VERSITA

Cent. Eur. J. Chem. • 11(3) • 2013 • 438-445
DOI: 10.2478/s11532-012-0175-2

Central European Journal of **Chemistry**

Composite membranes with poly(ether ether ketone) as support and polyaniline like structure, with potential applications in fuel cells

Research Article

Cristina M. Baicea[1*], Vlad I. Luntraru[1], Danut I. Vaireanu[1], Eugeniu Vasile[2], Roxana Trusca[2]

[1]*University POLITEHNICA of Bucharest, Str. Gheorghe Polizu 1-7, 011061 Bucharest, Romania*

[2]*Metav R&D, 020011 Bucharest, Romania*

Received 24 June 2012; Accepted 18 November 2012

Abstract: In this paper we present the synthesis of two composite membranes with sulfonated polyether etherketone as support polymer and as conductive polymers: polyaniline and poly(p-phenylenediamine) - which has a similar structure with polyaniline. The support membranes were obtained by the phase inversion process, the conductive polymers were added by in situ polymerization into the membrane pores, and to increase the conductive properties they were doped with polystyrene sulfonic acid. The synthesized membranes were characterized by FT-IR spectroscopy, SEM, EDAX and electrochemical impedance spectroscopy.

Keywords: *Composite membranes • Sulfonated polyether etherketone • Polyaniline • Poly(p-phenylenediamine) • Ionic conductivity*

1. Introduction

Fuel cells are considered to be a viable alternative of generating energy both economically and environmentally. Fossil fuels are increasingly rare and expensive, while fuel cells can be powered by hydrogen or fuels from renewable sources. As the technology advances and the production grows, the costs of fuel cells decline. Fuel cells have practically zero emissions, the only by-products of the energy conversion process, when hydrogen is used, being water and heat. The role of a membrane in a fuel cell is to allow the passage of the resulting protons from the electrochemical reaction taking place between a fuel and an oxidant in the presence of an electrolyte, from the anode to the cathode and prevent the crossover of fuel from one compartment to another [1-4].

The membrane materials used so far in fuel cells include: Nafion and Nafion modified with inorganic and organic phases (as silica, zirconium phosphate or various conductive polymers), polysulfones, polyetherketones, polyimides, polybenzimidazoles or their composite materials [5]. Undoubtedly, the most used membranes and with the best results, at least in the proton conductivity matter, are Nafion membranes and their composites [6,7]. These membranes have indeed a number of important advantages including: good chemical and oxidative stability, high proton conductivity at an operating temperature of 80°C, and a long operating time. However, as the operating temperature increases, its conductivity decreases, it also presents a high permittivity for methanol and a high cost, to add up [5,8]. Because of these limitations, a major scientific effort is put in the research and development of new proton exchange membranes (PEM), whose main requirement is high thermal stability, but equally important are good electrochemical properties and low cost [9].

Of the many alternative membrane materials mentioned above, polyether etherketone attracts a

* *E-mail: cristina_m_baicea@yahoo.com*

special attention, it is a semi-crystalline polymer with high thermal resistance - can be used at temperatures up to 250-260°C even in hot water or steam with good chemical stability [10]. At room temperature, it is almost insoluble in all solvents – except concentrated sulfuric acid, chlorosulfonic acid, hydrofluoric acid, nitric acid [11,12]. To obtain membranes from polyether etherketone, the polymer has to be sulfonated, operation which increases the ionic conductivity by enhancing acidity and hidrophilicity. The degree of sulfonation is a very important variable since membrane conductivity, permeability and integrity are strongly dependent on it. A high degree of sulfonation ensures high conductivity, but can lead to decreases of the membrane resistance; hence an average sulfonation degree - 50-70% - is preferable [13]. Even if sulfonation affects polymer properties, thermal stability is still high at more than 120°C, sufficient for the operating conditions of fuel cells, which makes polyether etherketone a successful replacement of the Nafion membrane [14].

