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Multilayered Proton-Electron Conductive Polymer Membrane for Fuel Cells

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1 Introduction

What we don't need is a polluting carbon based energy policy that exists simply because the supply side wants it that way. We really can't justify trashing the planet by burning carbon just because it is available. The Wind-Solar-Hydrogen Economy is achievable now. What we need is to improve hydrogen production, storage, transportation and usage methods. Very important for most of European countries is question about electricity generation power - an energy policy for future must be oriented to local renewables and clean generation technologies at amounts to satisfy self sufficiency.

Fundamental problem needs closer attention is the method of getting energy back from the hydrogen. One of the possibilities is direct burning, which is attractive because internal combustion engines can be transformed easy for hydrogen fuel. Nevertheless combustion engines have small efficiencies and great exhausts – nitrogen oxides, when hydrogen is burnt in air. As another way for regaining energy from hydrogen, the fuel cells are named, because of theoretically possible high energy recovery value [1]. One type of fuel cells is polymer electrolyte fuel cell. Advantages of this technology is comparably low working temperatures (typically till 100°C), which makes it interesting for application in portable devices and transport (bikes, cars, vehicles) [2].

Developing polymer membrane fuel cells one has to deal with several main topics: membrane itself, membrane-electrode assembly, catalyst etc. Our research group decided to elaborate advanced composite membranes for low temperature fuel cells, based on already well-known material – sulfonated poly(ether-ether-ketone) (SPEEK). As the second material polyaniline (PANI) was chosen as a electron conductive material, which also can reduce platinum load according to H.Gharibi *et.al.* [3]

2 Experimental

SPEEK was prepared from poly(ether-ether-ketone) (PEEK) supplied by Aldrich. The sulphonated SPEEK ionomers were synthesized using original and simple method [4]. Homogeneous proton-conducting membranes were developed from the obtained SPEEK by solvent casting method. Our idea is to make composite electron/proton conducting membrane from available non-expensive polymers - SPEEK and electron conducting material polyaniline (PANI). For synthesis we used PANI in non-conductive form (emeraldine base) with molecular weight of 60000 g mol⁻¹, supplied by Aldrich. Physical and chemical properties of separate polymers SPEEK and polyaniline (PANI) and SPEEK/PANI membrane were analysed.

The membranes were characterized by FTIR to confirm sulfonation [5]. FTIR spectra for both poly(ether-ether-ketone) (PEEK) and SPEEK were measured with a Bruker EQUINOX 55 spectrometer equipped with Praying Mantis TM (DDR) accessory designed for examining samples by diffuse reflection spectroscopy. The spectra were measured in transmittance mode and in DDR mode over a wave number range of 7000-400 cm^{-1} with resolution of 1 cm^{-1} . Thermogravimetric (TG) and differential thermal analysis (DTA) were performed with SHIMADZU DTG-60 instrument in Ar atmosphere (Ar 5.0 from AGA Ltd.) with flow 50 ml/min in temperature range from room temperature (RT) till 350 $^{\circ}\text{C}$ with heating rate 10 deg/min.

3 Results and Discussion

For wave number between 1700 and 500 cm^{-1} some changes indicate successful sulfonation. The peak at around 1500 cm^{-1} , which corresponds to C-C bond, splits into two (1470 cm^{-1} and 1493 cm^{-1}) in SPEEK sample due to hydrogen replacement with SO_3H group (marked with 1, Fig.1). Also new peaks appear due to sulphur and oxygen bonds (e.g. S=O bond at 1022 cm^{-1} ; O=S=O symmetrical and asymmetrical stretching vibrations at 1080 cm^{-1} and 1250 cm^{-1} accordingly) (2 and 3, Fig.1).

