Sulfonated poly (ether ether ketone) – activated polypyrrole composite membranes for fuel cells

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Sulfonated poly (ether ether ketone) membranes were obtained by the phase inversion process. These membranes were modified with chemically in situ polymerized polypyrrole in order to increase the ionic conductivity and to prevent the methanol crossover. For improving the polypyrrole ionic conductivity, this was activated with iron chloride and cerium sulfate. The new synthesized sPEEK/Ppy composite membranes were characterized by FT-IR spectroscopy, Scanning Electron Microscopy, Energy dispersive X-ray spectroscopy (EDAX), permeation measurements and the ionic conductive properties were evaluated by Electrochemical Impedance Spectroscopy.

1. Introduction

The issue of renewable energy is becoming pregnant nowadays due to increasing power demand, the scarce of oil and its rising prices and environmental problems. Among the various renewable energy sources, fuel cells are gaining more popularity due to their high-energy efficiency, near-zero emissions and vast applications [1]. The central core of a fuel cell is the membrane electrode assembly. The role of membrane between electrodes is the conduction of produced protons from anode to cathode and acts as a barrier to avoid the crossover of fuel [2-3]. Currently, the widely used PEM (proton exchange membrane) is Nafion membrane developed by Dupont, which exhibits excellent chemical and electrochemical stability as well as high proton conductivity at low temperatures. However, the high cost, the low conductivity at high temperatures and the high methanol permeability rate across the PEMs are critical problems which limit the use of Nafion membranes for DMFC (direct methanol fuel cell) [4]. In consequence, there are many materials studied for the development of alternative more economical non-perfluorinated PEMs.

In this paper a sulfonated poly (ether ether ketone) /polypyrrole (sPEEK/Ppy) composite membrane is studied. Sulfonated PEEK is a low cost polymer which exhibits high thermal stability and proton conductivity. A lifetime of more than several thousand hours for sPEEK membranes under fuel cell conditions was reported in Ref. [5], which also demonstrated the microstructure advantages of sPEEK over Nafion as the PEM in DMFCs [3]. To increase the conductivity of the material, the sPEEK support membrane is doped with a conductive polymer, in this case polypyrrole. It is already known that polypyrrole has been used to modify the Nafion membranes so they can be used in DMFCs [6]. Polypyrrole was reported to have high catalytic activity for the methanol oxidation and the Nafion/polypyrrole composite membranes showed extremely low methanol permeability [7-13]. Polypyrrole presents good environmental stability and it is chemically extremely resistant, being insoluble in many organic solvent. Compared with other polymers, Ppy has a high surface energy, also good electro-conductive and acid–base properties [14-16].

The synthesis and characterization of the new sPEEK/Ppy composite membrane are presented in this paper. The new material was characterized by FT-IR spectroscopy, Scanning Electron Microscopy, Energy dispersive X-ray spectroscopy (EDAX), permeation measurements and the ionic conductive properties were evaluated by Electrochemical Impedance Spectroscopy.

2. Experimental

2.1 Materials

For the composite membrane synthesis polyetheretherketone (Aldrich) (M = 150000 g/mol), sulfuric acid H_2SO_4 96% (Merck), pyrrole (Merck, analytic purity reagent), iron chloride $FeCl_3$ (Fluka) and distilled water were used. For membrane doping cerium sulfate $Ce(SO_4)_2$, $FeCl_3$ (both purchased from Fluka) and distilled water were used. For permeability experiments methanol, 2-propanol and distilled water were used.

