GAS SENSOR FOR TEMPERATURES ABOVE 100 ^{O}C BASED ON HYBRID INORGANIC-ORGANIC PROTON CONDUCTING PHOSPHOSILICATE POLYMER

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Introduction

In increasing demand for automatization of industrial processes precise sensors play an important role as a basic instrument to obtain desired information. Electrochemical sensors represent a significant part of the family of these devices. Their application is particularly attractive due to direct transformation of chemical quantities to an easily measurable electric signal, at low cost in comparison to the other sensor types based on other principles. Hydrogen and oxygen represent two of the most commonly used gases in industry. Theirs importance should even increase in near future with expected wider application of fuel cells.

Gas sensors based on potentiometric response of electrode separated from the reference electrode by suitable solid proton conducting electrolyte is known for a long time. Its application, however, is currently limited by various problems. Commonly used proton conducting membrane known under its commercial name Nafion^{R} is sensitive to insufficient low humidity of measured gases and in case of higher temperature or dry gas it rapidly looses its conductivity. Another problem represents reversibility of sensing and reference electrode.

In present work membrane based on hybrid inorganic-organic glass was used in hydrogen or oxygen gas sensor. Inorganic-organic glasses represent new attractive ionic conductive material. This is mainly because of its conductivity being apparently less dependent on the water content. It makes this type of materials promising for the electrochemical applications operating in dry environment and at the temperatures above 100 °C.

Experimental

Proton conductive material preparation

The synthesis of inorganic-organic structure has been realized by acid-base reaction of H3PO4 and (R)2SiCl2. On this way framework or organic functional groups bonded to Si tetrahedron can be build. In the present study the inorganic phosphate glass from crystalline H3PO4, (CH3)2SiCl2.and (C2H5O)4Si, with molar ratio of mentioned

component 2:0.9:0.1 respectively was synthesised. This is an amorphous transparent elastic material. As a reference material Nafion 117 membrane was used.

Sensor construction and measurement

The reference electrode based on TiH_x was prepared [1]. Ti plates were cleaned in concentrated HCl and heated to 550 °C in the flowing H_2 atmosphere for 3 hours. A Pt mesh was used as the sensing electrode. The sensor consisted from the membrane fixed between the Pt mesh and the TiH_x plate by a silicone gasket. The sensor has been pressed together by two terminal PTFE plates. A gas distribution serpentine was made in a PTFE plate at the side in contact with the Pt mesh. The sensor potential was measured by the pH/mV meter Orion 720 (Orion, USA).

Sensitivity towards H_2, O_2 and CO was tested. The gas mixtures of given compositions were prepared by two mass flow controllers. Measured gas was optionally passed through a bubble humidifier at given temerature to compare sensor behaviour in dry and partially humidified gas. All experiments were performed at atmospheric pressure.

Results and Discussion

In case of sensor equipped with membrane Nafion 117 fast response time below 10 s was observed. However it shows high sensitivity to the measured gas humidity. In case of humidification at 25°C it did not reach constant value at temperature above 50°C. This instability is caused by the continuous drying of the membrane that affects membrane's conductivity. The sensor quipped with our membrane shows negligible sensitivity towards gas humidification. In case of high humidity it is possible to suppose partial leaching of free phosphoric acid contained in membrane during long time operation.

The linear dependence of sensor potential on logarithm of H_2 mole fraction is shown on Fig. 1. It is in agreement with Nerst law. However, at temperatures 100°C and 150°C the slope of the calibration curve corresponds to the one and two electron reaction, respectively. A different reaction mechanism is not feasible explanation. Therefore, a possible explanation could be the influence of the ambient air atmosphere at the side of the TiH_x reference electrode resulting in the occurrence of a mixed potential. It is not in agreement with Alberti [2], where TiH_x electrode is considered as non sensitive to gas interference as it has no catalytic behaviour. Another factors could play important role, too. A different water content in the membrane and thus a different degree of hydration and dissociation of H_3PO_4 inside the membrane could cause changes of H^+ activity at the electrode surface. The variation of the activity of TiH_x reference electrode at different temperatures should be considered as well.

