Kinetics of the Proton Transport Through the New Types of Ion-Selective Membranes at Different Temperatures and Degrees of Swelling

Karel Bouzek, Martin Paidar, Zdeněk Samec[a] and Jan Schauer[b]
Institute of Chemical Technology
Department of Inorganic Technology, Technicka 5, 16628 Prague 6, Czech Republic
[a] J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic
Dolejškova 3, 18223 Prague, Czech Republic
[b] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic
Heyrovsky Sqr. 2, 16206 Prague, Czech Republic

Polymer electrolyte membrane represents up to now one of the weak points of the PEMFC. Several ways have been tested to solve this problem. One of them is synthesis of new, alternative membranes posing comparable, or even better properties at the conditions of the PEMFC at lower production costs (1).

In this work, new types of the homogeneous ion-exchange membranes based on the sulphonated poly(2,6-dimethyl-1,4-phenylenoxide) (SPPO) and SPPO intermolecularly complexed with poly(2-butylaniline) (PBA) or poly[2,2'-(m-phenylene)–5,5'-bibenzimidazole] (PBI) were synthesised. Intermolecular complexation enhances membrane mechanical properties, temperature and chemical stability. According to thermogravimetric analysis (TGA), these membranes exhibit good thermal stability at the temperatures up to 200 °C. The aim of this work was to examine transport properties of the new membranes as a function of theirs composition and thickness at the temperature between 20 and 60 ºC. Electrochemical impedance spectroscopy in four-electrode arrangement was used to fulfil this task.

As expected, conductivity of the membrane is negatively influenced by the increasing concentration of the complexing agent. This is because of occupation of the sulfogroup of SPPO by the quaternary nitrogen groups of the complexing agent responsible for the polymer cross-linking. This effect was more apparent for PBI than for PBA. This is because PBI poses two quaternary nitrogen groups compared to one group of PBA. Molecular weight of both materials is similar. These results point to the necessity of the careful optimisation of the membrane composition that would assure the sufficient membrane stability and the fast proton transport.

The results obtained were compared with those reported for the Nafion 117 membrane by Simonsson *et al* (2). At 100 % relative humidity (RH) and temperature of 20 ºC, the conductivities of the studied membranes and of Nafion 117 in proton cycle are comparable. Thus, a value of 8.52 S m^{-1} for Nafion 117 (2) is comparable with the values of 6.78 or 9.69 S m^{-1} that we measured for the SPPO membranes at the degree of sulfonation 25.4 or 42.4 %, respectively. It is to be noted, that the conductivity of the membrane complexed with PBI in not influenced by the addition of the first 10 % of complexing component.

On the other hand, when temperature is increased from 20 to 45 ºC, the conductivity of Nafion 117 decreases from 8.52 to 3.17 S m^{-1} (2), while the conductivity of the studied membranes exhibit the opposite behavior. This difference may stem from the different experimental arrangement. The conductivity of the Nafion membrane was measured in the longitudinal direction, which in the case of Nafion may lead to the results different from those for the transversal direction. To avoid any doubts, the conductivity of the SPPO membranes was determined also in the transversal direction using the two-electrode arrangement and the mercury contact to the membrane. Very good agreement between results in both arrangements was reached indicating that the present arrangement does not introduce any uncertainty.

Dependence of the membrane conductivity on the degree of the membrane swelling shows the characteristics that are slightly worse than for Nafion 117. On lowering RH from 100 to 50 %, the conductivity of the studied membranes decreases by approximately one to two orders of magnitude, whereas the Nafion conductivity exhibits a decrease less than one order of magnitude, *i.e.* from 8.52 to 1.25 S m^{-1} (2).

We conclude that the membranes based on the sulfonated polyphenylenoxide show promising properties for the future application in PEMFC. However, their further study is needed in order to optimize the membrane composition.

ACKNOWLEDGEMENTS

The financial support of this research by the Grant Agency of the Czech Republic under project number 203/99/0575 and by the Ministry of Education, Youth and Sports under project number CEZ: MSM223100001 is gratefully acknowledged. The Alexander von Humboldt Foundation purchased the Electrochemical Impedance Spectroscopy equipment.

REFERENCES

1. C.A. Linkous, Int. J. Hydrogen Energy, **18**, 641 (1993).
2. Y. Sone, P. Ekdunge and D. Simonsson, J. Electrochem. Soc.**, 143**, 1254 (1996)

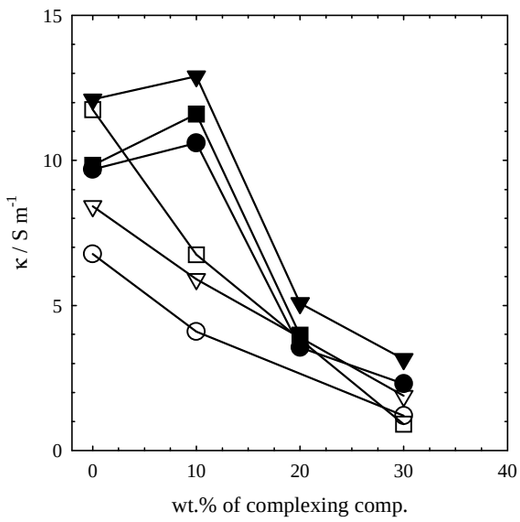

Figure: Dependence of the membrane conductivity on the content of the complexing compound, temperature: O - 20 °C, ∇ - 40 °C and □ - 60 °C, open symbols - membrane complexed with PBA, full symbols - membrane complexed with PBI.