

Comparative Study of Polysulfone Matrix Based Composite Membranes Designed for Fuel Cells

MIRCEA SEGARCEANU¹, ALEXANDRA RALUCA MIRON¹, CARMEN GEORGIANA LICA¹, OVIDIU OPREA¹,
ABBAS ABDUL KADHIM KLAIF RIKABI^{1,2}, DANUT IONEL VAIREANU^{1*}

¹Politehnica University of Bucharest, Faculty of Applied Chemistry and Materials Sciences, Dept. of Analytical Chemistry and Environmental Engineering, 1-7 Gheorghe Polizu Str., 011061, Bucharest, Romania

²Technical college of Al-Mussaib (TCM), Al-Furat Al-Awsat Technical University, Foundation of Technical Education, Baghdad, Iraq

In this work, the synthesis and characterization of new types of composite membranes with polysulfone matrix and ionomeric polymer electrolyte: polysulfone-sulfonated polyetherether sulfone (PSf-SPEEK) or polysulfone - poly (styrene sulfonic acid-co-vinylpyridine (PSf-PSSA), with sulfonic groups, with high performances, but especially economically viable, are studied. The composite membranes have different behavior depending upon the two ionofores. This is both due to the different temperatures of the total dehydration and to the decomposing temperature specific to each combination. The most unfavorable observation is the weight loss of PSf_D-PSSA and PSf_N-PSSA at temperatures under 170°C, most probably due to improper reticular degree. Nevertheless, the thermals diagrams of the composite membranes slightly differ for the same ionofore, suggesting the possibility of usage of the composite membrane on a polysulfone support - obtained from either the available or more accessible solvent. This observation is not yet valid neither from the ionic interchange nor from the conductivity point of view, since the performances of the two composites drastically differ with respect to the supports used here (PSf-D and PSf-N). Comparing the thermic performances, the recommended usage order to consider for the composite membranes is: PSf_N-SPEEK = PSf_D-SPEEK > PSf_D-PSSA = PSf_N-PSSA. From the electrical performances point of view, the composites classify in the following order: PSf_D-PSSA > PSf_N-PSSA >> PSf_D-SPEEK > PSf_N-SPEEK. At this time of research, it is difficult to establish an optimal composite membrane for fuel cell, although the composite PSf_D-PSSA seems to be preferred.

Keywords: composite membranes, polysulfone, polysulfone-sulfonated polyetherether sulfone, polysulfone - poly (acid styrene sulfonic-co-vinylpyridine), fuel cell

Membrane and membrane processes researches are now geared towards obtaining new, hybrid or intelligent membrane materials. These materials, more resistant, more efficient and less costly, have as main goal to overcome performance limits in achieving advanced technologies [1-3].

In this context, the development of composite materials and membranes for the use in combustion cells as future green energy sources is a priority objective [4, 5]. Fuel cells have a high efficiency for energy conversion, low noise, low pollution, and low maintenance costs [6-8].

The combustion cell is a type of generator that produces electrical energy following an electrochemical reaction that takes place inside it. This reaction is produced by introducing a fuel which generates a chemical oxidation reaction at the anode while at the cathode level, in the presence of an oxidant, a reduction reaction takes place [7-12].

The most frequently used fuel is hydrogen, but other fuels, such as methanol or carbon monoxide can be also used [7-9]. A great advantage of hydrogen combustion cells, unlike those with alcohols, is that the chemical reaction does not produce environmental pollutants with reference to carbon dioxide [13, 14].

The main features underlying the selection of fuel cells for different practical applications are given by the nature of the electrolyte used. Thus, are distinguished the following types of solid electrolyte (PES) [13-19]:

- PEMFC - solid state electrolyte type cells (Polymer Electrolyte Membrane Combustion cells);

- Alkaline electrolyte cells - AFC (Alkaline Combustion cells);

- Fosforic acid electrolyte cells-PAFC (Fosforic Acid Combustion cells);

- Molten carbonate electrolyte cells-MCFC (Molten Carbonate Combustion cells);

- Solid Oxides Fuel electrolyte cells-SOFC (Solid Oxides Combustion cells).