In case of the O_2 sensor the response time decreases with temperature similarly to the H_2 sensor. The calibration slope again exhibits a linear dependence of the sensor potential on O_2 mole fraction logarithm. Surprisingly, very interesting effect was observed. The slope of the calibration curve -155.5 mV/ decade corresponds to approx. 0.5 electron electrode reaction. Because the measured gas consist only from N_2 and O_2 no additional reaction than formation of water by interaction with H^+ and Pt surface can be expected. Only possible explanation is a presence of a mixed potential. Detailed study of mentioned mixed potential occurrence should be subject of further work.

In case of CO only preliminary experiments was done showing expected blocking of Pt surface by adsorbed CO. Therefore it is necessary to operate at elevated temperatures to obtain repeatable results.

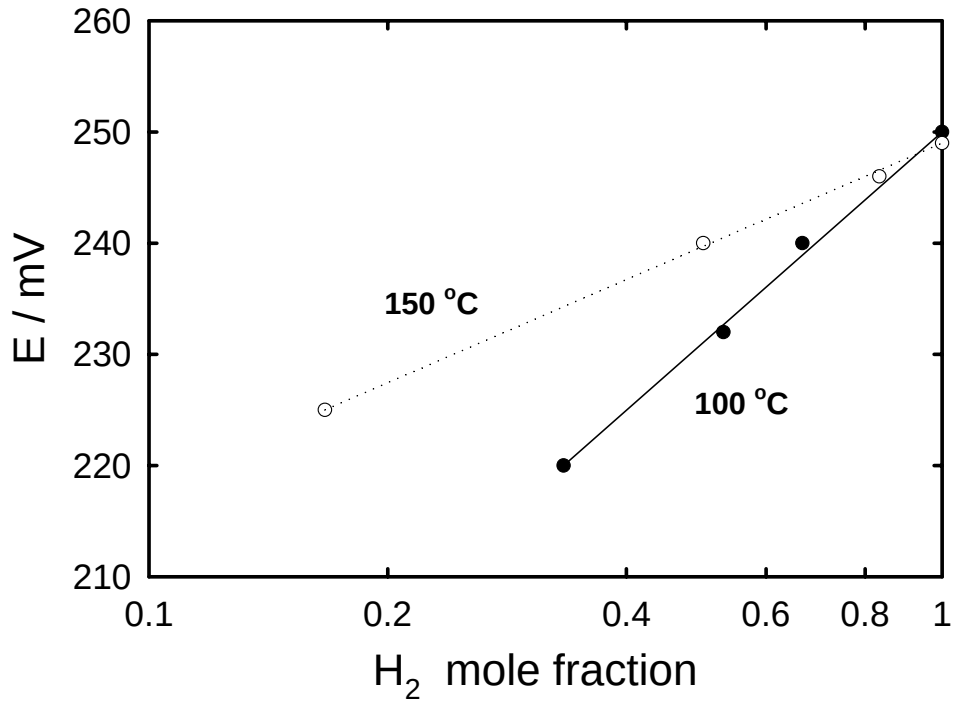

Fig. 1 *The calibration curves of the potentiometric H_2 sensor at 100 °C and 150 °C. Potential of Pt sensing electrode against TiH_x reference electrode.*

Conclusions

Prepared inorganic-organic glass membrane shows good potentiometric response In comparison to Nafion membrane the response delay is longer. It is probably due to its high thickness. On the other hand, sensitivity of sensor response to the relative humidity of measured gas is significantly lower in comparison to the Nafion membrane. It is much more evident especially at temperature increased to 100°C, where possible application of hybrid membranes is supposed. Further hybrid membrane optimisation should make this material promising for the proposed type of application.

Acknowledgements

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References

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2. G. Alberti, M. Casciola, Solid State Ionics **145** (2001) 3.