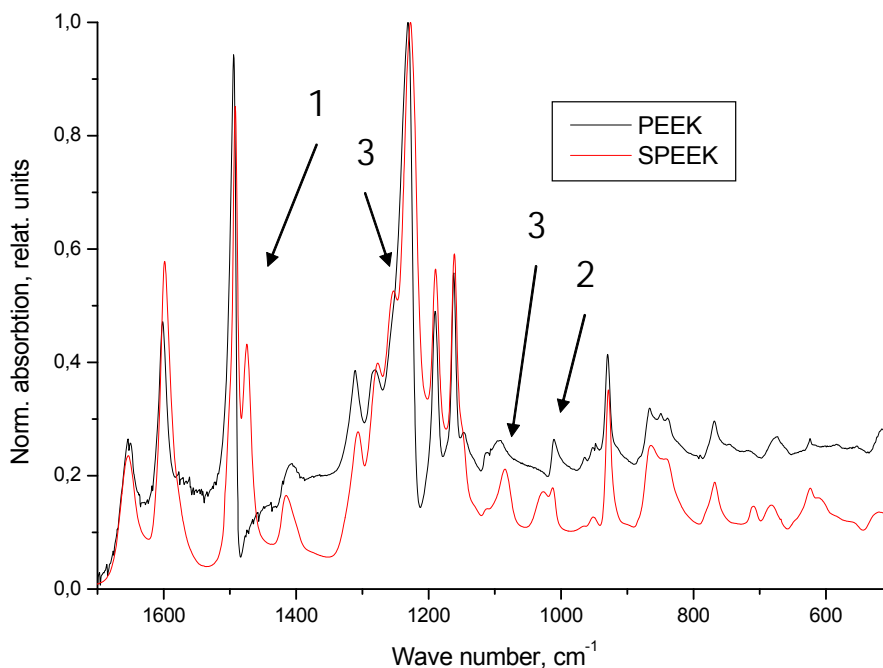


Figure 1: Spectrum of poly(ether-ether-ketone) and sulfonated poly(ether-ether-ketone).

New synthesized SPEEK membrane was compared with Nafion membrane with a help of thermogravimetric (TG) analysis. Fully hydrated samples were used for TG measurements. As it is seen from obtained results (Fig. 2), in region around 100 $^{\circ}\text{C}$, which corresponds to water loss, the higher temperature is necessary for our SPEEK material to lose the water. Conclusion is that SPEEK membrane indicates better behaviour comparing with Nafion of membrane in case of reaching higher end of working temperature range (Fig.2).

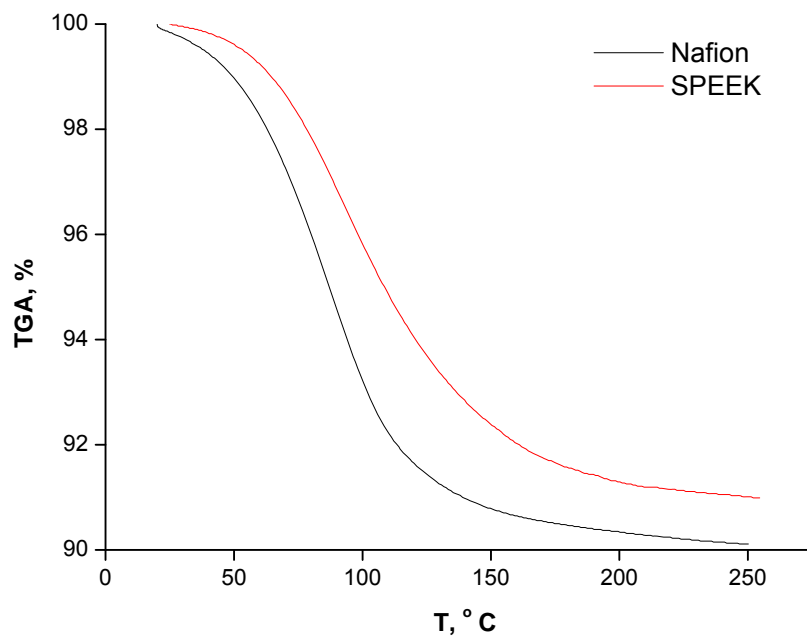


Figure 2: Thermogravimetric measurements in a region from room temperature till 250°C for new synthesized SPEEK and Nafion membranes.

The proton conductivities of our SPEEK membranes were found to be excellent in the order of 10^{-2} S/cm in the fully hydrated condition at room temperature. Testing samples in temperature range till 90°C, the steady grows was observed, reaching values around 50 mS/cm (Fig.3).

