in inert gases, Journal of The Electrochemical Society, **169** (2022) 057530. https://doi.org/10.1149/1945-7111/ac725d

32. Bao J, Okuyama Y, Shi Z, Ohno H, et al., Properties of Electrical Conductivity in Y- Doped $CaZrO_3$. Mater. Trans., **53** (2012) 973–979. https://doi.org/10.2320/matertrans.m2012017

33. Goppel W, Reinhardt G, Rasch M, Trends in development of solid state ampermetric and potentiometric high temperature sensors, Solid State Ion, **136(1–2)** (2000) 519–531. https://doi.org/10.1016/S0167-2738(00)00410-0

34. Kalyakin AS, Volkov AN, Meshcherskikh AN, Dunyushkina LA, Dual chamber YSZ based sensor for simultaneous measurement of methane and water vapor concentrations in CH_4 + H_2O+ N_2 gas mixtures, Journal of Solid State Electrochemistry, **26** (2022) 739–747. https://doi.org/10.1007/s10008-022-05116-y

35. Somov SI, Reinhardt G, Guth U, Göpel W, Tubular amperometric high-temperature sensors: simultaneous determination of oxygen, nitrogen oxides and combustible components, Sens. Actuators B: Chem., **65(1–3)** (2000) 68–69. https://doi.org/10.1016/S0925-4005(99)00341-X

36. Katahira K, Matsumoto H, Iwahara H, Koide K, Iwamoto T, A solid electrolyte steam sensor with an electrochemically supplied hydrogen standard using proton-conducting oxides, Sens. Actuators B: Chem., **67(1–2)** (2000) 189–193. https://doi.org/10.1016/S0925-4005(00)00400-7

37. Uchida H, Maeda N, Iwahara H, Relation between proton and hole conduction in $SrCeO_3$-based solid electrolytes under water-containing atmospheres, Solid State Ionics, **11(2)** (1983) 117–124. https://doi.org/10.1016/0167-2738(83)90048-6