
Conductive Polymer-Based Membranes

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Abstract

This review focuses on an important theme of conductive polymer domain: preparation and applications of advanced materials with permselective properties, such as conductive polymer-based membranes. The most common groups of conductive polymers, their particularities, their use in membranes preparation together with main specific obtaining methods/techniques and conductive polymer-based membrane applications are presented based on a comprehensive documentary study.

Keywords: polymers, conductive polymers, membranes, membrane processes, conductive polymers membranes applications

1. Conductive polymers general data

1.1. Introduction

Polymers represent a larger class of organic compounds, in terms of both diversity and industrial-scale applications. They are used in the majority of industrial branches and have contributed decisively to the last century economic development. Polymers' impact upon the human society progress showed a positive effect, but nowadays, more attention is given to the mitigation of negative environmental impact induced by their intensive use. As a consequence of exponential growth of researches in the polymers field, the macromolecular compounds' chemistry became a distinct science within organic chemistry, a well-defined domain, in connection with other natural sciences areas. The turning point in the development of macromolecular compounds chemistry as an exact science was the transition from semi-empiric researches to rigorous experiments marked in 1925–1930 period by Staudinger and

Carothers researches [1–4] that led to highlighting of polymer structures, defining the notions of macromolecule, macromolecular chain, homologous polymeric series, etc.

Polymers led to rapid development of plastic materials science due to their specific properties: chemical stability on acids, bases and solvents (higher than gold and platinum in some cases), high thermal stability, elasticity, plasticity, excellent mechanical strength, non-permeability to gases, low density, electrical insulation properties and also electroconductive properties. The latest characteristics referring to electroconductivity was thoroughly studied during the last 60 years, leading to the development of a new polymer chemistry subdomain, and dedicated to conductive polymers. The results, reported within research works focussed on conductive polymers, materialized in two Nobel prizes in chemistry [5]:

- Rudolph A. Marcus (1992) for his works on electron transfer theory in redox processes, with direct applications in biopolymers science and
- Alan J. Heeger, Alan G. Mac Diarmid and Hideki Shirakawa (2000) for development of intrinsic electroconductive polymers through researches related to polyacetylene.

At the same time, with macromolecular compound chemistry, a new domain related to the preparation and use of membrane-type advanced materials was developed. Membrane science developed continuously as an interdisciplinary science in which polymers have a central role. With the progress of research works dedicated to conductive polymers, researches on conductive polymers membranes preparation and their application were also initiated and developed.

1.2. Conductive polymers classes, specific characteristics, preparation methods and general applications

Classification of conductive polymers can be done based on various criteria. The most important criterion is related to the electric charge movement type which depends on the polymer chemical structure. Thus, two groups of electronic conductive polymers are formed:

- Redox polymers: polymers that possess redox potential within their structure groups (reduction/oxidation capacity);
- Intrinsic electroconductive polymers: polymers with conjugated π - π or p - π systems.

In the case of redox polymers, the movement of electrons is realized through reversible chemical reactions “donor-acceptor” type, in accordance with Eq. (1):



where “ n ” is the number of transferred electrons.

The standard potential (E^0) is determined by Eq. (2):

$$E^0 = -\Delta G^0/nF \quad (2)$$

where F is the Faraday constant and ΔG^0 is the standard Gibbs free energy, calculated in accordance with Eq. (3):

$$\Delta G^0 = \Delta G^0_{\text{Red}} - \Delta G^0_{\text{Ox}} \quad (3)$$

In the case of redox polymers, the essential condition needed for continuous electron transport, which defines the “electronic conductive polymer” property, is that groups with redox potential have to be distributed one next to the other within the macromolecular structure (its spatial configuration) in such a way that electron jump between groups is possible (**Figure 1**).

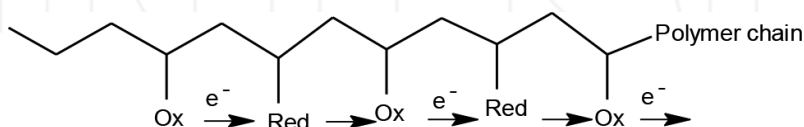


Figure 1. Electric charges movement within redox polymers.

Such polymers are those based on substituted nitro-styrene, quinones, dopamines and polymers which have within structure coordinative ligands based on Ir, Co, Re, Ru or Os [6].

The electrons transport principle of intrinsic electroconductive polymers consists of electrons transfer from π type bonds to nearby simple σ bonds, due to repulsion effect of same type charges.

The mandatory condition is that double bonds alternate with the simple ones (conjugated π - π systems), as shown in **Figure 2**.

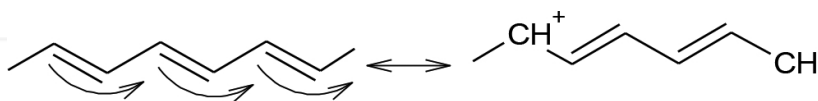


Figure 2. Electric charges movement in “ π - π ” conjugated systems.

The same principle applies to the continuous transport of electrons in the case of polymers which contains heteroatoms N, S or O types within the macromolecular chain. Heteroatoms must be bonded to C atom that is involved in a double bond. Practically, non-participating p electrons of the heteroatom move to σ single bond, and through electrostatic repulsion effect, they further induce the movement of π electrons from the nearby double bond. That type of electrons transport is specific to conjugated p- π systems (**Figure 3**).

Intrinsic conductive polymers have the capacity to conduct electricity better than the majority of plastic materials which do not contain conjugated electron systems. For example, polyace-

tylene has a conductivity of 10^{-8} – 10^{-7} S m^{-1} in the form of “cis” isomer and 10^{-2} – 10^{-3} S m^{-1} in the form of “trans” isomer, compared with Teflon which has a conductivity of 10^{-16} S m^{-1} . However, compared with the conductivity of metals with best electric properties (Ag and Cu), which is of order 10^8 S m^{-1} , the conductivity of these polymers is very low, having semiconductor properties. Through doping process, similar with that applied to classic inorganic semiconductors, the conductivity of intrinsic conductive polymers significantly grows, being closer to metals properties. Thus, polyacetylene doping with halogen vapour made (Cl, Br, I) the conductivity grow up to 10^5 S m^{-1} [5].

