SYNTHESIS AND PROPERTIES OF POLYAMIDE PROTON-CONDUCTING MATERIALS FOR ELECTROCHEMICAL DEVICES

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Introduction

Development of the technologies concerning design of high-performance electrochemical equipment (fuel cells, sensors, etc) is impossible without production of polymer materials with high ionic conductivity, chemical and thermal stability, as well as with high mechanical strength within the high temperature range. Among a great variety of the materials used for these purposes, ionogenic polymers considered as promising polymer matrixes of proton-conducting membranes and electrode materials are of undoubted interest.
Perfluorinated materials like Nafion are widely used as the proton-conducting membrane of fuel cells. However, high cost of this class materials, operational only at positive temperatures (up to 90°C) has necessitated development of the principally new non-fluorinated materials for production of fuel cells membrane-electrode assembly (MEA). Before, there were attempts to produce ion-conducting materials based on polyarylenes (poly-n-xylylene, poly(phenylene oxides), polysulfone, polyester sulfone, polyester ketone) which are the polymers with a high chemical and thermal stability. Sulfonation of this class polymers allows to produce the materials with a proton conductivity, including water-soluble ones. However, realization of this process even in a homogeneous medium does not allow to produce the materials by regular alternation of ionogenic groups and, accordingly, with the well reproducible properties.
One more important factor is synthesis of the sulfonated materials with a high value of ion exchange capacity (IEC), which characterizes concentration of ionogenic sulfo-acid groups per the mass of dry polymer membrane (for Nafion it is ~1 meq/g). However, polymers with the high value of IEC, as a rule, are the materials well soluble in water and methanol. This makes problematic their use as a membrane material for electrochemical devices.
In the connection with the above, development of the synthesis methods of polycondensation polymers with participation of sulfonated monomers resulting in film cross-linked polymer materials with a high value of IEC and regular alternation of ionogenic groups is rather promising.
In the work, there are presented the results concerning development of the synthesis methods of polyamide sulfo-acid materials promising for use in fuel cells.

Experimental

The films of sulfonated polyamide derivatives were produced by the polycondensation reaction of polyamide, aromatic sulfo-acid, aldehyde and catalytic quantity of sulfuric acid

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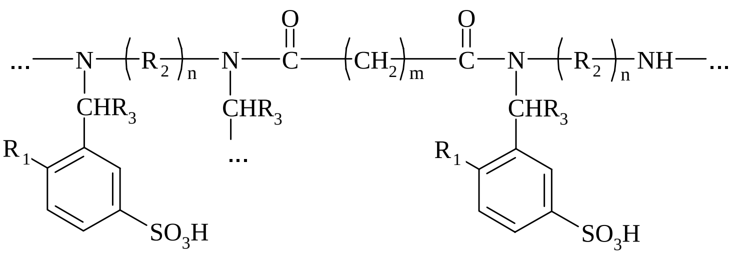
in the medium of organic solvent. Proton-conducting membranes were formed by a casting method of the prepared solution on a glass surface followed by temperature treatment at 50-80°C for 5-10 hours. Then the film was removed from a substrate and immersed into distilled water for one day for washing from unreacted monomers. The washing operation was repeated 2-3 times with distilled water changing.
After drying, the synthesized membranes were semi-transparent films with a good mechanical strength and well swelling in water and the water solutions of sulfuric acid.

Result and Discussion

We have developed the synthesis method of proton-conducting film materials on the basis of the polycondensation products of polyamides, aromatic sulfo-acids and aldehydes in the presence of catalytic quantities of sulfuric acid. The synthesized films are the materials with cross-linked structure:



The films washed out in water and dried in air up to the constant mass of film are insoluble none of the organic solvents, that indicates formation of cross-linked products. By the physical-mechanical properties, the synthesized membranes both in dry and swelled states are practical identical to polyamides used for their synthesis. In this case they show thermal stability up to 250-300°C (Fig. 1).

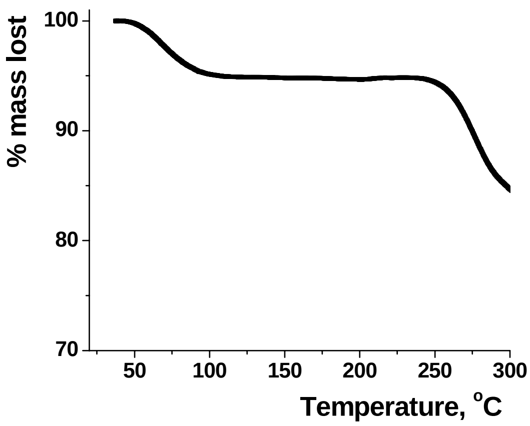


Fig. 1 *Data of thermogravimetric analysis of polyamide sulfo-acid membranes.*

The carried out investigations have shown that the properties of film materials (like water absorption, IEC and ion conductivity) depend significantly on the nature and the ratio of initial components used for their synthesis.
Water concentration in the investigated membranes is ~40-80%, in this case it should be noted insignificant change of membrane geometric sizes at swelling in water or sulfuric acid solutions. IEC of the synthesized materials ranges from 1.63 up to 2.29 meq/g.
In Fig. 2 the typical changes of the resistance of synthesized polyamide membranes at swelling are shown.

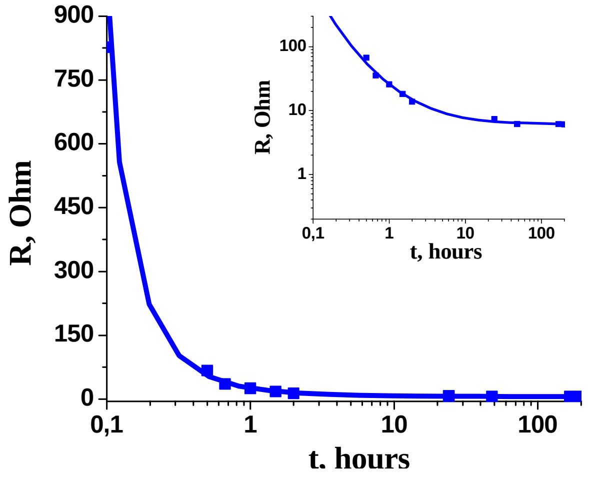


Fig. 2 *Change of proton conducting membrane resistance of composition polyamide : phenol sulfo-acid : CH_2O = 1:0.5:1 (molar ratio) at swelling in 1M H_2SO_4 solution.*

In this case, membrane conductivity of the composition shown in Fig. 2 is ~10^{-4} $\Omega^{-1}.cm^{-1}$ (see Table 1).

Table 1 *Conductivity of non-modified and modified polyamide membranes at room temperature*

Swelling time (t, hours)	Thickness (mm)	Conductivity (σ, $\Omega^{-1}.cm^{-1}$)
Non-modified membrane of composition polyamide : phenol sulfo-acid:CH_2O = 1:0.5:1		
24	317	$6.18 . 10^{-4}$
48	317	$7.37 . 10^{-4}$
168	317	$7.42 . 10^{-4}$
Modified membrane of composition polyamide : alkyl ether of phenol sulfo-acid:CH_2O = 1:0.5:1		
24	399	$3.78 . 10^{-3}$

Significant increasing is reached at the expense of using alkyl ester of phenol sulfo-acid.

Conclusions

Thus, the synthesis method of new film materials with the high complex of physical-mechanical properties and proton conductivity has been developed. This allows to recommend them for approbation as membranes for fuel cells and other electrochemical devices.