INORGANIC ACID-IMPREGNATED INTERPOLYMER COMPLEXES FOR FUEL CELL MEMBRANES

O.Chervakov[1], E.Shembel[2], V.Ryabenko[1], Yu. Polischuk[1], K.Kylyvnyk[2], P. Novak[2]

[1] Ukrainian State Chemical Technology University, 49005 Dnipropetrovsk, Ukraine
[2] Ener1, Inc, Fort Lauderdale, FL, 33309

Introduction

Perfluorosulfonated polymers are the most widely used as the proton conducting matrixes for fuel cell membranes. But their high cost and operation temperature up to 90°C are two main limitations of their promising use. Above this temperature, water evaporation from the membrane leads to a dramatic drop in conductivity. Thermal stability of perfluorosulfonated polymers is insufficient. For example, lifetime of Nafion 117 at 120°C is 30-45 days.

There has increased interest in development of new non-fluorinated proton-conducting materials with a low cost and high service properties at the temperatures higher than 120°C in recent years. Two main reasons of the increased interest to high-temperature membranes may be selected:

- kinetic rates of electrochemical reactions generally increase with increasing temperature resulting in improved fuel cell performance;
- at high temperatures (~150°C) the reason for Pt catalyst poisoning by the traces of CO, which can be in H_2 fuels is excluded.

Among a great variety of the already developed proton-conducting materials, a special interest is shown in the polymer systems based on polybenzimidazoles (PBI) and cation polymers doped by inorganic acids (H_3PO_4 or H_2SO_4) [1, 2]. Phosphoric acid-doped PBI is not such expensive as Nafion is gas and methanol impermeable, does not require humidification in PEMFC applications, and has effective working temperature reaching almost 200°C [1].

Blends consisting of cationic polyelectrolyte and phosphoric acid have been also reported in [2]. Accordingly, polydiallyl-dimethylammonium-dihydrogen-phosphate ($PAMA+H_2PO_4^-$) electrolyte is blended with H_3PO_4 to give the system ($PAMA+H_2PO_4^-$)–H_3PO_4, which is stable at about 150°C. Its conductivity increases with H_3PO_4 concentration and can reach 10^{-2} S/cm at 100°C [2].

In the work we present the synthesis and investigation results of the properties of proton-conducting materials based on inorganic acid-impregnated interpolymer complexes, produced by the interaction between polyvinylpyridine and polyethylene oxide derivatives.

Corresponding author: Oleg Chervakov
E-mail: chervakov@email.dp.ua
Phone: (38-0562) 47-24-91, Fax: (38-0562) 47-03-91

Experimental

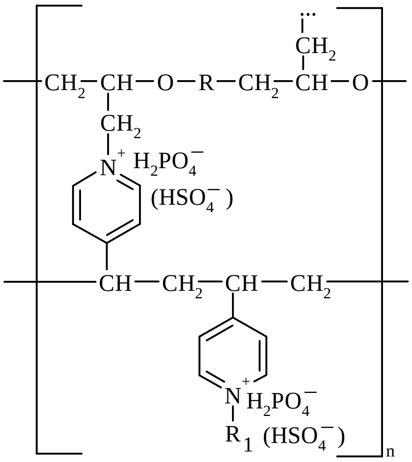
Synthesis of the films of proton-conducting membranes was carried out by macromolecular condensation of polyethylene oxide derivatives with active chloromethyl groups and polyvinylpyridine in the medium of aprotic organic solvent (tetrahydrofurane, acetone or their mixture) during some stages.

The first stage envisages interaction of the functional groups of polyvinylpyridine (pyridine groups) and polyethylene glycol derivative (of chloromethyl groups) for example, in acetone, up to the 10-15% conversion degree, nearly the point of gelation. Then, the obtained solution of for-interpolymer complex is deposited on glass or PTFE substrate where the stage of membrane formation occurs at the expense of the further interaction of functional groups up to the deeper conversion degrees and removal of solvent.

After drying the produced at 50-80°C polymer film and its washing from unreacted products, it is prepared for activation (doping) by inorganic acids.

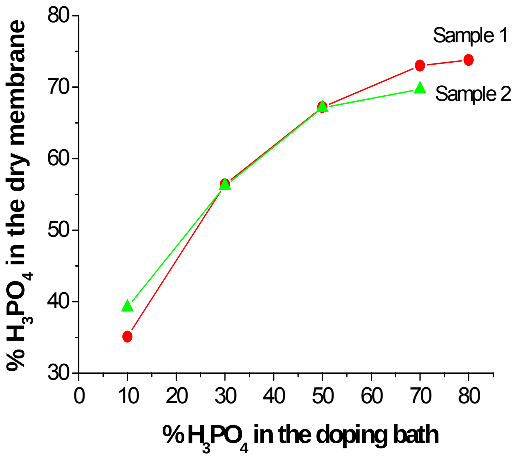
In case of need, membrane may be modified by its treatment by low-molecular amines for the conversion of unreacted chloromethyl groups into ammonium.