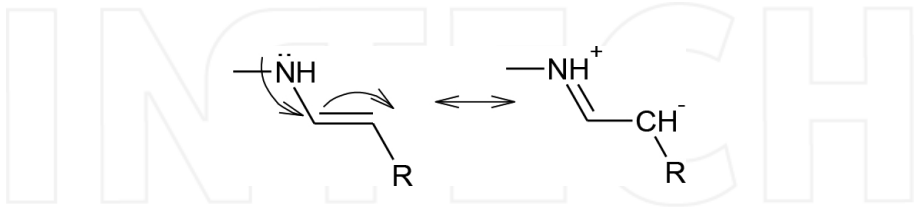
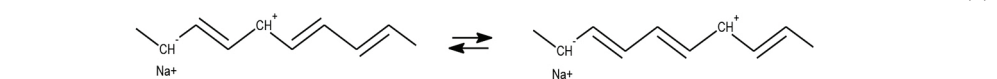
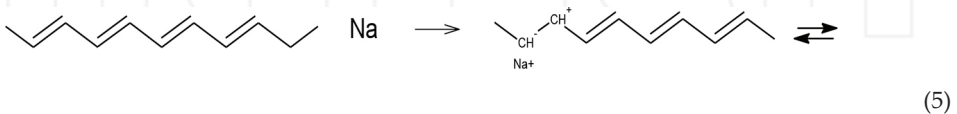
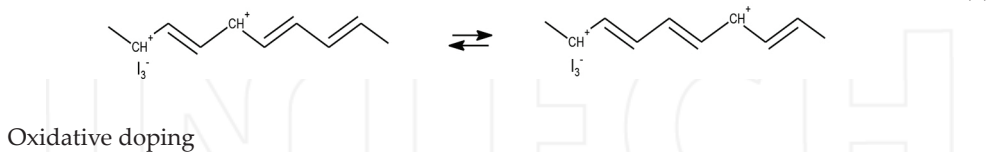
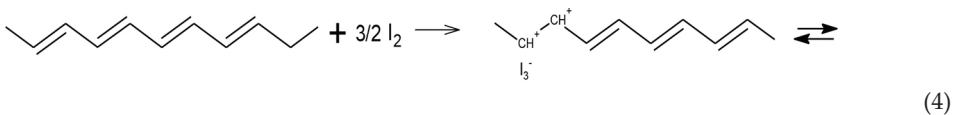


Figure 3. Electric charges movement in “p- π ” conjugated systems.

Doping process involves the introduction of atoms capable of extracting or providing electrons to polymer’s conjugated system, within its macromolecular chain. Introduction of such defects within the structure of macromolecule results in a more rapid jumping of electrons from created polar centres, assuring a better conductivity for the polymer. Usually, two distinct doping processes are applied [5]: oxidative doping (or p-doping) through which electrons are abstracted from the structure of polymer and reductive doping (or n-doping) through which electrons are introduced within the structure of polymer.

The two mentioned reactions are the processes for polyacetylene in Eqs (4) and (5):



Reductive doping

In the first case, iodine is abstracting electrons from double bonds and in the second case, sodium atoms are releasing electrons to the double bonds bond resulting in their polarization. Both electric charges are migrating within the polymeric chain, adding the electric conductivity property, as shown in Eqs (4) and (5).

Doped intrinsic conductive polymers are obtained through one of the two main methods: chemical or electrochemical [7, 8]. Through chemical synthesis processes, monomers are polymerized/polycondensated by mixing with specific oxidative reagents such as ferric chloride or ammonium persulphate, at a specific pH. The method presents two main advantages compared with the electrochemical method: can be used to obtain polymeric powders or films that can be further processed and used at industrial level and can be used also in the synthesis of conductive polymers via electrochemical methods. Drawbacks of the methods are related to the fact that is highly sensitive, being dependent on reaction conditions (solvent nature, solvent and reagents purity, reagents' molar ratios, temperature, mixing mode and speed, reaction time, etc.). Electrochemical synthesis method is based on polymerization/polycondensation of monomers dissolved in a specific solvent through appliance of electricity between two electrodes. The monomer solution also contains the doping agent. Through this method, polymeric films (nanometers order thickness) with controlled/predefined structure are obtained. Electrochemical synthesis can be realized through three techniques: galvanostatic, potentiostatic and potentiodynamic [8]. The method presents the following disadvantages: limited polymer doping, conductive polymer quantity and polymeric film size are limited by electrode geometry and surface, difficulties in appliance for composite materials preparation (compared with the chemical synthesis).

No.	Chemical name	Abbreviation
1	Polyacetylene	PAC
2	Polyaniline	PANI
3	Polypyrrole	PPy
4	Polythiophene	PTh
5	Poly(p-phenylene)	PPP
6	Polyazulene	PAZ
7	Polyfuran	PFu
8	Polyisopren	PIP
9	Polybutadiene	PBD
10	Poly(isothianaphtene)	PITN
11	Poly(α -naphthylamine)	PNA

Table 1. A list of representative polymers and their abbreviations.

At the 2014 year level, more than 25 intrinsic conductive polymers [8] were known and used in various applications: electrochemical sensors [9–11]; gas sensors [12]; biosensors for medicine, food industry and environmental monitoring [13–15]; functionalized biomaterials with application in medicine [8, 16]; corrosion inhibitors [17]; fuel cells [18], etc. One of the main applications of conductive polymers is the development of optoelectronic devices based on electroluminescence phenomenon (field-effect transistors, FET; photodiodes; and light-emitting diodes, LEDs) [19]. The most representative polymers from those classes and their abbreviations are presented in **Table 1**.

For each basic polymer, a larger number of derivatives with electroconductive properties suitable for various applications were studied, and the research results were reported within the literature.

Many of the listed conductive polymers can be used for the preparation of polymeric membranes used in advanced separation processes, which is presented in the next section.

2. Membranes based on conductive polymers and their applications

2.1. General data on membranes and membrane processes

Membranes are advanced materials used for separation of compounds of sizes between 0.1 nm and 1 μm (from suspensions, dissolved macromolecules to simple or complex ions) from liquid and gaseous mixtures. It is difficult to find a membrane definition that covers simultaneously the issues related to its structure, separation mechanism and utilization domain. A generally accepted definition presented within the literature is as follows: *membrane is a selective barrier which actively or passively participates to the mass transfer between the phases separated by it* [20]. The membrane selectivity is determined by the material from which it is made, its structure (form, dimensions and pores distribution) and the force responsible for the separation process.

Membranes are classified based on material type and nature, structure and application domain. Based on these criteria, membranes are as follows:

- *Depending on material nature:* natural or synthetic;
- *Depending on material type:* polymeric or inorganic;
- *Depending on structure:* porous or dense (non-porous);
- *Depending on utilization domain:* microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), dialysis (D), electro-dialysis (ED), membrane distillation (MD), pervaporation (PV) and electro-osmosis (EO).

Considering the pores' form and distribution within the porous or non-porous membranes, they can be classified as

- *Symmetric structure:* straight or inclined cylindrical pores, uniformly distributed of mono-disperse microspherulites;

- *Asymmetric structure*: micropores with variable diameters forming a very thin layer 0.1–1 μm named active layer and non-regulated macropores forming the macroporous layer 100–200 μm ;
- *Composite structure*: an active compact symmetric or asymmetric layer, an intermediary layer and a macroporous layer.