2.2. Methods

Sulfonated polyetheretherketone was obtained by dissolving PEEK in H_2SO_4 (5 wt.%) at room temperature, under stirring for 24 h. From the resulting polymer solution, membranes were cast in the form of thin films on a cleaned glass plate and immersed in water for coagulation (phase inversion process). Consequently with the solubilization of PEEK in sulfuric acid, the polymer is functionalized with sulfonic acid groups resulting sulfonated poly (ether ether ketone) – sPEEK.
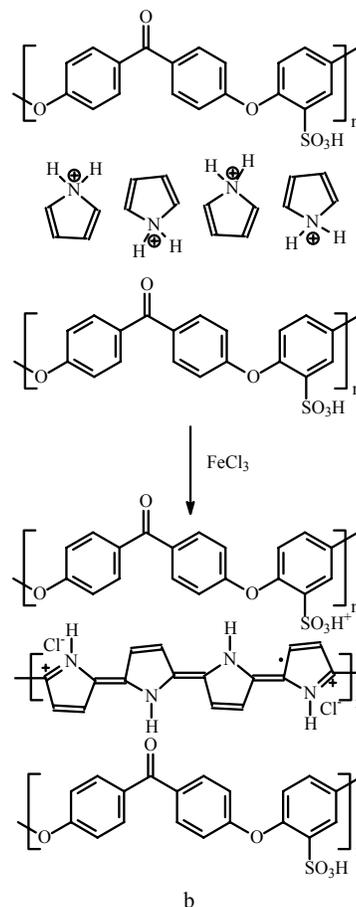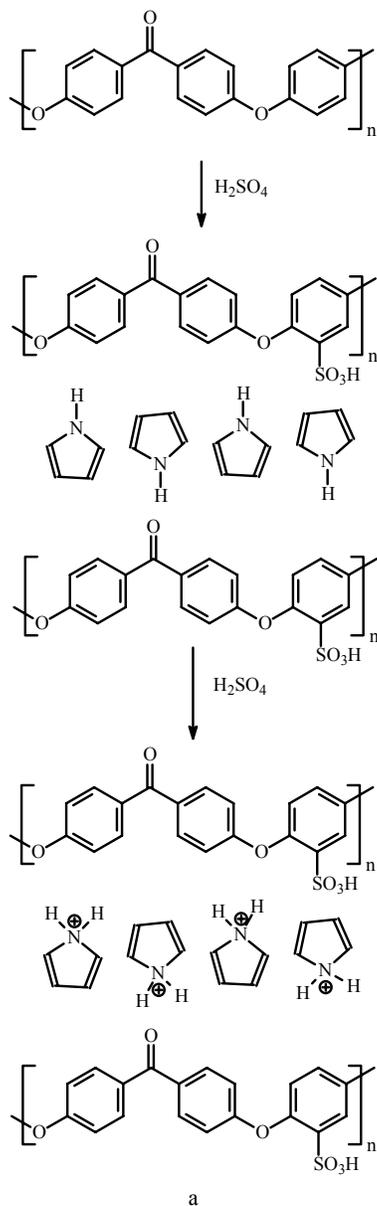

a

b

Fig. 1. Schematic representation of composite membrane synthesis: sulfonation of poly (ether ether ketone) and protonation of pyrrole from membrane pores (a) and oxidation-polymerization of pyrrole to polypyrrole (b).

The synthesis mechanism is presented in Fig. 1. The resulting membranes were washed several times with water to remove the traces of sulfuric acid. For the preparation of sPEEK/Ppy composite membranes pyrrole was sprayed on the support membranes then they were immersed into a bath which contained a $FeCl_3$ solution in water. First of all, the pyrrole is protonated by the remaining sulfuric acid in membrane pores. The polymerization of pyrrole at the surface and within the pores can be easily observed due to a change of color of membrane from white to black, the color of polypyrrole. The polypyrrole from the obtained membranes was doped with cerium sulfate and excess of iron chloride by immersing the membranes in a solution of $Ce(SO_4)_2$ in distilled water 1M, respectively in a solution of $FeCl_3$ in distilled water 1M.