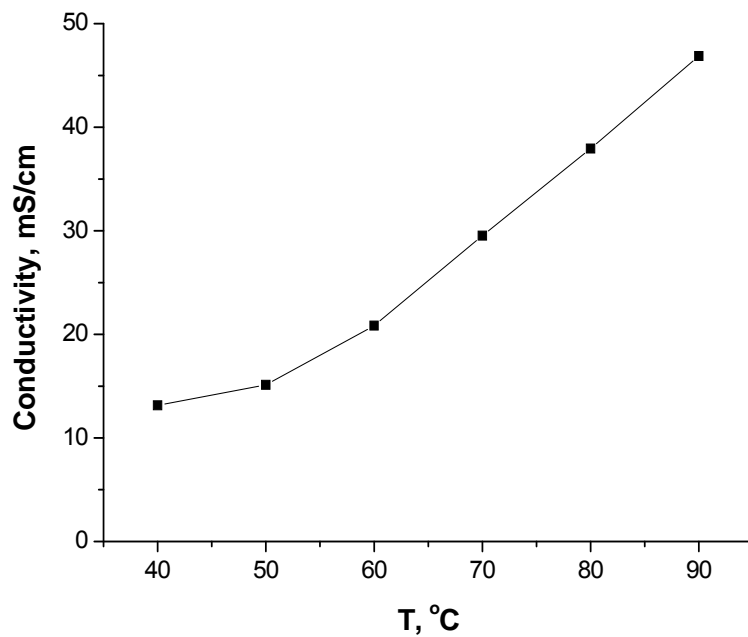


Figure 3: Conductivity measurements for new synthesized SPEEK polymer membrane.

The most important parameter for membranes is proton conductivity, and measured values showed (Figure 4), that for composite membrane with 10 wt% PANI the conductivity decreased significantly (3-4 times depending from temperature region).

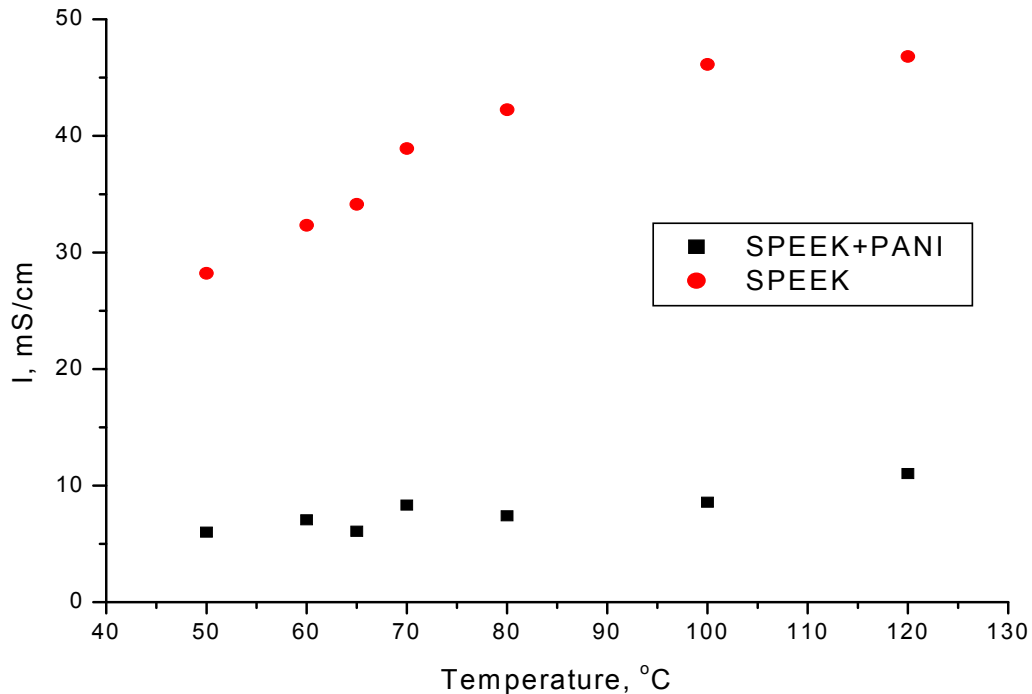


Figure 4: Conductivity measurements for SPEEK and SPEEK with 10 wt% PANI.

One of the possible reason for significant conductivity decrease could be the possibility of SPEEK polymer to play the doping role in PANI polymer. This process decreases the number of SO_3H groups, which are responsible for proton conductivity in membrane. To increase the proton conductivity, another doping polymer could be used, e.g. some acid. As it was seen from preliminary impedance spectra of composite SPEEK/PANI membrane, an electronic conductivity is found to be insignificant. It would be suggested that PANI transformation to electron conductive form also would increase the conductivity of composite membrane. Adding a doping would result in next two processes. Firstly, PANI will transform to electron conductive form, allowing reaching our goal of developing material with both types of conductivity. Secondly, doping will increase proton conductivity, because SPEEK partly reacts with PANI and acts as doping, at the same time decreasing proton conductivity.

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