The membranes are activated by their immersion into the solution of inorganic acid of a suitable concentration. In the end, the proton-conducting membrane of the following common structure is produced:



Result and Discussion

The synthesized membranes were used for PEM production by their impregnation in the solutions of orthophosphoric acid of different concentration. In Fig. 1 it is presented the data of the quantity of absorbed acid in a membrane depending on the acid concentration in the doping bath where membrane is immersed into.



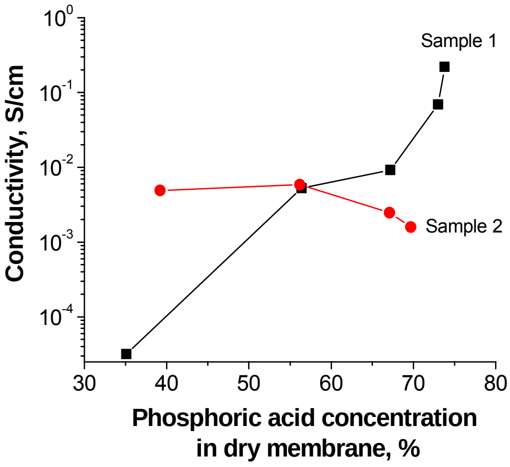
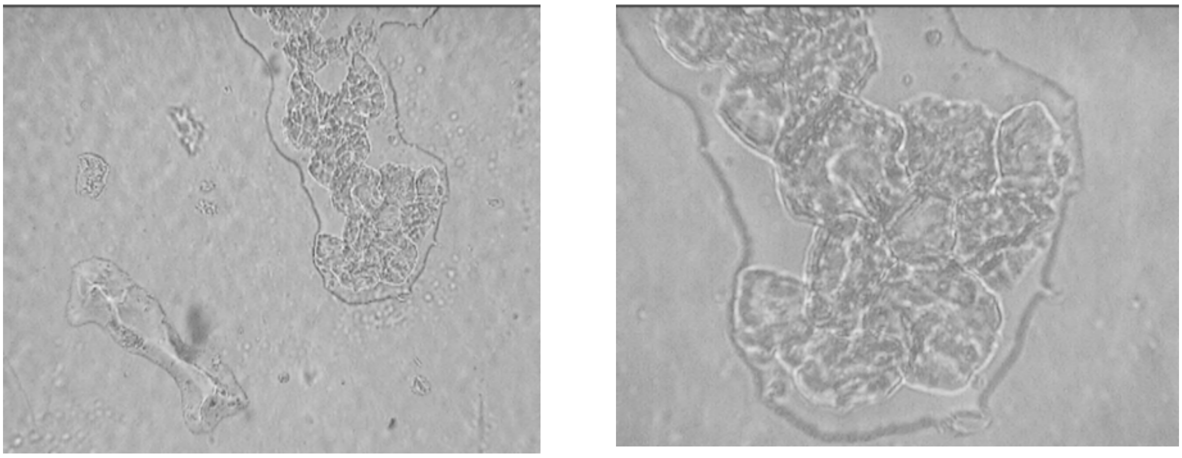


Fig. 1 *(left) Phosphoric acid percentage absorbed in the dry membrane as a function of concentration of H_3PO_4 in the doping bath*

Fig. 2 *(right) Conductivity of non-humidified IPC membranes at room temperature as a function of phosphoric acid percentage absorbed by dry membranes.*

Sample 2 is the membrane additionally treated by trimethylamine, unlike Sample 1.
Investigation of non-humidified membrane conductivity has shown that their conductivity depends significantly on the composition of synthesized interpolymer complex, and concentration of absorbed acid in membrane ranges from $1.59 \cdot 10^{-3}$ to $2.2 \cdot 10^{-1}$ S/cm (See Fig. 2).
During carrying out of works the influence of composition and conditions of membrane synthesis on their morphology (homogeneity) was investigated. It has been established that at a synthesis, it is possible the premature formation of space cross-linked product (gel), which availability results in defect appearance in membrane structure.



Magnification X100 **Magnification X400**

Fig. 3 *Micrograph of proton-conducting membranes based on interpolymer complexes.*

Thus, as a result of our carried out works, the synthesis methods of new polymer matrixes have been developed for proton-conducting membranes of fuel cells and the main approaches to the synthesis of the membranes with increased conductivity and optimal morphology have been determined.

References

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