Depending on the separation surface, geometry membranes are plane, tubular hollow fibre type (inner diameter < 0.5 mm), tubular capillary type (0.5 mm $<$ inner diameter < 5 mm) and tubular type (inner diameter > 5 mm).

There are five main methods for membrane preparation: sintering, lamination, irradiation, phase inversion and deposition on thin layers [21]. Among them, phase inversion is the most commonly used method and is applied for membrane preparation at both laboratory and industrial level. Phase inversion concept was introduced in the literature by Kesting [22], and the concept implies transformation of one homogeneous polymeric solution in a two-phase system: one rich in polymer which forms the continuous part of porous membrane and other lacking polymer which fills the pores from membrane structure. The process has three main stages: polymer solubilization in a suitable solvent, skinning of polymer solution on a plane or tubular surface and polymer precipitation (phase inversion). The stage responsible for membrane structure is the precipitation one. Frequently, one of the following techniques for polymer transformation from liquid to solid phase is used: *vapour phase precipitation* [23], *controlled evaporation precipitation* [24], *thermal precipitation* [25] and *immersion precipitation* [26, 27]. Through phase inversion and immersion-precipitation techniques, membranes from various polymers are obtained: polysulphone, polyether sulphone, nylon 6,6, cellulose derivatives, polycarbonate, polyphenylenoxide, polyimides, polyamides, etc. These are used in both base form and modified (functionalized) form via various chemical reactions [28, 29].

Membrane processes are determined by the membrane structure and differentiated after the transport mechanism of chemical species through the membrane. Passing of one component from one side of the membrane to the other is defined as *permeation*, which is dependent on the driving force that generates it. After this criterion, membrane processes are classified as follows:

- Microfiltration, ultrafiltration and reverse osmosis (*driving force—pressure gradient*);
- Pervaporation, gas permeation, dialysis, separation through liquid membranes (*driving force—concentration gradient*);
- Thermo-osmosis and membrane distillation (*driving force—temperature gradient*);
- Electrodialysis and electro-osmosis (*driving force—electric potential gradient*).

Practical realization of membrane separation processes involves specific installations for each application field, in which the core element is represented by the equipment that contains the membrane, named *membrane module*. Depending on membrane shape there are two types of modules: *plane* and *tubular*. Plane membranes can be used in various geometries within modules similar to classic plate filters. Plane membranes can also be used within filter modules

with both spiral and folded configurations. Tubular membranes can be used within tubular, capillary or hollow fibre modules.

Membranes and membrane process applications cover a vast area: treatment of water intended for human consumption from various sources (surface water including marine water, ground water), wastewater treatment, separation and concentration of proteins and enzymes from various natural and biosynthesis media, preparation of ultrapure water, development of medical devices (artificial kidneys, artificial lungs), development of sensors and biosensors with multiple applications, gas separations, fuel cells, ultrapure compounds via membrane distillation and pervaporation, etc.

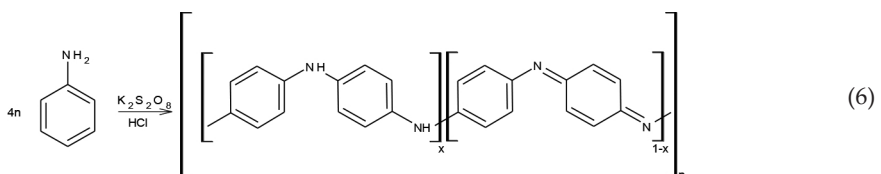
Recent works in the field of membranes and membrane processes are focussing on obtaining cost reduction, improvement of separation characteristics (flow rate, selectivity, limitation of clogging) and extension of application domains at industrial scale [30]. Among these domains, the use of conductive polymer-based membranes is envisaged.

2.2. Membranes based on conductive polymers and their applications

Membranes based on conductive polymers represent a new class of advanced materials that can be used for separation or for interphase transfer processes of some chemical species based on their electrical properties. These membranes can be obtained through the previously described processes for preparation of classic membranes, their particularities being linked to polymers' "doping" methods in order to improve their conductive properties. Membranes of this type are obtained mainly from the polymers mentioned within **Table 1**, but considering the number of citations from the literature, the most used polymers are polyaniline (PANI) and polypyrrol (PPy). Apart from these polymers, during the last period, the use of functionalized polyetheretherketone (PEEK) as conductive polymer and of a considerable number of other polymers in fuel cells were thoroughly researched. Based on these facts, three main classes of conductive polymer-based membranes are presented. All the above-mentioned polymers have physical-chemical properties that do not allow the preparation of membranes using only the specific polymer but only in combination with other polymers. Such membranes usually lack conductive properties but have excellent mechanical strengths. Therefore, the majority of conductive polymer-based membranes are "composite membranes".

2.2.1. Membranes based on polyaniline (PANI) and their applications

Polyaniline (PANI) is a macromolecular compound obtained through oxidative polymerization of aniline in accordance with Eq. (6):



In its structure, there are structural units formed from benzene rings linked through aminic groups (-NH-) and structural units formed from a benzene ring linked with a quinone diimine. The ratio of the two structural units within polymeric chain is varying depending on its degree of oxidation. There are three particular structures of the polyaniline, which differentiate among them the function of the two structural units' ratio (**Figure 4**).

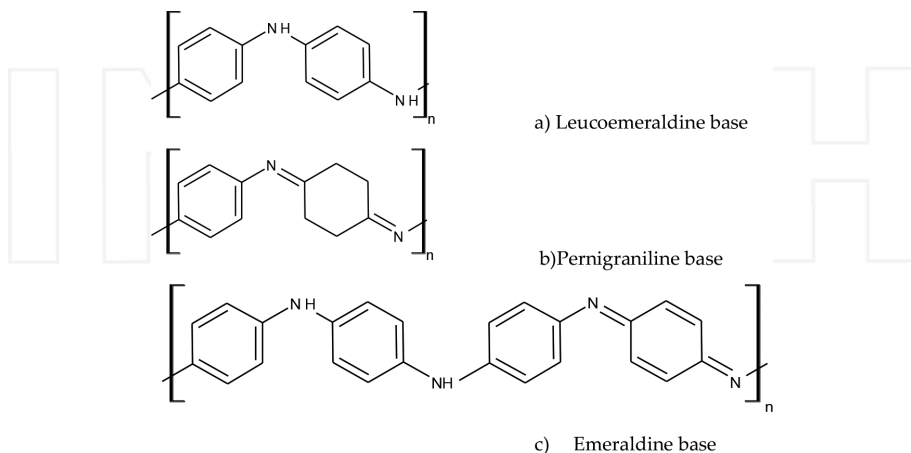


Figure 4. Structural PANI forms. (a) Leucoemeraldine base, (b) pernigraniline base and (c) emeraldine base.