3. Results and discussion

3.1. Scanning electron microscopy analysis

The SEM analysis, performed with a FEI instrument, offers important information about the morphology of the membranes.
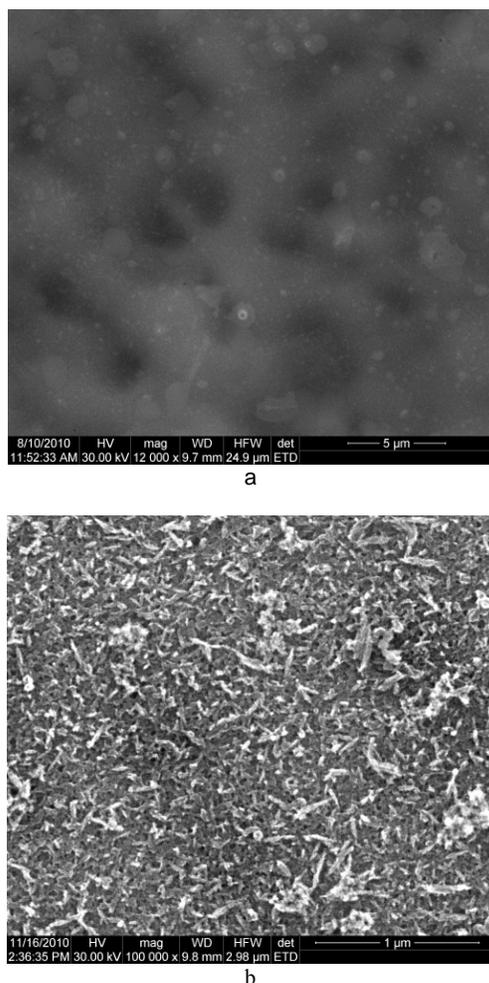

a

b

Fig. 2. SEM images of sPEEK membrane (a, surface) and sPEEK/Ppy composite membranes (b, surface).

Fig. 2a presents the SEM images for the sPEEK membrane, it can be observed that the membrane pores size is between 1 and 3 µm in diameter. In the SEM image for the sPEEK/Ppy composite membrane (Fig. 2b), it can be observed that the Ppy is formed in filiform shape at the surface and in the pores of the sPEEK membrane. The pores size of sPEEK/Ppy composite membrane is between 3 and 25 nm in diameter.

3.2. Energy dispersive X-ray spectroscopy analysis

The EDAX spectrums (Fig. 3) performed with a FEI instrument, present the elemental composition of the

membranes. For the sPEEK membrane (Fig. 3a) beside the characteristic membrane elements, such as carbon (C), oxygen, sulphur, calcium can be observed. The presence of Ca is due to the complexation of the sulfonic groups from the membrane. The formation of PPy (Fig. 3b) can be observed due to the presence of nitrogen, also chlorine and iron as the Ppy is activated with chloride anions used in the polymerization process. As well the Ppy is a complexing agent for magnesium and silicon beside calcium.
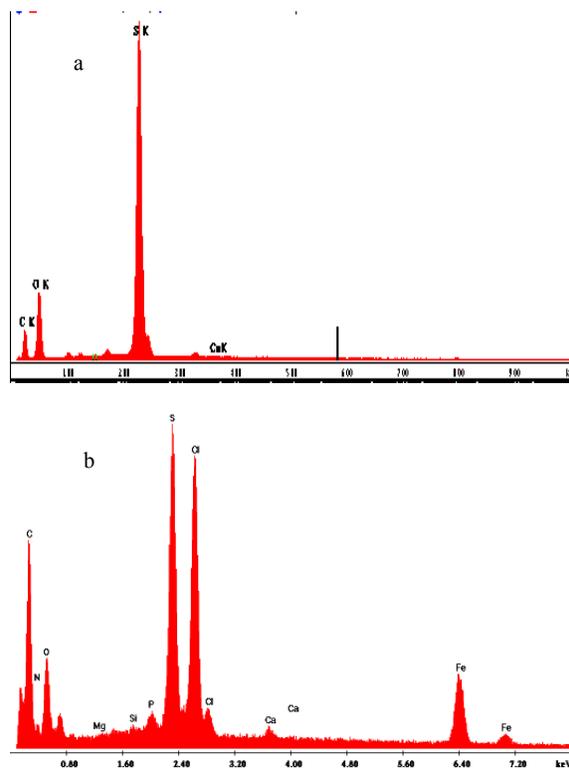

Fig. 3. EDAX images of sPEEK membrane (a, compact surface) and sPEEK/Ppy composite membrane (b, surface).