To increase the membrane conductivity, substrate doping with a conductive polymer is practiced. Among the conductive polymers we can number: polyacetylene, polyaniline, polypyrrol, polythiophene and suchlike, these present electronic, magnetic and optical properties similar to those of metals, but conserve the mechanical properties characteristic of polymers [15]. Of these, polyaniline (PANi) presents a great interest due to the wide range of conductivity, environmental stability, low cost, simple method of synthesis and applicability in various fields. PANi can be synthesized by chemical oxidation of aniline with a suitable oxidant in acid, neutral or alkaline medium or by electrochemical anodic oxidation [15]. A new approach in synthesis of conjugated polymers is the polymerization of aromatic diamines, which can lead to materials with mechanical, thermal and chemical properties better than those of PANi [16]. Thus, through oxidative polymerization of p-phenylenediamine, a polymer that has a similar structure with polyaniline in the pernigraniline base form or a doped-PANi like structure is obtained [16]. The conductivity of the polymer can be affected by molecular weight, degree of crystallinity, degree of oxidation and molecular arrangement and the degree of doping and dopant type [17]. The doping process and the dopant used are the most important factors for achieving high conductivity of polyaniline and conserve it. So, for acid polymer dopants, the conductivity at room temperature and at temperatures of 180°C, is higher for those with higher molecular weight and dopants with a high basicity confer a lower conductivity [18].

The synthesis and characterization of two new composite membranes: sulfonated polyether etherketone/polyaniline - sPEEK/PANi and sulfonated polyether etherketone/poly(p-phenylenediamine) - sPEEK/PpPD are presented in this paper. The membranes were obtained by polymerization of aniline, p-phenylenediamine respectively, in the sulfonated polyether etherketone membrane pores. The new materials were characterized by FT-IR spectroscopy, Energy dispersive X-ray spectroscopy (EDAX), Scanning Electron Microscopy (SEM).The ionic conductivities were evaluated by Electrochemical Impedance Spectroscopy.

2. Experimental procedure

2.1. Materials

For the composite membrane synthesis polyether etherketone, M = 150000 g mol^{-1} (Aldrich), sulfuric acid H_2SO_4 96% (Merck), aniline, p-phenylenediamine, HCl 37%, iron chloride $FeCl_3$ (Fluka), ammonium persulfate $K_2S_2O_8$ (Fluka), polystyrene sulfonic acid (Fluka) and distilled water were used.

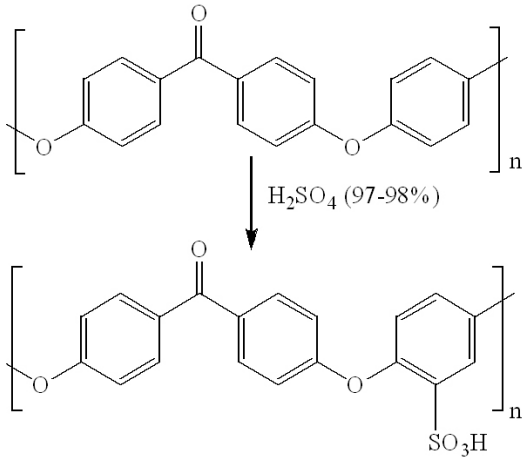
2.2. Methods

Sulfonated polyether etherketone was obtained by dissolving PEEK in H_2SO_4 (5 wt%), as shown in Scheme 1, at room temperature, under stirring, for 24 hours, till the obtaining of a dark orange-red sPEEK solution. From this solution membranes were cast in the form of thin film on a cleaned glass plate and immersed in water for coagulation (phase inversion process). The resulting membranes were washed several times with water to remove the traces of sulfuric acid.

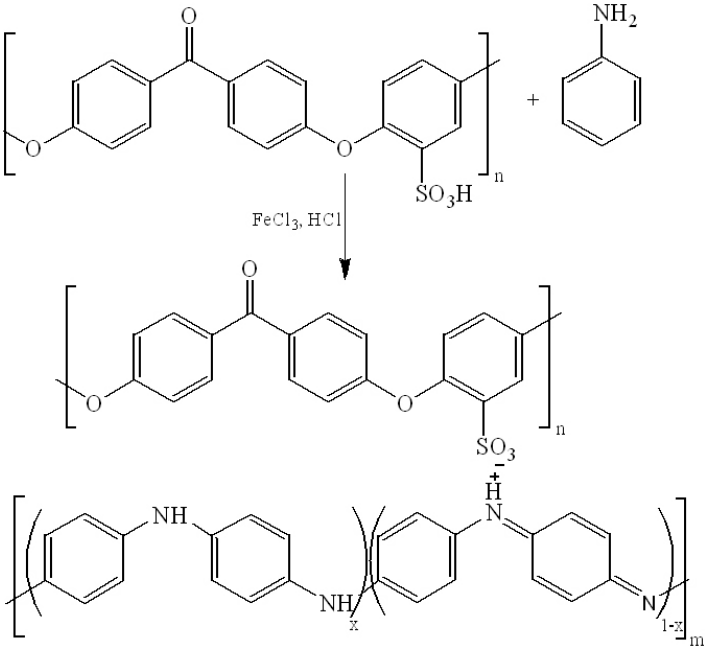
The doping process of the support membrane with the conductive polymer was carried out in two ways.