Thus, in the limit case of PANI containing only structural units formed from benzene rings linked through aminic groups ($x=1$), the compound is named *PANI-leucoemeraldine base* (**Figure 4a**), and in the limit case in which within the structure are only structural units formed from one benzene ring linked with a quinone diamine ($x = 0$), the compound is named *PANI-pernigraniline base* (**Figure 4b**). The third particular case is that in which within the macromolecular compound structure, the proportions of the two structural units are equal ($x = 0.5$), the compound being named *PANI-emeraldine base* (**Figure 4c**). Through treatment of these forms with acids or bases (“doping”), the polymer reversible passes from one form to other and gains electroconductive properties.

PANI in the base form has properties that do not allow obtaining simple membranes (low solubility in the majority of solvents commonly used for membranes preparation, low plasticity, thermal instability at temperatures above 160°C, etc.). For this reason, PANI-based membranes are obtained through blends with other polymer (usually chemically inert) suitable for membranes preparation. Composite membranes based on PANI with conductive properties are obtained. There are a large number of inert polymers used for PANI-based composite membranes preparation, the most used being cellulose and its derivatives, polysulphone, polystyrene and polypropylene.

PANI-based composite membranes are used in the majority of domains mentioned for conductive polymers, mainly for selective separation processes of some chemical species from

complex liquid solutions, selective separation of gases, development of biosensors, electric and electronic devices (LED, photovoltaic cells), anticorrosive films and fabrication of antistatic textile materials.

The most recent scientific researches on preparation and specific applications of PANI-based composite membranes are presented in the following paragraphs.

Fibre-type cellulose was used in nanocomposites fabrication through oxidative in situ polymerization of aniline within fibres microstructure [31]. Polymerization was made in oxidative conditions using ammonium peroxydisulphate in hydrochloric acid aqueous solutions in which cellulose fibres impregnated with aniline are suspended. From the fibres separated at the end of the process, which contain PANI in their microporous structure, polymeric films were obtained via phase inversion process. Similarly, a composite material using nanofibrils bacterial cellulose as support material for PANI was obtained [32]. Research works showed the growth of PANI content within the composite material at the same time with the increase of its electric conductivity, with the prolonged reaction time from 30 to 90 min. Prolonging reaction time more than 90 min resulted in a decrease of electric conductivity due to aggregation of PANI particles and creation of discontinuities within nanocomposite structure. At the optimum time, a nanomaterial with the best conductivity of cca. 5.0 S m^{-1} was obtained. Using this composite material, a flexible film (conductive membranes) that synergetically combines PANI conductive properties with mechanical strength (Young's modulus is 5.6 GPa and tensile strength is 95.7 MPa) provided by bacterial cellulose is obtained. The membranes obtained are applied in the field of electrochemical sensors, flexible electrodes and flexible displays. Compared with the processes in which first a nanocomposite material is obtained and then is used for conductive membrane preparation following a classic technique (phase inversion through immersion-precipitation technique), research works were conducted with the aim to obtain PANI-based composite conductive membranes following the next sequence: first, a semipermeable cellulose membrane is obtained and then on its surface, a thin layer of PANI is applied [33]. Deposition of the thin layer at membrane interface is realized via in situ polymerization of aniline with oxidative mixture containing ammonium peroxydisulphate in hydrochloric acid aqueous solutions. An aniline conversion of 80% was obtained after 24 h reaction time. At the end of the process, residual aniline was found on the active side of PANI membranes and secondary reaction products (ammonium hydrogen sulphate) obtained from ammonium peroxydisulphate were found on both sides of the membrane.

Cellulose esters are representing another class of polymeric materials used as support in preparation of PANI-based composite membranes. Investigations on PANI deposition on the surface of some microporous cellulose ester membranes were performed using two distinct techniques: deposition of PANI layer on membrane surface through in situ aniline polymerization in liquid phase or aniline polymerization in vapour phase [34, 35].

In situ polymerization of aniline in liquid phase was performed through dipping of one membrane from cellulose esters mixture in an aniline solution (PANI monomer) and FeCl_3 as oxidant [34]. In other experimental variant, aniline polymerization in liquid phase is made by immersion of pre-formed cellulose esters membrane in a solution that contains aniline and HCl followed by the addition (at a certain time) of oxidative agent such as ammonium

peroxydisulphate solution [35]. Aniline polymerization in vapour phase is done by soaking cellulose ester-based membrane in a solution of aniline and HCl and maintaining it in a closed tank with an oxidizing agent (ammonium peroxydisulphate and HCl solution)-saturated vapour atmosphere heated at 65–70°C [34, 35]. Cellulose acetate–PANI composite membranes with electric conductivities from 10^{-3} and 11 S m^{-1} (using the liquid phase polymerization) [34] and respectively 98 S m^{-1} (using the vapour phase polymerization) [35] were obtained.

Polysulphone (Psf) is another frequently used polymer in the preparation of polymeric membranes used in membrane processes based on gradient pressure driving forces (microfiltration, ultrafiltration, reverse osmosis). This diversity of uses is due to polymers physical-chemical characteristics (chemical inertness, very good plasticity, excellent solubility in usual solvents used within phase inversion process, good mechanical strength, etc.). Psf is used as a substrate for the preparation of Psf–PANI composite membranes designed for advanced separation of compounds with polar groups from various mixtures, capitalizing the conductive properties of PANI from their structure.

Within the Psf – PANI composite membranes, PANI is present in the whole membrane's microporous structure, not only on surface. Preparation method is also a specific one and is differentiating from those already described. Thus, research works aimed to prepare Psf–PANI composite membranes through simultaneous formation of Psf-base membrane and aniline polymerization in oxidative conditions within membranes under formation pores [36]. Practically, the process consists of solubilization of Psf polymer within a specific solvent (N-methyl-pyrrolidone or dimethylformamide) and aniline (PANI monomer), skinning of polymeric solution on a plane surface and immersion of polymeric film within an oxidative coagulation solution (ammonium peroxydisulphate and HCl). As the phase inversion process advances, Psf membrane is formed and within its pores PANI resulted from aniline polymerization in oxidative conditions.