3.3. Infrared spectroscopy

In the FT-IR spectrums, performed using a Bruker Tensor 27 Instrument with ATR diamond annex, the specific bands for sulfonated poly (ether ether ketone) and polypyrrole can de observed (Fig. 4a). The specific bands for sPEEK are represented by the peak at 1250 cm^{-1} attributed to the etheric bond (C-O-C), the peak at 1640 cm^{-1} attributed to conjugated ketonic bond (C=O) and the peaks characteristic for sulfonated polymers at 1030 and 1096 cm^{-1}. The specific bands for polypyrrole are represented by the peak at 880 cm^{-1} attributed to =C– bond outside the vibration plane and the large band from 3310 to 3350 cm^{-1} given by the secondary N-H stretch vibration. In the spectrum of sPEEK/Ppy membrane doped with Ce(SO$_4$)$_2$ (Fig. 4b) it can be observed that the total intensity of the material decreases from 0.6 to 0,35 in absorbance units, hence the intensities of the polymers decrease. The cerium peak can't be seen due to fact that its

band is outside the vibration plane. The FT-IR spectrum in Fig. 4b can be characteristic to the sPEEK/Ppy membrane doped with $FeCl_3$ too.
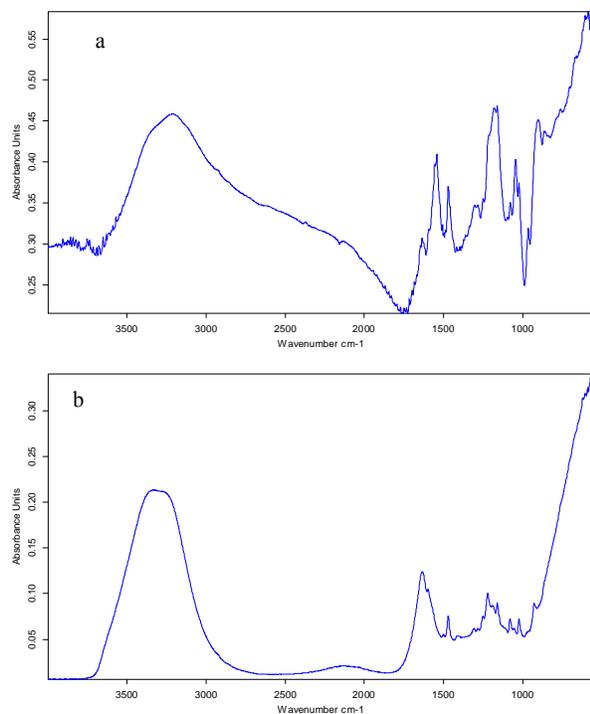

Fig. 4. FT-IR spectrum of sPEEK/Ppy composite membrane (a) and sPEEK/Ppy composite membrane doped with $Ce(SO_4)_2$ (b).

3.4. Permeation tests

The permeation measurements were performed in order to study the transport through the membrane. 100 mL of distilled water, methanol and 2-propanol were passed through a sPEEK/Ppy membrane with a diameter of 0.04 m (surface of 0.005 m^2). The time in which the liquid has passed through the membrane and the volume of liquid passed from 5 to 5 minutes through the membrane were measured.

The permeation fluxes are presented in Table 1, wherefrom it can be observed that water passed through the membrane in 2 minutes with a permeation flux of 561,783 L/m^{2}h. The methanol passed through the membrane in 21 minutes and it can be observed that the permeation flux decreases from 107,484 to 53,162 L/m^{2}h. The flux for 2-propanol decreases also from 100,318 to 44,232 L/m^{2}h. The decrease in the permeation fluxes is induced by the reduction of the membrane pores size due to the retention of liquid molecules within the pores.

Table 1. The permeation fluxes of water, methanol and 2-propanol through the sPEEK/Ppy composite membrane.