The electrolyte is a substance capable of dissociating into ions in the presence of a protic solvent, so that the solution conducts the electrical current. In PEMFC type cells (fig. 1), the electrolyte is a solid polymer film known as a membrane. The thickness of the membrane is between 50 and 200 micrometers. The membrane prepared for the combustion cells has to be solvated, in particular and most often, hydrated [7-12]. By water using, the membrane adsorbs negative ions (e.g. OH⁻) that remain bounded in its structure, while positive ions (eg. H₃O⁺) can move between anode and cathode.

For ion-based polymer membranes, the positive ions are protons, which is why the cell is also known as PEM (Proton Exchange Membrane). The displacement of H₃O⁺ ions through the membrane only from the anode to the cathode is essential for closing the electrical circuit [14, 15].

The membrane must be a very good separator between fuel and air, avoiding their mixing, followed by combustion, and also must be a good electrical insulator to prevent electrons from moving through the electrolyte [16, 17].

The electrons formed at one of the electrodes move toward to the other electrode through a resistive type

* email: di_vaireanu@yahoo.co.uk

consumer inserted into the external circuit, making the electrical current [12-19].

Within this class are distinguished the cells with polymer membranes powered directly with methanol (Direct Metanol Fuel cells - DMFC) membrane membranes.

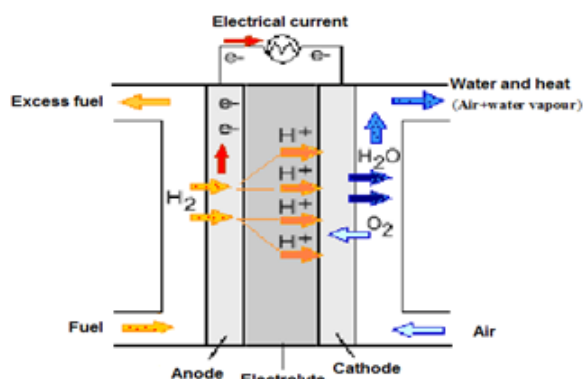


Fig. 1. Fuel cell with solid state electrolyte (PEM)

Unlike PEMFC this type of combustion cells directly extract hydrogen from the introduced fuel.

This combustion cell has the advantage of an operating temperature of 50 to 100 °C and the efficiency is around 40%, being mainly used in the supply of portable electronic equipment [17-19].

In the present paper, the synthesis and characterization of new types of composite membranes with polysulfone matrix and ionomeric polymer electrolyte: polysulfone-sulfonated polyetherether sulfone (PSf-SPEEK) or polysulfone - poly (styrene sulfonic acid-co-vinylpyridine (PSf-PSSA), with sulfonic groups, with high performances, but especially economically viable, are studied.

Experimental part

Materials, apparatus and methods

Polysulfone (PSf) Udel type (Aldrich - $M = 22000$ Da), was used as basic material for all the variants of membranes prepared with solvents purchased from Merck: N-methyl pyrrolidone (NMP) or dimethylformamide (DMF). Sodium salt of 4-styrenesulfonic acid (4-NaSSA), was purchased from Alfa Aesar, with a molecular weight of 206.20 g/mol, 80% purity, $\rho = 1.043$ g/mL at 25°C, 4-vinylpyridine (4VP), containing 100 ppm hydroquinone as inhibitor, 95% from Aldrich, with molecular weight of 105.14 g/mol, $\rho = 0.975$ g/mL at 25°C, and Merck reagents for synthesis: sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), potassium metabisulfite ($\text{K}_2\text{S}_2\text{O}_5$), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). Hydrochloric acid (37%) and sulfuric acid (96%) used for electrochemical studies and sulfonate polymers used for synthesis were provided from Merck.

The water required for solution preparation was obtained with a Millipore System and the solvents: acetone, lower alifatic alcohols (methanol, ethanol and isopropanol) were purchased from Merck.

Morphological analysis of samples was performed by scanning electron microscopy (SEM). It used a high-resolution microscope, FEI Instrument with dual beam and equipped with X-ray (EDX) dispersive detector, the samples were covered with a thin layer of gold.

Gravimetric measurements were performed using a thermal analysis (TGA-DSC) using a Universal V4.5A TA Instrument set to 1000° C, in static air atmosphere, with a heating rate of 10 K min.