Six types of composite membranes were obtained, using three polymeric solutions with 10, 12 and 14% Psf and two types of coagulants (distilled water and distilled water with 1.9% aniline). In all polymeric solutions, Psf was dissolved in a mixture of N-methylpyrrolidone and aniline. Obtained membranes were characterized from the point of view of flow and electroconductive properties through flows determination for solutions with variable pH (1, 3, 5, 7, 9 and 11), and selective separation properties were emphasized via determination of retention degree for standard proteins (albumin from bovine serum—BSA). BSA separation experiments proved that membranes obtained through coagulation from water and aniline solution present higher flows and retention degree compared to the membranes obtained by coagulation with only distilled water. For example, membranes obtained from 10% solution coagulated with water and aniline present a flow of $151.2 \text{ L/m}^2\text{h}$ at $\text{pH}=4.9$ and $196.3 \text{ L/m}^2\text{h}$ at $\text{pH}=7.4$ compared with membranes obtained from the same solution but coagulated in distilled water that showed a flow of $140.1 \text{ L/m}^2\text{h}$ at $\text{pH}=4.9$ and $189.4 \text{ L/m}^2\text{h}$ at $\text{pH}=7.4$. Retention degrees for membranes coagulated in water and aniline varied between 81.84 and 92.16% compared with 75.36–81.4% determined for membranes coagulated in distilled water.

Through this process composite membranes with conductive properties are obtained, having separation characteristics superior to those obtained using similar polymeric conditions that

contains only Psf. Performed research emphasized the dependence of Psf/aniline ratio from polymeric solution and structural and hydrodynamic characteristics of Psf-PANI composite membranes.

In order to diminish the errors at laboratory level, mainly the manual skinning of polymeric solution and variation during the phase inversion process of the coagulation solution composition, Psf-PANI-based composite membrane preparation was studied in a steady-state installation [37]. That induces a modification of composite membrane preparation technology such that in one tank Psf membrane forming takes place. Psf membrane has in its pre-formed pores a certain quantity of aniline, and finalization of its structure is made in a reaction tank filled with oxidative mixture in which polymerization of aniline from pores occurs.

Using a 10% Psf solution (MW = 22,000 Da) dissolved in a mixture of N-methylpyrrolidone and aniline, membranes in a continuous system in the following working conditions were prepared: thickness of the polymeric film is equal to 0.2 mm, speed of the carrier in the tanks is equal to 1 m/min, temperature of the oxidative solution is equal to 25°C and reaction time is equal to 2 h. Characterization via distilled water flow for nine samples from the same membrane led to a maximum relative deviation of flow values of 2.45%, proving that through this approach, Psf-PANI composite membranes with reproducible hydrodynamic and conductive properties both in the entire surface and from one batch to other are obtained.

Other polymers studied as support materials in order to develop composite membranes based on PANI, with conductive polymers, are polystyrene [38, 39] and polypropylene [40]. Thus, from blends containing PANI and polystyrene in various ratios, dissolved in N-methyl-2-pyrrolidone, flexible polymeric films were obtained via phase inversion process, phase changing taking place through precipitation in vapour phase [38]. The particularity of the method consists in the fact that PANI was obtained in a separate oxidative polymerization process: a reaction media formed from aniline and alcoholic solution of 0.1 M H₂SO₄ in a volumetric ratio of 1/25 is cooled to -5°C; a solution containing ammonium peroxydisulphate as initiator is slowly added in a 2-h period within the reaction mixture; obtained PANI polymer is filtered and washed with acetone and a solution of 0.1 M NH₄OH and mixed for 24 h; after that the polymer is filtered again, washed with distilled water and dried at 60°C for 24h. After drying, PANI and polystyrene are dissolved in N-methyl-2-pyrrolidone, the solution being coated on a support that is heated in an oven at 60°C for 24 h. Finally, the composite membrane obtained is removed from the support and subjected to doping process by immersing in a 5 M HCl solution for 9 min and dried afterwards [38].

Obtained polystyrene-PANI composite membranes present conductive properties depending on polystyrene/PANI ratio within the solution.

Polystyrene is used also in functionalized sulphonated form for the preparation of PANI-based composite materials [39]. Both polymers are obtained simultaneously in the same reaction environment consisting of aniline (PANI monomer), 4-styrene sulphonic acid sodium salt hydrate (sulphonated polystyrene monomer), ammonium peroxydisulphate and HCl (for oxidative polymerization).

The working procedure is the following: within a 3.47 mM aqueous solution of 4-styrene sulphononic acid sodium salt hydrate, heated at 80°C, the oxidant ammonium peroxydisulphate (aqueous solution 4.86 M) was added drop wise in a volumetric ratio of 1/7 to styrene solution, under mixing for 1 h; after that an aqueous solution of aniline chlorhydrate 0.58 M (volumetric ratio of 1/8 to mixture) is added and after another 15 min a new quantity of 4-styrene sulphononic acid sodium salt hydrate (aqueous solution with a concentration of 0.72 M in a ratio of 1/9 to reaction media) was added drop wise; the reaction media is maintained under mixing at 80°C for 3 h, and afterwards the temperature drops to ambient temperature in a 24-h period. The composite polymer is precipitated in iso-propanol for 24 h without mixing and is washed with ethanol and dried at 70°C.

Obtained composite material contains in its structure PANI and sulphonated polystyrene macromolecular linked with chemical bonds (ionic bonds) through diimino protonated groups of PANI and sulphonic groups of sulphonated polystyrene. Due to these bonds, the conductive capacity of the composite material is lower compared with the above-presented composite materials, being practically a semiconductor. This composite material is used for polymeric membranes preparation through classic processes, dense films for antistatic packages, anticorrosive material or semiconductors.

Polypropylene is used as support material for preparation of PANI-based composite materials in the form of microporous membrane film through biaxial stretching technique [40]. PANI is formed within the polypropylene pores membrane through soaking of polymeric film in aniline followed by aniline oxidative polymerization using ammonium peroxydisulphate and HCl. Polypropylene—PANI composite membranes maintain the microporous structure of the support polymer, with various pores diameters and present conductive properties. These composite membranes are used in selective separation of chemical species from various liquid media through microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

Besides polymeric materials, inorganics can be used as support for PANI-based composite materials. Thus, zeolites were used for new zeolite-PANI composite materials preparation due to their microporous structure and adsorption capacities [41]. Method consists of polymerization of aniline retained within zeolite matrix (Molecular Sieve 13X – SUPELCO Analytical) in oxidative conditions similar to those described previously (ammonium peroxydisulphate and HCl). The composite material is included within a quartz filter structure resulting in an inorganic-organic membrane with ultrafiltration flow rate properties. Conductive properties of these membranes (due to the PANI inclusion within their structure) allow separation of chemical species with high pollution potential from wastewater, such as heavy metals ions (Pb, Cu, Zn) and phenol derivatives (phenol, aminophenols or nitrophenols). Thus, retention degrees determined for heavy metal ions were 72.59% for Pb²⁺, 87.48% for Zn²⁺ and 99.55% for Cu²⁺. Phenol derivatives from wastewater were removed using these composite materials with efficiencies above 98% (phenol, 98.15%; aminophenol, 99.78%; nitrophenol, 99.23%).