Time (min)	Permeation fluxes (L/m^{2}h)		
	Water	**Methanol**	**2-propanol**
2	561.783	-	-
5	-	107.484	100.318
10	-	81.210	77.627
15	-	67.675	64.490
20	-	55.832	50.159
25	-	-	46.815

3.5. Ionic conductivity measurements

The ionic conductivity and capacitance for obtained membranes were determined by Electrochemical Impedance Spectroscopy. The Niquist representations for measured membranes are presented in Fig. 5.
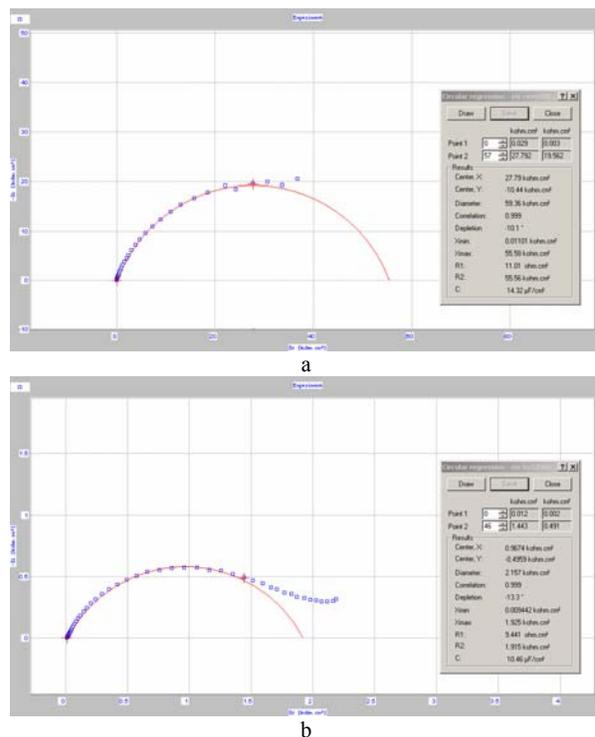

Fig. 5. EIS spectrum for sPEEK – activated Ppy with $Ce(SO_4)_2$ composite membrane (a) and sPEEK – activated Ppy with $FeCl_3$ composite membrane (b), Niquist representation in normal impedance coordinates.

The measurements were made using a platinum cell with two electrodes with a specific surface of 0.9503 cm^{-2} in frequency range 100 kHz-100 mHz at 25 ^{o}C.

At a thickness of 374 μm, the measured capacitance for the sPEEK/Ppy membrane doped with $Ce(SO_4)_2$ was C = 14.32 μF/cm^2 and the ionic conductivity is σ = 34 × 10^{-4} S/cm. The sPEEK/Ppy membrane doped

with $FeCl_3$, for a thickness of 266 μm, has the capacitance $C = 10.46$ μF/cm^2 and the ionic conductivity $\sigma = 28 \times 10^{-4}$ S/cm.

4. Conclusions

The synthesis and characterization of a new sPEEK/Ppy composite membrane was presented in this paper. The material was synthesized by *in situ* polymerization of polypyrrole, in the presence of iron chloride, in the sPEEK membrane also obtained by phase inversion process. Scanning Electron Microscopy and Energy dispersive X-ray spectroscopy were performed in order to observe the structure of the membranes and the formation of polypyrrole. To study the transport through the membrane, permeation measurements were done, which showed that the permeation fluxes for methanol and 2-propanol decrease in time. To evaluate the ionic conductive properties Electrochemical Impedance Spectroscopy analyses were performed. For the sPEEK/Ppy membrane doped with $Ce(SO_4)_2$ the measured capacitance was $C = 14,32$ μF/cm^2 and the ionic conductivity was $\sigma = 34 \times 10^{-4}$ S/cm and for the sPEEK/Ppy membrane doped with $FeCl_3$ the measured capacitance was $C = 10,46$ μF/cm^2 and the ionic conductivity was $\sigma = 28 \times 10^{-4}$ S/cm.

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