Polysulfone membranes matrix formation

In an Erlenmeyer flask with ground glass stopper, the required amount of solvent and portions from the purified

polymer up to the desired concentration (12.5% polysulfone in solvent NMP or DMF) were added under magnetic stirring. Using precipitated and dried polymer, the desired polymer solution was obtained within 4 h. Before use, the solution is deaerated by standing in a vacuum ejector for 30 min [20-23].

A determined amount of polymer solution, 5mL, is deposited on a spectral glass support, and with a chromatographic type scraper is extended to a 250 μm standard thick. The polymer film deposited on the glass is submerged in a coagulation bath (I), especially prepared containing lower alifatic alcohols [23-25].

PSf-SPEEK composite membranes

PEEK (350P, grey powder) was dried in a drying stove with vacuum at 100°C. PEEK (10 g) pellets were gradually added in 100 mL H_2SO_4 (96%) under magnetic stirring at room temperature (approx.22°C).

After a maturing time of 72 h, the sulfonate polymer was recovered by precipitating the polymeric acid solution in a large amount of water (ice) under mechanical stirring for a period of time, ranging from one hour to two hours, observing the formation of a SPEEK white gel. The white SPEEK gel was allowed to stabilize overnight.

SPEEK was washed with deionized water by introducing the polymers into a dialysis tube and dialysis of the acid from the polymers until the wash water reached a pH of between 6 and 7 [24-26].

The PSf-SPEEK composite membranes were formed by drying the white gel of SPEEK deposited by ultrafiltration in the polysulfone matrix selected in a drying stove at 70° C and 100 °C, appearing the white to yellowish-orange composite membranes.

The PSf-PSSA composite membranes

The acid stiresulfonic-co-4-vinylpyridyn (PSSA) copolymer was synthesized through free radical's polymerization process using distilled water at 70°C, under nitrogen atmosphere and continuous blending for 8 hours. The reaction conditions were as follows: the molar ratio of the monomers 1: 1, the mass of monomers in solution and of the initiator 10wt%, the equimolar mixture of ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and of sodium metabisulfite of approximately 1wt% of the monomers mass [28-30].

The PSf-PSSA composite membranes were formed by PSSA gel deposition onto the polysulfone matrix within a vacuum oven, both at 70 and 100°C, thus leading to the apparition of the cream-colored composite membranes.

The conductivity of the membrane

The conductivity of the membrane, k_m , was measured under atmospheric pressure and in the membrane's thickness, using as electrolyte various solutions with different concentrations. A glass cylindrical support at 25°C was used. The measurement method used was the AC method (fig. 2) [28, 30]. The membrane was pressed in-between two wire electrodes connected to the measurement apparatus. The voltage used was 7.5 mV. Before any measurement, the membrane was firstly balanced, for at least 30 min.

The membrane resistance (R) was determined by subtracting the resistance of the electrolytic solution (R_s is the resistance of the solution, determined in absence of the membrane) from the resistance of the membrane, balanced in the electrolytic solution (R_{s+m}):

$$R = R_{s+m} - R_s \quad (1)$$

The proton conductivity was computed by measuring the impedance of the membrane R (ohm) using a RLC

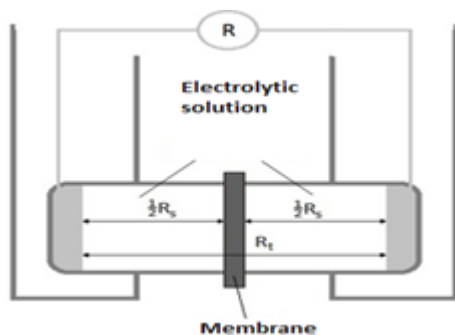


Fig. 2. The schematics of the conductivity measurement cell, R-LCR

measurement apparatus. The proton conductivity of the membrane was computed as follows:

$$\kappa_m = \frac{1}{S_m(R_{z+m} - R_z)} \quad (2)$$

where κ_m is the proton conductivity [Scm^{-1}], l is the thickness of the membrane [cm], S_m is the area of the membrane's section [cm^2] (which measures 1 cm in diameter) and R is the impedance [ohm] measured at a frequency of 1 KHz, in DC (direct current) [29, 30].