2.2.2. Polypyrrol-based membranes and their applications

Polypyrrol (PPy) is a polymer obtained by pyrrol oxidation (Py) in the form of a black powder. This polymer has poor mechanical strength and thus low processibility. Its conductive

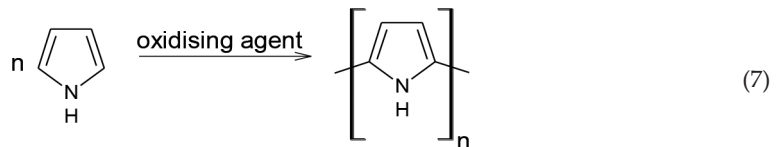
properties in natural state are very low, and it is rapidly oxidized in contact with air, changing its properties. PPy conductivity is given by the existence within its structure of π conjugated electron systems (from pyrrol ring) with p electrons available at N atom from pyrrol ring. This property is significantly improved by PPy "doping" with anions such as chloride, sulphate, perchlorate, dodecylsulphate and other organic compounds. Doped PPy is a polymer characterized by good chemical and thermal stability and better conductivity compared with other conductive polymers. Disadvantages related to PPy mechanical strength, plasticity and elasticity are improved both through doping process and by inclusion (as doped form, similar with PANI) within the polymeric and inorganic composite materials structure. PPy-based composite materials are frequently used as membranes within the processes in which driving force is no longer the pressure gradient but concentration gradient (gas separation from complex mixtures and pervaporation) and electric potential gradient (electro-dialysis).

During the last period, the research works related to PPy-based composite materials studies are focussed on their application in electro-analysis, medical field (systems for controlled release of drugs and use as biomaterial for artificial muscles) and antistatic and anticorrosive protection.

PPy polymerization in PPy-based composite materials is done through two methods: *polymerization through chemical oxidation* and *electrochemical polymerization* [42].

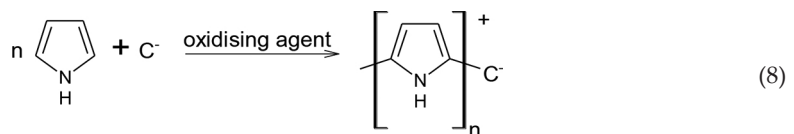
Ammonium peroxydisulphate, hydrogen peroxide and various compounds based on transitional metals salts (Fe^{2+} ; Cu^{2+} ; Cr^{6+} ; Mn^{2+} ; etc.) are frequently used as oxidative agents for the polymerization through chemical oxidation.

The process is presented in Eq. (7):



PPy polymeric chain can contain Py linked with three types of dimer sequences [8], presented in **Figure 5**.

Addition within the chemical oxidation reaction media of surfactants such as sodium dodecylbenzenesulphonate and sodium alkylsulphonate and alkylnaphtalenesulphonate results in an increase of electric conductivity of the composite material and Py polymerization efficiency [42]. Electrochemical polymerization is performed in conditions mentioned within Section 1.2 based on application of an electric current between two electrodes immersed in a Py solution that contains also the dopant, in accordance with Eq. (8):



where C^- is counterion.

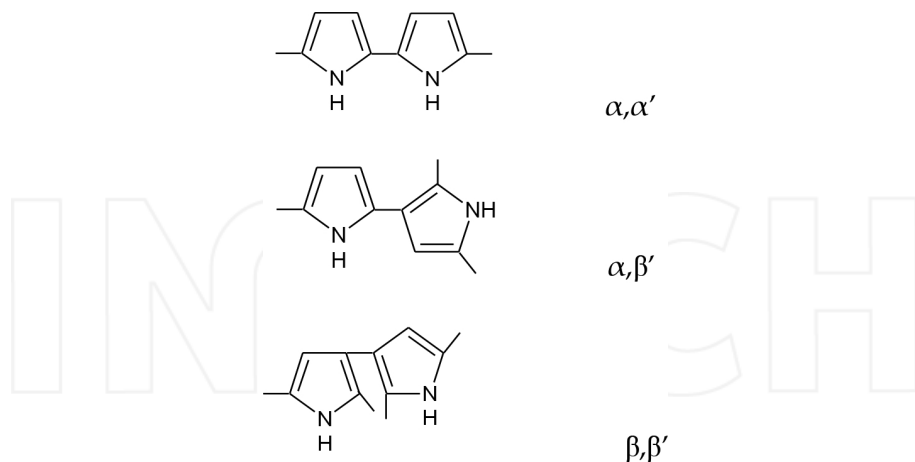


Figure 5. Dimer sequences within PPy structure. (a) α, α' , (b) α, β' and (c) β, β'

The Py chemical oxidative polymerization was applied to obtain membranes with high permeability for gas separation. Membranes were obtained through the technique of deposition in thin layers through interfacial polymerization [43, 44]. A freestanding polymeric film, 200–300 nm thick, was obtained by Py polymerization on an inert glass support through mixing of oxidative agent aqueous solutions containing ferrous chloride (0.4 M) and ferric chloride (0.5 M) with a solution of Py dissolved in an organic solvent (n-hexane) [43]. The membranes were prepared by pouring a solution of polydimethylsiloxane dissolved in n-hexane on PPy surface, after oxidant excess removal and polymeric film washing with methanol. The contact between components was maintained for 24 h and after that the composite membrane was annealed in air at 80°C for 15 min. Finally, the composite membrane is removed from the glass surface by simple washing with water. Obtained composite membranes present high selectivity for separation of oxygen and nitrogen from various mixtures, separation ratios O_2/N_2 of 17.2 being reported. The permeability for O_2 was 40.2 barrer. Using the same method of interfacial polymerization through chemical oxidation of Py or its derivatives (N-methylpyrrole), PPy-based conductive composite membranes with applications in the field of gas separation and pervaporation were obtained on a surface of microporous membrane supports [44]. Polymerization was performed at chamber temperature for 4 h using an aqueous 0.5 M Py solution and ferric chloride solutions (0.5, 1, 2 or 3M) as oxidative agent. The obtained membranes were washed with deionized water and stored in a 1 M HCl solution, and the operation was repeated daily for a week. In the final, membranes were stored in deionized water prior to characterization and use.