a) Aniline was sprayed on the sPEEK membranes then they were immersed into a bath which contained a $FeCl_3$ solution in water and HCl 37%. The polymerization of aniline at the surface and within the pores can be easily observed due to a change in color of membranes from white to black transiting light and dark green. The polymerization reaction that takes place in the sPEEK membrane is presented in Scheme 2.

b) The sPEEK membranes were immersed in water with HCl and sprinkled with p-phenylenediamine, then they were let to react in this solution for 2 hours for p-phenylenediamine to enter within the pores, which can be observed from the changing colour of membranes from white to yellow. Then, $K_2S_2O_8$ and HCl were added to this solution so that the p-phenylenediamine can polymerize. The polymerization is evidenced by the blue colour of the membranes which after 4 hours, when the



Scheme 1. Schematic reprezentation of the sulfonation reaction of polyether etherketone.



Scheme 2. Schematic representation of the polymerization reaction of aniline at the surface and within the pores of the sulfonated polyether etherketone membrane.

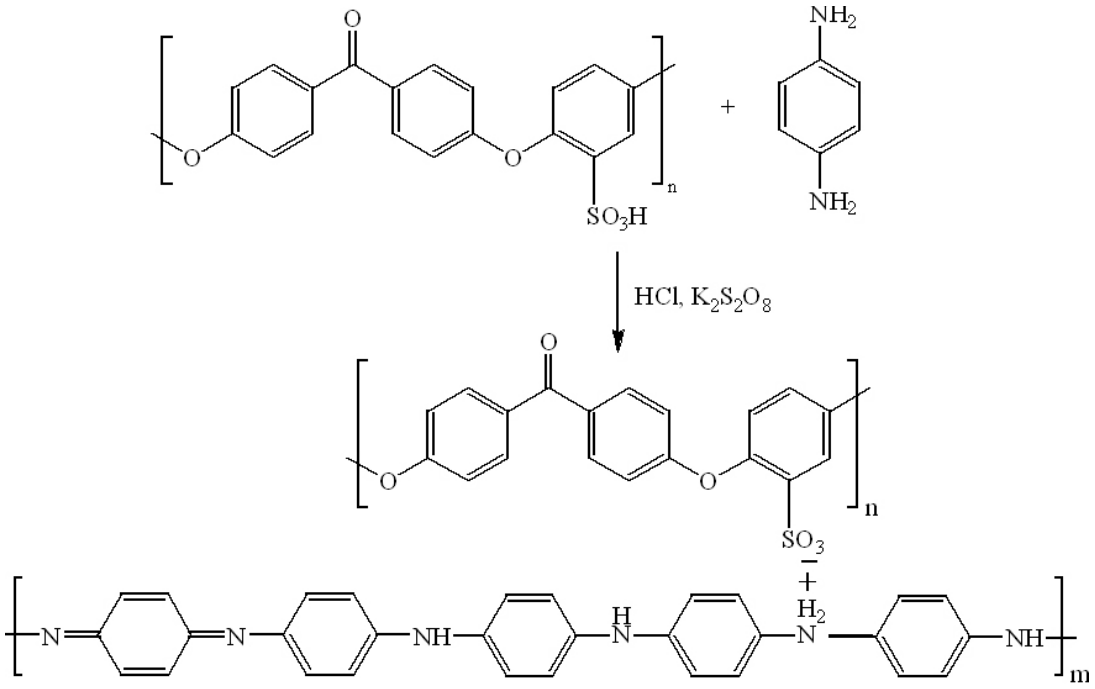
reaction stops, turns to black. The reaction takes place as presented in Scheme 3.

The conductive polymers from the composite membranes were doped with polystyrene sulfonic acid, process that took place by immersing the membranes in a solution of polystyrene sulfonic acid in water.