The ionic exchange capacity (IEC)

The determination of the ionic exchange capacity is made by titrating the inert atmosphere of the polymer solution (1g of polymer) with potassium hydroxide. The ionic exchange capacity is given in milliequivalents for each gram of solid polymer (meq/g) [30].

Results and discussions

The ion exchange membranes are classified with respect to the ionic groups attached to the matrix of the membrane. The cations exchange membranes contain negatively charged groups like $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3\text{H}^-$, $-\text{PO}_3^{2-}$, $-\text{C}_6\text{H}_4\text{O}^-$, which are fixed on the matrix of the membrane and therefore allow the passage of cations only. The anions exchange membranes contain positively charged groups like $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}_3^+$, $-\text{PR}_3^+$, $-\text{SR}_3^+$, are fixed on the matrix of the membrane and allow the passage of anions only [27-29]. According to the link mode of the charged groups in the matrix or to their chemical structure, the ions exchange membranes can be further classified in homogenous and heterogenous membranes. Nevertheless, most of the homogenous ions exchange membranes comprise of polyolefins or poly-fluoride olefins which contain ionic groups [12-16, 31-35].

The proton exchange membranes for combustion cells use a membrane with sulfonic groups. Nowadays, the most known such membrane is Nafion (perfluorinated ionomer - poly (perfluoro-sulfonic acid)). This one offers both an exceptional oxidative stability and high proton conductivity. A version of Nafion membrane is the one having a $-\text{COOH}$ group; its name is Flemion. Both types have high methanol permeability and rather low glass transition temperatures, which make them, unfit for the combustion cells' specific applications [11, 15-17].

The operating temperatures for such membranes are comprised between 60 and 130°C , with a typical value of 80°C [8-19].

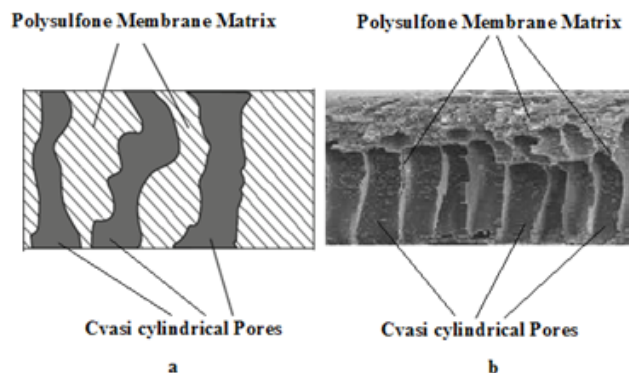
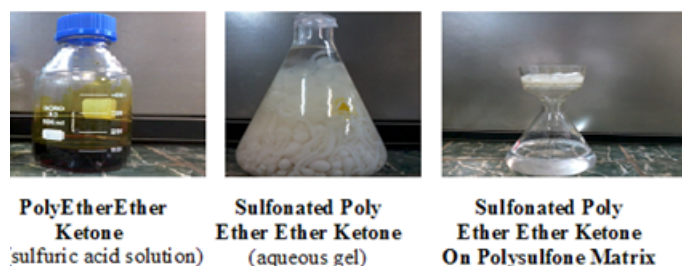


Fig. 3. The microstructure of the polysulfone matrix and of the macropores for ionofore potting (a- conceptual scheme; b-the real situation)

Lately, the proton exchange membranes (PEM) containing cationic exchange groups (SO_3^-) are based on cheaper materials, such as poly (styrene sulfonic acid) (PSSA) along with their co-polymers or sulfonated polyetheretherketone (SPEEK) [24-30].

In the present study, two polysulfone based polymeric matrices are used, both being obtained by fase inversion from polymer solution in dimethylformamide (PSf-D) and N-methyl pyrrolidone (PSf-N). The microstructure of these matrices (fig. 3) allows the incorporation of the desired ionofore into the parallel quasi-cylindrical pores: sulfonated polyether ether ketone or poly (acid styren sulfonic -co-vinylpyridine) thus obtaining the composite membrane of polysulfone matrix type with insertions of either sulfonated poly-ether etherketone (PSf-SPEEK) or poly (styrene sulfonic acid-co-vinylpyridine) (PSf-PSSA).