The Py chemical oxidative polymerization was used also for the preparation of PPy-based composite membranes having pre-formed membranes from sulphonated poly(styrene-co-divinylbenzene) as support, with its biotechnological applications and applications in

wastewater treatment through electro-dialysis [45]. PPy polymer was formed through chemical oxidation within the structure of a commercial membrane with cationic exchange properties (Selemion CMT, manufactured by Asahi Glass Co.). The process consists of immersion of commercial membrane soaked in a ferric chloride oxidant solution in a Py aqueous solution at chamber temperature for about 4 h.

Similar properties related to ion exchange and possibility to apply in electro-dialysis also present PPy-based membranes obtained via Py chemical oxidative polymerization within the microporous structure of some inert polymeric supports [46] or inorganic supports [47]. In the first case [46], composite membrane is formed in one single stage through phase inversion techniques and chemical oxidation reactions. A solution of polysulphone and PPy dissolved in a N,N-dimethylformamide/methanol solvent system is coated on a plane surface and then immersed in a ferric chloride oxidant solution. At the same time, with formation of microporous polysulphone support, the chemical oxidative polymerization of Py within the preformed pores takes place. In the second case [47], the process consists of polymerization of adsorbed Py into silica through chemical oxidation, resulting in PPy inorganic-organic composite membranes.

PPy obtained through chemical oxidative polymerization is used as base material for medical devices [48, 49] due to its conductive properties. Py polymerization takes place in controlled conditions, a special attention being given to PPy doping and modification in order to be biocompatible. On PPy structure are engrafted biomolecules or cells (mammalian cells, endothelial cells, mesenchymal stem cells, etc.) through adsorption of covalent bonding [48]. Other studies emphasized the use of PPy incorporated in poly(ϵ -caprolactone) and gelatin nanofibres for cardiac tissues [49]. Performed experiments proved that increase of PPy concentration up to 30% within the composite material resulted in a reduction of average diameter of fibres from 239 ± 37 to 191 ± 45 nm, at the same time, with an increase of about six times of tensile modulus (7.9 ± 1.6 MPa initial and 50.3 ± 3.3 MPa after introduction of PPy).

Other applications of PPy-based composite membranes prepared through Py chemical oxidation is in the antistatic and anticorrosive materials field. Polyethylene used as natural [50] or modified [51] polymer constitutes an excellent polymeric material for the preparation of PPy composite membranes due to its properties (good mechanical strength, plasticity, elasticity) needed for membranes preparation. Thus, within the pores of polymeric films obtained through melt extrusion with subsequent annealing, uniaxial extension and thermal fixation, PPy was deposited through Py chemical oxidative polymerization [50]. Using another technique [51], polyethylene polymeric film is modified through engraftment within its structure of another polymer realized through acrylic acid irradiation with γ rays. Obtained material is highly hydrophilic which contributes to a better Py retention through surface adsorption that is further polymerized through chemical oxidation using iron chloride (III) or ammonium peroxydisulphate. Performed researches [51] were focussed on increase of electric conductivity of the composite material through increase of Py concentration within the reaction media from 0.3 to 0.9 M, but obtained results proved that this was insignificant (from 162 to 166 S m⁻¹). Introducing a new Py polymerization phase resulted in an increase of electric conductivity from 166 to 543 S m⁻¹.

PPy obtained via electrochemical method has similar application with those of PPy obtained through chemical oxidation.

Thus, PPy membrane formed on stainless steel net is used for separation of ethanol and cyclohexane mixtures through pervaporation [52]. Electrochemical polymerization takes place in a four-cell installation with porous glass walls and three electrodes. One of the electrodes is made from stainless steel net obtained through weaving of stainless steel fibre with 25 or 18 μm diameter. Within the cell that contains this electrode, a solution of 0.1M Py, acetonitrile as solvent and a doping agent (Me_4NBF_4 0.05 M, Bu_4NBF_4 0.1 M or Bu_4NPF_6 0.1 M) are administered. Formed pervaporation membranes were tested in a specific installation and are proved to be selective for ethanol, permeation being dependent on Py polymerization degree and dopant type.

Using a similar method, electrochemical polymerized PPy deposited onto platinum sputter-coated polyvinylidene filters was obtained [53]. Process was realized through introduction within the cell containing filters of a Py aqueous solution containing as doping agents 8-hydroxyquinoline-5-sulphonic acid (HQS) or 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline disulphonic acid (BCS). PPy/BCS-type conductive membranes are permeable to a series of ions such as Co^{2+} , Ni^{2+} , Zn^{2+} , K^+ , Mg^{2+} , Ca^{2+} , Mn^{2+} , Fe^{3+} and Cu^{2+} . PPy/HQS conductive membranes are not permeable to all above-mentioned ions, significant results being obtained only for K^+ , Co^{2+} and Cu^{2+} . Moreover, ion fluxes are much higher (more than 10 times in case of Cu^{2+}) for PPy/BCS compared with PPy/HQS membranes. Conductive membranes with permeability for Na^+ , K^+ , Ca^{2+} and Mg^{2+} ions were obtained in similar conditions with those described above with the difference that PPy was deposited onto platinum sputter-coated polyvinylidene fluoride filters and polystyrenesulphonate/dodecylbenzenesulphonate (1%) or polyvinylphosphate/dodecylbenzenesulphonate systems were used for doping [54]. It was proved that ions transport fluxes are varying in the following order: $\text{Na}^+ > \text{K}^+ > \text{Ca}^{2+} > \text{Mg}^{2+}$.

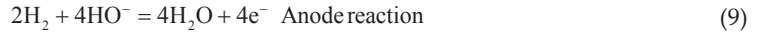
Another domain that was thoroughly studied in the last period and uses PPy polymers obtained in the form of membrane films via electrochemical polymerization is that of electroanalysis. Through deposition of PPy membrane on the Al_2O_3 surface of one electrode, amperometric sensors with multiple uses in the field of analytical chemistry is obtained [55]. PPy membrane is prepared through electrochemical polymerization of Py on the electrode surface using an aqueous solution 0.2 M Py and 0.1 M KCl (dopant) or 0.1 M Py and 0.5 M $\text{K}_4[\text{Fe}(\text{CN})_6]$ (dopant).

PPy based membranes applications within fuel cells domain should be mentioned also. The conductive polymers applications in the field of fuel cells are presented within the next section.

2.2.3. Conductive polymers based membranes used for fuel cells

Fuel cells are devices that generate electricity based on the free energy of a chemical reaction. A classical fuel cell consists of a porous anode fed with gas fuel that after oxidation led to electrons release; a porous cathode fed with oxidant, which generates protons and an electrolyte located between the two electrodes; and two bipolar plates and electric connectors that

are linking electrodes through an exterior circuit. Chemical reactions for a classic combustion cell are presented in Eqs (9–11).



where E = electrical energy and H = heat.

