PROTON CONDUCTING PHOSPHOSILICATE MEMBRANES

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Introduction

The growing number of research works in the field of proton conducting inorganic-organic membranes reflects the increasing interest to apply these advanced materials as fast proton conductors operating at increased temperature and low humidity in the H_2/O_2 fuel cells or in various sensors [1-3]. Character of the phosphosilicate membranes strongly depends on a fabrication procedure and enables to achieve sufficient conductivity at low humidity conditions. This makes this type of materials promising for the electrochemical applications at temperatures above 100 °C at ambient pressure. A typical example represents PEM (proton exchange membrane) type fuel cell. For such devices an elastic material is preferred, because electrochemical reactions at the glass-electrode interface could result in volume changes with subsequent risk of material rupture. Desired glass elasticity and ion-selectivity can be attained by the incorporation of suitable organic compounds. The substitution of the bridging oxygen atoms by organic groups can also decrease material's viscosity that facilitates the migration of ions and a viscous flow can suppress a mechanical tension in the material.

Experimental and Results

The creation of inorganic-organic structure without the decomposition of organic moiety is not easy. It can be obtained by the sol-gel technique, but the problem is the presence of a solvent in gels. Its evaporation can cause cracking or shrinking of the material. The alternative synthesis of hybrid materials is offered by acid-base reactions, such as the reaction of H_3PO_4 melt with liquid $(R)_2SiCl_2$. This way, a framework where organic groups are bonded to Si tetrahedron, e.g., $-Si(CH_3)_2-O-PO(OH)-O-$, can be build. In our work we has used this approach to synthesize the inorganic-organic hybrid phosphosilicate membranes from H_3PO_4, $(CH_3)_2SiCl_2$ and $(C_2H_5O)_4Si$. We obtained a transparent elastic material (Fig. 1) of amorphous character as was verified by X-ray diffraction.

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Fig. 1 *Prepared elastic inorganic-organic phosphosilicate membrane exhibiting proton conductivity.*

An electrochemical impedance spectroscopy was used in order to determine proton conductivity of the prepared membrane and its dependence on temperature at ambient atmosphere relative humidity. At low relative humidity (~35%), the conductivities were roughly 10^{-1}- 10^{0} S/m for the temperature range from 25 to 110°C and the conductivity was dependent on the composition of a membrane and its preparation procedure.

Discussion and Conclusions

The low atmosphere humidity affected the conductivity much less comparing to the classical polymeric proton exchange membranes, which makes this material promising for the proposed applications. At higher temperatures, the increase of the mobility of protons in our membranes compensated the negative effect on conductivity caused by a water content decrease and thus we did not observed a drop of conductivity. We started to apply the prepared membranes in the H_2/O_2 fuel cell and in the electrochemical sensors for H_2, O_2, and CO_2 gases.

Acknowledgements

This study was funded by the GACR grant 106/04/1279 and was a part of the research program MSM 6046137302 “Preparation and research of functional materials and material technologies using micro- and nanoscopic methods”.

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