In order to illustrate the attainment of composite membranes, the succession of operations is presented (fig. 4) for the case of composite polyetheretherketone membrane deposited on polymeric, polysulfone based matrix, already presented in figure 3. Thus, after obtaining the polyether etherketone solution in sulfuric acid 96%, this is inserted in water with ice and washed until the polyetherether sulfonated gel is obtained, the ionofore is deposited - through vacuum filtration - on the polysulfone matrix. Eventually, it is dried at $60-70^\circ\text{C}$ using a controlled vacuum oven [35, 36].

Table 1 presents the main characteristics of the composite membranes based either upon sulfonic polyetheretherketone (PSf-SPEEK) or upon poly (styrene sulfonic acid-co-vinylpyridine) (PSf-PSSA) on polysulfone support, obtained out of dimethylformamide or N-methylpyrrolidone. The electronic microscopy (see table 1) highlights the porous structure of the polysulfone support (PSf-D and PSf-N) as well as the ionofore inclusions (PSf_N-SPEEK, PSf_D-SPEEK, PSf_D-PSSA, PSf_N-PSSA). For the composite membranes we can see a slight exfoliation of the superficial ionofore layer, more obvious in case of PSf_D-PSSA. The thermal analysis (TG) shows a similar behavior of the two polysulfone matrices (PSf-D and PSf-N) with mass losses which are noticeable at temperatures over 170°C , and accelerated or almost total decomposition at temperatures over 500°C . For thermal decomposition (in

Fig. 4. The succession of operations for composite membrane of polyEtherEtherKetone deposited on polymeric, polysulfone based, matrix

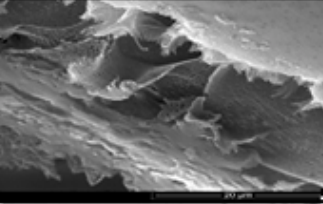
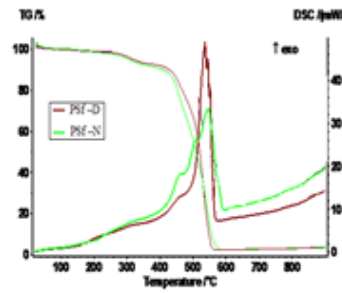
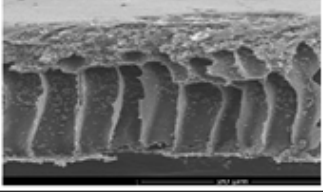
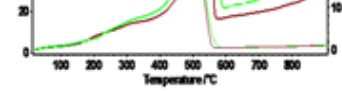
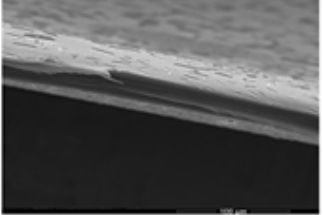
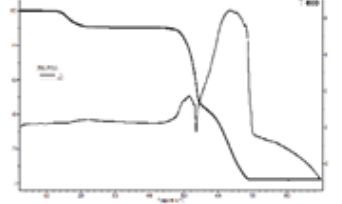
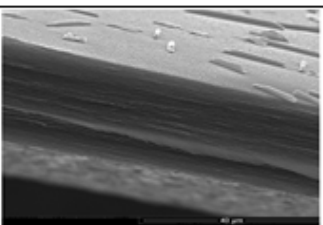
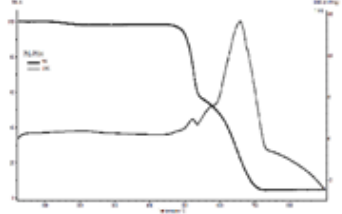
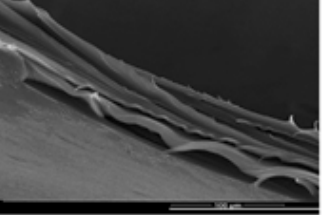
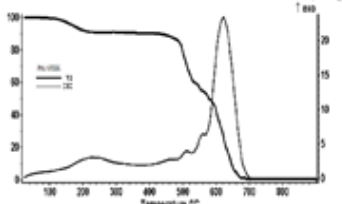
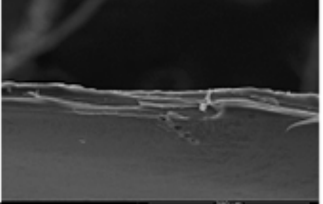
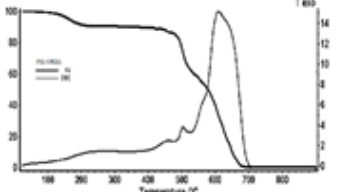
Membrane type	Electronic Microscopy (SEM)	Thermal Analysis (TG /DSC)	Ion Exchange Capacity (meq/g)	Conductivity σ (S/cm)
PSf-D matrix			-	-
PSf-N matrix			-	-
PSf _D -SPEEK			0.879	0.136
PSf _N -SPEEK			0.793	0.081
PSf _D -PSSA			1.920	0.198
PSf _N -PSSA			1.567	0.143