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. Fig. 1a) presents the SEM images for the sulfonated polyether etherketone membrane, wherefrom it can be observed that the membrane pores size is between 1 and 3 μm in diameter. Fig. 1b presents the SEM image for the sPEEK/PANi composite membrane; it can be observed that polyaniline is formed at the surface and in the pores in little stars shape with 3 to 7 μm in size, also the pores size of sPEEK/PANi membrane is between 1 and 10 μm in diameter. Fig. 1c presents the SEM image for the sPEEK/PpPD composite membrane where it can be observed that the conductive polymer synthesized at the surface and within the pores of the sulfonated polyether etherketone membrane, as conglomerates with the magnitude between 0.35 and 0.6 μm.



Scheme 3. Schematic representation of the polymerization reaction of p-phenylenediamine at the surface and within the pores of the sulfonated polyether etherketone membrane.

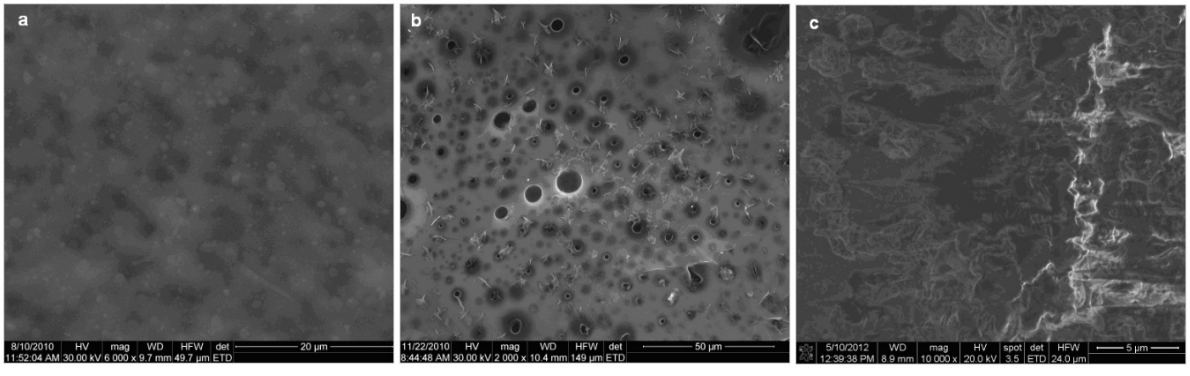


Figure 1. SEM images of: a) sPEEK membrane, b) sPEEK/PANi composite membrane, c) sPEEK/PpPD composite membrane.

3.2. Energy dispersive X-ray spectroscopy analysis

The EDAX analysis (Fig. 2), performed with a FEI Instrument, presents the elemental composition of the membranes. In the first image Fig. 2a – is presented the EDAX image for the sulfonated polyether etherketone membrane where it can be observed from the characteristic membrane elements, such as carbon, oxygen, sulphur and beside them, calcium, it's presence can be explained due to the complexation of the sulfonic groups from the membrane. Fig. 2b – presents the EDAX image for the sPEEK/PANi composite membrane, where, beside the above mentioned elements, chlorine and iron are present as the $FeCl_3$ is used in the polymerization process.

3.3. Infrared spectroscopy

The results of the Infrared Spectroscopy are presented as spectra of the intensity of IR radiation, in terms of absorbance units, as a function of wavenumber. From the spectra images, presented in Fig. 3, it can be observed that the sPEEK/PANi spectrum improves after the doping with polystyrene sulfonic acid, the rest of the spectra are practically the same, some minor differences being detected in the intensity and also in the localization of some peaks. The assignments of the peaks identified in each spectrum are presented in Table 1.

3.4. Ionic conductivity

The advantage of using the a.c. impedance spectroscopy for the evaluation of the ionic conductivity method is

