Sulfonated Poly(p-phenylene sulfide) as proton conducting material

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INTRODUCTION

The interest in modern energy conversion technologies has increased the demand for novel ion-conducting materials. In fact, interesting applications of these materials are, for example, as electrolytes hydrogen/oxygen and methanol fuel cells. For such applications, polymer electrolytes must combine a number of properties, i.e. excellent chemical and environmental resistance, high thermal and dimensional stability and high ion conductivity. Poly(*p*-phenylene sulfide) (PPS) appears to be a promising candidate, since it possesses good thermal, chemical and mechanical characteristics but is a poor ion-conductor. Conductivity may be remarkably improved by chemical introducing sulfonated groups in the polymer chain. In this way water is absorbed within the polymer, allowing the solvation and transport of H^+ ions. Ion conductivity is related to the amount of water molecules and thus to the number of $-SO_3H$ groups in the membrane.

The development of this work is divided in two parts:

ØSulfonation of PPS and chemical and physical characterization,

ØPreparation and characterization of conducting membranes that contain $PPS-SO_3H$.

SULFONATION

The material used in this research is a Poly(*p*-phenylene sulfide) commercially named Fortron (by Ticona). This polymer has an high molecular weight (M_W = 90000 u.m.a.); it is insoluble in all commonly used solvents at temperature < 200 °C.

The sulfonation procedure implies an excess of chlorosulfonic acid as reagent, and the product of reaction is the chlorosulfonated polymer, which is converted into the corresponding acid by hydrolysis in hot water.

The scheme of these reactions is the following (Fig 1, 2):

The reaction product is controlled by FT-IR; in particular, the signal at 1442 cm^{-1}, corresponding to the stretching of the third substitution on the aromatic ring, was considered. Fig. 3 shows the PPS spectra before (—) and after (—) sulfonation reaction. The acid groups amount were determined by titration and the results, as mol. weight/n $-SO_3H$, are reported in Tab. 2.

PREPARATION AND CHARACTERIZATION MEMBRANES

The sulfonated PPS result to be very brittle and no membrane with appreciable mechanic strength could be obtained. By blending sulfonated PPS with sulfonated

PEEK [1], bi-phasic membranes with good mechanical characteristics were prepared (Fig. 6)
The two materials were dissolved in N-methylpirrolidinone, the solution spread on glass support and the solvent evaporated in oven at 100 °C. Constant thickness films (20-45 mm) were obtained.
The conductive membranes products were characterized by conductivity measures with spectroscopy impedance method. The proton conductivity was determined at a voltage of 10 mV and in the frequency range from 1 KHz to 100 Hz. [2] (Table 3).

REFERENCES

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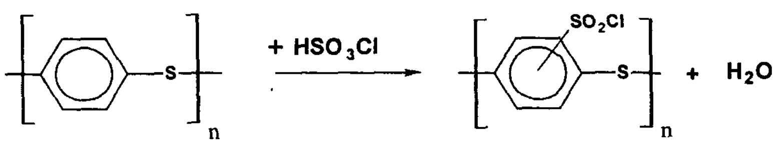

Fig. 1: Sulfonation reaction with an excess of acid chlorosolfunic

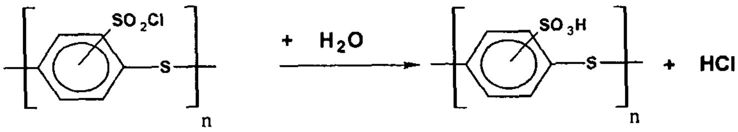

Fig. 2: Hydrolysis reaction leading to the acid group form.