Table 1

air) the exothermic effect is especially emphasized for PSf-N matrix. The slightly different thermal behavior of the two polysulfone matrices is caused both by the residual solvent within the membrane's micro-pores (dimethylformamide or N-methylpyrrolidone) and by their very different porosity.

The composite membranes have different behavior depending upon the two ionofores. This is both due to the different temperatures of the total dehydration and to the decomposing temperature specific to each combination. The most unfavorable observation is the weight loss of PSfD-PSSA and PSfN-PSSA at temperatures under 170°C, most probably due to improper reticular degree. Nevertheless, Table 1 shows that the thermals diagrams of the composite membranes slightly differ for the same ionofore, suggesting the possibility of usage of the composite membrane on a polysulfone support - obtained from either the available or more accessible solvent.

This observation is not yet valid neither from the ionic interchange nor from the conductivity point of view (table

1), since the performances of the two composites drastically differ with respect to the supports used here (PSf-D and PSf-N).

Comparing the thermic performances, the recommended usage order to consider for the composite membranes is:

$PSf_N-SPEEK = PSf_D-SPEEK > PSf_D-PSSA = PSf_N-PSSA$

From the electrical performances point of view, the composites classify in the following order:

$PSf_D-PSSA > PSf_N-PSSA >> PSf_D-SPEEK > PSf_N-SPEEK$

At this time of research, it is difficult to establish an optimal composite membrane, although the composite PSfD-PSSA seems to be preferred.

The performance improvement of the two types of composite membranes of the matrix type made out either of polysulfone with sulfonic polyetheretherketone (PSf-SPEEK) inclusions, or of composite membranes of polysulfone with poly(styrene sulfonic acid -co-vinylpyridine) (PSf-PSSA) inclusions, assumes the

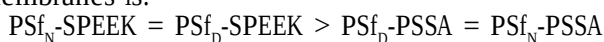
increasing the degree of sulfonation of polyetheretherketone in order to increase both the conductivity and capacity of ionic interchange and the reticular degree of poly(styrene sulfonic acid-co-vinylpyridine), necessary for a good thermal behavior (avoiding weight loss under 170°C).

Conclusions

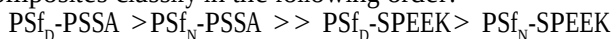
New types of composite membranes with polysulfone matrix and ionomeric polymer electrolyte: polysulfone-sulfonated polyetherether sulfone (PSf-SPEEK) or polysulfone - poly (styrene sulfonic acid-co-vinylpyridine (PSf-PSSA), with sulfonic groups, with high performances, but especially economically viable, are obtained.

In the present study, two polysulfone based polymeric matrices are used, either being obtained by fase inversion from polymer solution in dimethylformamide (PSf-D) or N-methyl pyrrolidone (PSf-N).

Comparing the thermic performances, the recommended usage order to consider for the composite membranes is:



From the electrical performances point of view, the composites classify in the following order:



At this time of research, it is difficult to establish an optimal composite membrane for fuel cell, although the composite PSf_D-PSSA seems to be preferred.

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Manuscript received: 15.10.2017