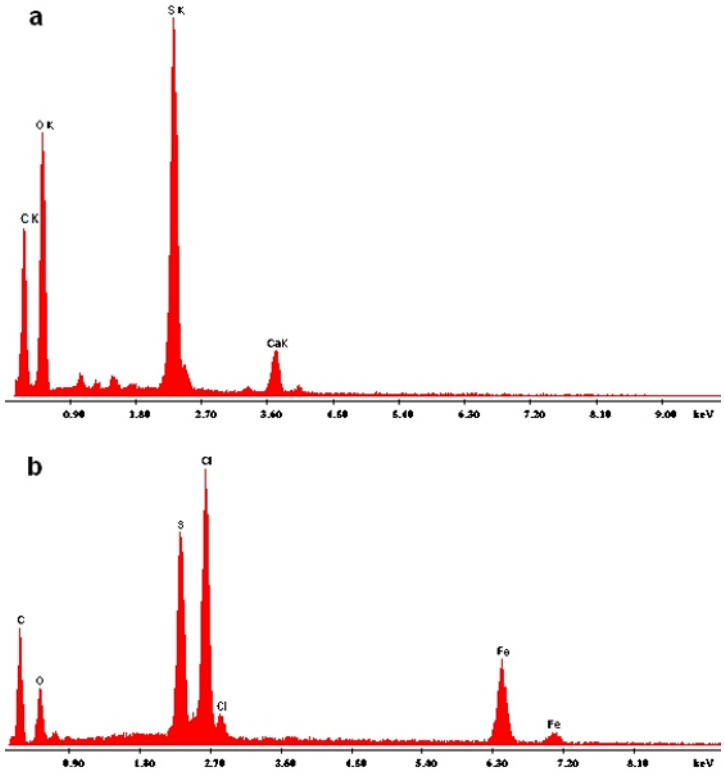


Figure 2. EDAX images of: a) sPEEK membrane, b) sPEEK/PANi composite membrane.

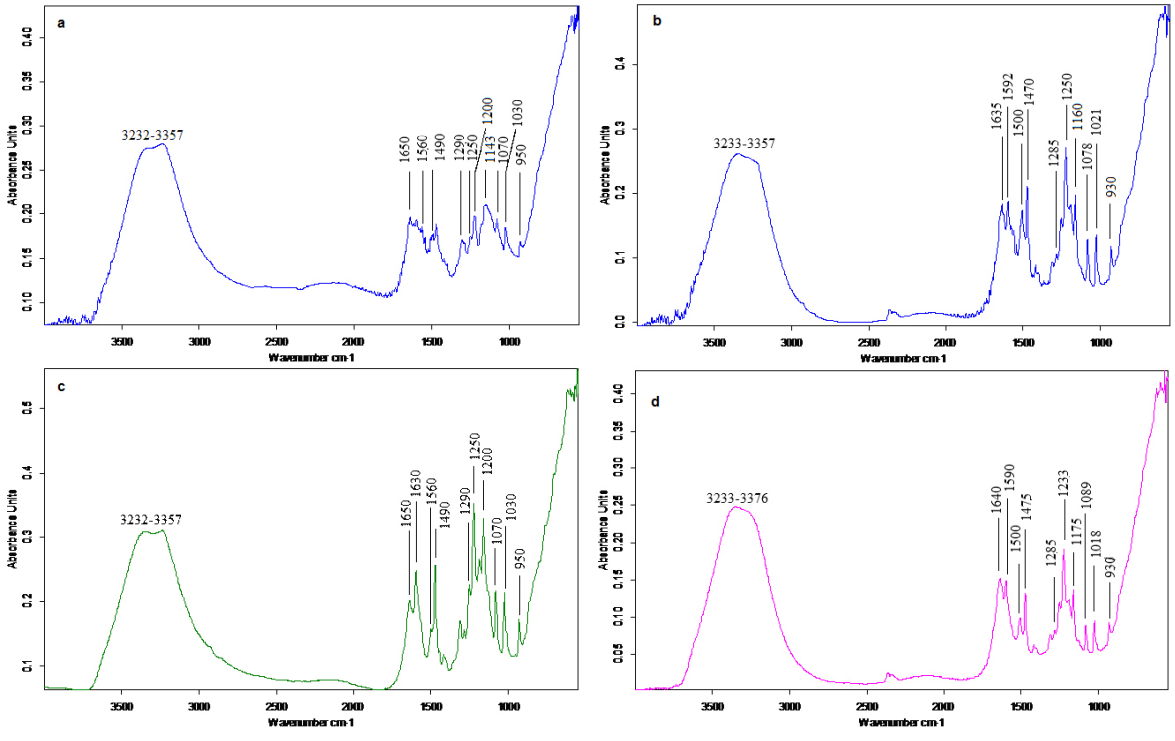


Figure 3. FT-IR spectra for the composite membranes: a) aniline polymerization, b) p-phenylenediamine polymerization and of composite membranes with the conductive polymer doped with polystyrene sulfonic acid: c) sPEEK/PANi membrane, d) sPEEK/PpPD membrane.

Table 1. The assignments of peaks in the IR spectra.

Fragment/Figure	a	b	c	d
peaks assigned to PEEK				
etheric C-O-C bond	1143 cm^{-1}, 1200 cm^{-1}, 1250 cm^{-1}	1160 cm^{-1}, 1250 cm^{-1}	1200 cm^{-1}, 1250 cm^{-1}	1175 cm^{-1}, 1233 cm^{-1}
conjugated ketonic C=O bond	1650 cm^{-1}	1635 cm^{-1}	1650 cm^{-1}, 1630 cm^{-1}	1640 cm^{-1}
peaks assigned to conductive polymers				
C-N stretching vibration of the aromatic secondary amino group	1290 cm^{-1}	1285 cm^{-1}	1290 cm^{-1}	1285 cm^{-1}
secondary N-H stretch vibration	3232-3357 cm^{-1}	3233-3357 cm^{-1}	3232-3357 cm^{-1}	3233-3376 cm^{-1}
peaks assigned to both polymers				
C=C-C aromatic ring stretch	1560 cm^{-1}	1500 cm^{-1}, 1592 cm^{-1}	1560 cm^{-1}	1500 cm^{-1}, 1590 cm^{-1}
C=C stretching vibration	1490 cm^{-1}	1470 cm^{-1}	1490 cm^{-1}	1475 cm^{-1}
=C-bond outside the vibration plane	950 cm^{-1}	930 cm^{-1}	950 cm^{-1}	930 cm^{-1}
peaks assigned to sulfonic groups				
symmetric O=S=O stretch	1070 cm^{-1}	1078 cm^{-1}	1070 cm^{-1}	1089 cm^{-1}
S=O symmetric stretch	1030 cm^{-1}	1021 cm^{-1}	1030 cm^{-1}	1018 cm^{-1}

that there is no net movement of ions, and therefore no need for an ion source [19]. When one scans a wide range of a.c. frequencies, at high frequencies only the uncompensated resistance ohmic resistance contributes to the real part of impedance, while in the case of very low frequencies the polarization resistance or charge transfer resistance has also a contribution. By representing the electrochemical impedance spectra as Nyquist plots one may easily determine the real part of impedance R1 (multiplied with the electrode surface), taken when the value of the imaginary part of impedance equals to zero and hence the possibility of computing the value of the ionic conductivity for the measured sample. The ionic conductivity and the corresponding capacitance for the obtained membranes were determined by Electrochemical Impedance Spectroscopy using a procedure identical to the one presented in details in [19].

The measurements were carried out using parallel opposed dual electrode platinum cell with a common surface area of 0.9503 cm^2 placed inside the jaws of a digital precision micrometer provided with mobile reference origin, having as electrolyte the membranes that are subjected to analysis placed between the above said electrodes. The frequency was scanned between 100 kHz and 100 mHz, and the working temperature was 25°C [20]. The applied potential perturbation was 10 mV. The ionic conductivities were determined from the electrochemical impedance spectra presented in the form of Nyquist diagrams and depicted in the form of screen captures, Figs. 4a and 4b, as the ratio between the membrane thickness, d, measured during the determination with the digital micrometer, and the ohmic resistance component of the impedance, R1, supplied by the circular regression procedure carried out by the associated software (see Fig. 4b) taken as the first intersection of the circular regression curve with the real impedance axis, $\sigma = \frac{d}{R1}$, the unit of measurement being S/cm ($[\sigma] = \frac{cm}{\Omega \cdot cm^2} = \Omega^{-1} \cdot cm^{-1} = S \cdot cm^{-1} = S/cm$). Thereby at a mean thickness of 0.0713 cm, for the sPEEK/PANi membrane doped with polystyrene sulfonic acid, the value for R1=30.6 Ω cm^2 and the ionic conductivity is σ = 0.0023 S cm^{-1}. The measured capacitance for the assembly platinum electrodes and sPEEK/PANi membrane doped with polystyrene sulfonic acid determined also from the circular regression is C = 86.63 μF cm^{-2}. For the sPEEK/PpPD membrane doped with polystyrene sulfonic acid, at a mean thickness of 0.0365 cm, the value for R1=13.33 Ω cm^2 and hence the ionic conductivity σ = 0.0027 S cm^{-1} and the corresponding capacitance for the assembly platinum electrodes and sPEEK/PpPD membrane doped with polystyrene sulfonic acid is C = 1.776 μF cm^{-2}.

From this results it can be observed that the two composite membranes studied have similar ionic conductivities but these values are smaller than those reported in the literature for Nafion membranes - 0.083 - 0.1 S cm^{-1} [21,22].

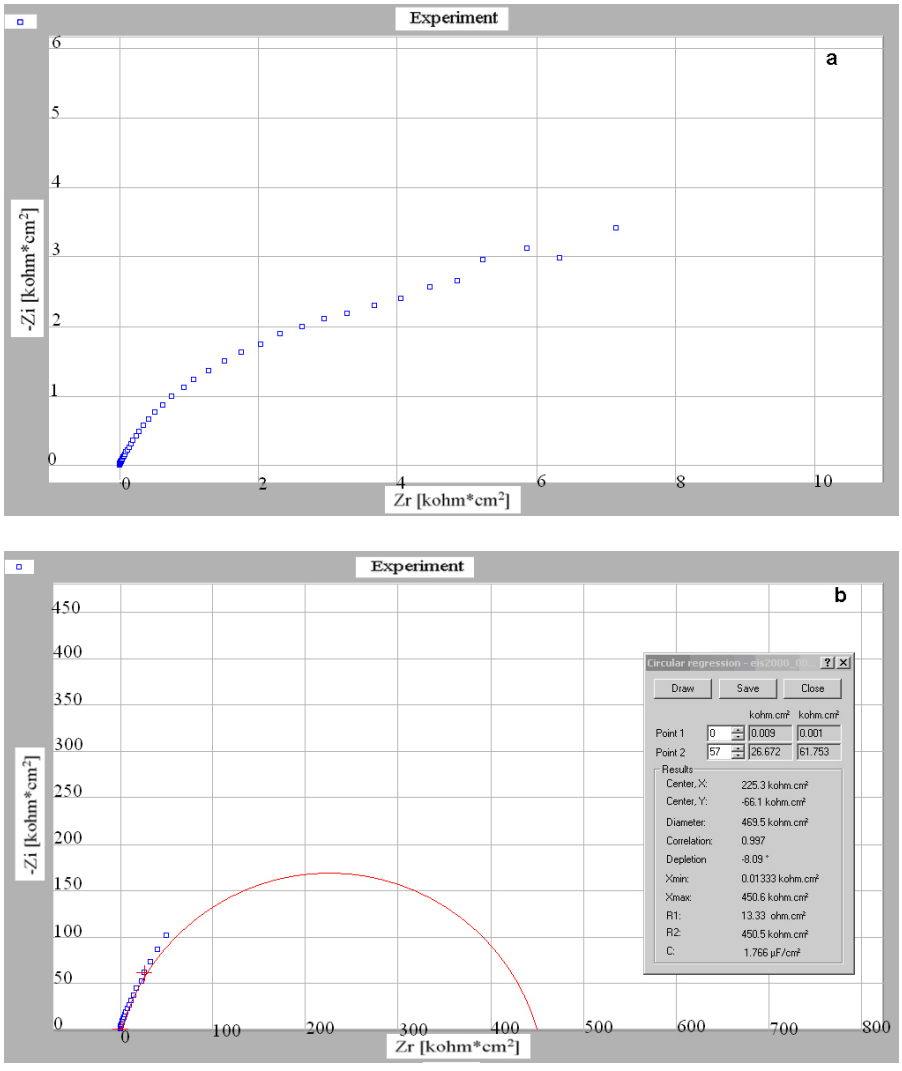


Figure 4. Screen capture of Nyquist diagrams for: a) sPEEK/PANi membrane – polystyrene sulfonic acid and b) sPEEK/PpPD membrane – polystyrene sulfonic acid.

4. Conclusions

The synthesis and characterization of new composite membranes with sulfonated polyether etherketone as support and conductive polymers, like polyaniline and poly(p-phenylenediamine), with a polyaniline like structure, were reported in this paper. The support membranes were synthesized by phase inversion process, a known and employed method for the synthesis of polymeric membranes, while, for the doping process with conductive polymers new, simple and inexpensive methods were used. The obtained membranes were characterized by classical procedures. Thus, by SEM and EDAX analyses the structure and morphology of the membranes have been observed, by FT-IR spectroscopy the proposed chemical structures have been demonstrated and it have been marked out the fact that the structure of poly(p-phenylenediamine) is almost identical with that of polyaniline. By using electrochemical impedance spectroscopy the ionic conductivity of the membranes could be evaluated, an important characteristic for fuel cell applications. From this analysis it could be observed that the two obtained composite membranes have similar values for the ionic conductivity: σ = 0.0023 S cm^{-1}, for sPEEK/PANi membrane and σ = 0.0027 S cm^{-1}, for sPEEK/PpPD membrane, measured at room temperature, but these values aren't even close to those of Nafion membrane. However, taking into account that sPEEK membranes are less expensive than Nafion and have better chemical and thermal stability one may consider them as an attractive potential candidate for application in the field of fuel cells development.

Acknowledgment

The work has been funded by the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/60203.

References

[1] A. Kirubakaran, S. Jain, R.K. Nema, Renewable and Sustainable Energy Reviews, 13, 2430 (2009)
[2] S.J. Peighambardoust, S. Rowshanzamir, M. Amjadi, International Journal of Hydrogen Energy, 35, 9349 (2010)
[3] G. Nechifor, S.I. Voicu, A.C. Nechifor, G. Nechifor, Desalination 241, 342 (2009)
[4] F.D. Balacianu, A.C. Nechifor, R. Bartos, S.I. Voicu, G. Nechifor, Optoelectronics and Advanced Materials – Rapid Communications, 3(3), 219 (2009)
[5] R.K. Nagarale, G.S .Gohil, V.K. Shahi, Journal of Membrane Science 280, 389 (2006)
[6] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chemical Reviews 104, 4587 (2004)
[7] H. Lin, C. Zhao, W. Ma, H. Li, H. Na, International Journal of Hydrogen Energy 34, 9795 (2009)
[8] A. Siu, B. Pivovar, J. Horsfall, K.V. Lovell, S. Holdcroft, Journal of Polymer Science Part B: Polymer Physics 44, 2240 (2006)
[9] A. Basile, L. Paturzo, A. Iulianelli, I. Gatto, E. Passalacqua, Journal of Membrane Science 281, 377 (2006)
[10] P. Patel, T.R. Hull, R.W. McCabe, D. Flath, J. Grasmeder, M. Percy, Polymer Degradationand Stability, 95, 709 (2010)
[11] J. Wang, In: T. Sabu, P.M. Visakh (Eds.), Handbook of Engineering and Speciality Thermoplastics, Volume 3: Polyethers and Polyesters (John Wiley & Sons, Hoboken, NJ, USA 2011)
[12] J.K. Fink, High performance polymers (William Andrew Inc., Norwich, NY, 2008)
[13] S. Zhou, J. Kim, D. Kim, Journal of Membrane Science 348, 319 (2010)
[14] B. Lakshmanan, W. Huang, D. Olmeijer, J.W. Weidnera, Electrochemical and Solid-State Lett. 6, A282 (2003)
[15] S. Palaniappan, A. John, Prog. Polym. Sci. 33, 732 (2008)
[16] R.H. Sestrem, D.C. Ferreira, R. Landers, M.L.A. Temperini, G.M. do Nascimento, Polymer 50, 6043 (2009)
[17] S. Bhadra, S. Chattopadhyay, N.K. Singha, D. Khastgir, J. Appl. Polym. Sci. 108, 57 (2008)
[18] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, Progress in Polymer Science 34, 783 (2009)
[19] D.I. Vaireanu, I. Maior, A. Grigore, D. Savoiu, Rev. Chim. 59, 1140 (2008)
[20] C. Baicea, A.C. Nechifor, D.I. Vaireanu, O. Gales, R. Trusca, S.I. Voicu, Optoelectronics and Advanced Materials – Rapid Communications 5(11), 1181 (2011)
[21] S.J. Kim, H.M. Kim, Y.T. Yoo, J.R. Haw, S.G. Kim, M.H. Jang, S.K. Lim, Journal of Ceramic Processing Research 10(2), 176 (2009)
[22] K.Y. Cho, H.Y. Jung, K.A. Sung, W.K. Kim, S.J. Sung, J.K. Park, J.H. Choi, Y.E. Sung, Journal of Power Sources 159, 524 (2006)