Type of fuel cell	Operating temperature (°C)	Electrolyte	Reaction
			At the anode (A) At the cathode (C)
AFCs	60–90	KOH (liquid)	(A) $\text{H}_2 + 2\text{HO}^- = 2\text{H}_2\text{O} + 2\text{e}^-$ (C) $1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- = 2\text{HO}^-$
PEMFCs	60–120	Polymer- SO_3H (solid)	(A) $\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$ (C) $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$
DMFCs	60–120	Polymer- NR_3 (liquid)	(A) $\text{CH}_3\text{OH} + 6\text{HO}^- = \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$ (C) $3/2\text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- = 6\text{HO}^-$
PAFCs	160–220	Phosphoric acid H_3PO_4 (liquid)	(A) $\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$ (C) $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}$
MCFCs	600–800	Molten salt $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ (liquid)	(A) $\text{H}_2 + \text{CO}_3^{2-} = \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ (C) $1/2\text{O}_2 + \text{CO}_2 + 2\text{e}^- = \text{CO}_3^{2-}$
SOFCs	800–1000	Ceramic $\text{ZrO}_2/\text{Y}_2\text{O}_3$ (solid)	(A) $\text{H}_2 + \text{O}^{2-} = \text{H}_2\text{O} + 2\text{e}^-$ (C) $1/2\text{O}_2 + 2\text{e}^- = \text{O}^{2-}$

Table 2. Main combustion cell type's characteristics.

These devices present large spectra of applications due to the fact that global efficiencies obtained for electricity are higher than those of classical systems (thermic engines or hydroelectric turbines). At the same time, the effects induced upon the environment are less harmful than those produced by other electricity-producing systems such as fossil fuels burning.

Fuel cells can be classified based on two main criteria: electrolyte nature (charge carriers HO^- , H^+ , CO_3^{2-} or O^{2-}) and operation temperature. Based on the latter criterion, fuel cell types are: *low temperature*—alkaline fuel cells (AFCs— $T < 100^\circ\text{C}$), polymer electrolyte fuel

cells (PEMFCs— $T = 60\text{--}120^\circ\text{C}$), direct methanol fuel cells (DMFCs— $T = 60\text{--}120^\circ\text{C}$), phosphonic acid fuel cells (PAFCs— $T = 160\text{--}220^\circ\text{C}$) and *high temperature*—molten carbonate fuel cells (MCFCs— $T = 600\text{--}800^\circ\text{C}$), solid oxide fuel cells (SOFCs— $T = 800\text{--}1000^\circ\text{C}$).

Table 2 is summarizing the main combustion cell types depending on operating temperature, electrolyte nature, anode (A) and cathode (C) reactions.

Conductive polymer membranes are thoroughly studied due to advantages offered by the fact that they function both as solid electrolytes and as selective separation barriers for the species implied in electricity generation within the fuel cells.

First applications were based on preparation and inclusion within the fuel cells structure of protons exchange membranes—Nafion, obtained from persulphonic acid and PTFE by Dupont Company 30 years ago. Nowadays researches are focussed on preparation of conductive polymers membranes with improved electric and mechanical properties. The most recent researches in preparation of both conductive membranes with protons exchange properties, applicable in PEMFCs, and conductive membranes applicable to AFCs are reviewed in the following paragraphs.

In a study dedicated to this domain [56] are emphasized the large number of composite membranes based on conductive polymers used for fabrication of high temperature proton exchange membrane fuel cells. Both organic composite membranes based on polymers with electric properties such as sulphonated poly (p-phenylene), sulphonated poly(ether ether ketone), sulfonated polysulfone, sulfonated poly (arylene ether sulfone), sulfonated poly(aryl ether ether nitrile), sulfonated poly(sulphide ketone), and organic-inorganic composite membranes such as fluorinated polymer/SiO₂, polyalkoxysilane/phosphotungstic acid, Nafion/PTFE/zirconium phosphate, Nafion/TiO₂ and Nafion/SiO₂ are reviewed.

One of the most studied polymers for organic composite membranes with applications in fuel cells is poly(ether ether ketone) (PEEK), which is used in base or modified form. Thus, from sulfonated poly(ether ether ketone) (SPEEK), asymmetric microporous membranes can be obtained via phase inversion method and immersion-precipitation technique. The SPEEK polymer was obtained by dissolving PEEK in concentrated H₂SO₄ added in a proportion of 5 wt%, at room temperature, reaction media being maintained by mixing for 24 h. From the resulted solution, a membrane was prepared by coating on a plane glass surface, followed by immersion in a coagulation bath containing distilled water (phase inversion method, immersion-precipitation technique). The obtained membrane is modified through in situ polymerization (within membrane pores) of Py doped with iron chloride and cerium sulphate [57]. Electroconductive properties of PPy from composite membrane structure (ionic conductivity of 0.34 S m⁻¹) made the membrane suitable for fuel cells.

Composite membranes are obtained, using SPEEK as base material, through inclusion within its structure of heteropolycompounds based on tungsten, molybdenum or wolfram [58]. Obtained composite membranes present a conductivity of 1 S m⁻¹ at chamber temperature and 10 S m⁻¹ at 100°C temperature, being used in PEMFC-type fuel cells.

Other studies on SPPEK applications for fuel cells showed that it can be functionalized with quaternary amine hydroxide and imidazolium hydroxide [59] (resulting membranes with 10^{-3} S m⁻¹ conductivity) or by PANI inclusion within membrane structure [60].

Polysulfone [61] and poly(1,4-phenylene ether ether sulfone) [62] are other polymeric materials that can be used to obtain composite membranes with conductive properties for fabrication of fuel cells. Using polysulfone, asymmetric membranes can be obtained via classical process of phase inversion and afterwards functionalized through incorporating acrylamide-based ionomers having proton-conducting sulphonics groups. Incorporation process of the new polymer is based on photopolymerization [61]. At the surface of membranes prepared from poly(1,4-phenylene ether ether sulfone) modified through addition of tungstophosphoric acid, a layer of PPy polymer is applied via chemical oxidation, resulting in composite membranes used for fabrication of DMFC [62]-type fuel cells.

Fuel cells protons exchange composite membranes, which can be used at temperature above 100°C, were obtained from poly(2,6-dimethyl-1,4-phenylene oxide), N-(3-aminopropyl)-imidazole and metal – organic frameworks [63].

Composite membranes with applications at high temperatures, for fuel cells, are obtained also from bi-functionalized copolymer prepared through radical copolymerization, having SiO₂ [64] within in its structure.

Another point of interest within the literature is represented by preparation of membranes for alkaline fuel cells. Studies performed in this domain [65, 66] classify conductive membranes for preparation of AFCs in heterogeneous and homogeneous membranes, each with their specific polymers and preparation methods. One of the most recent researches related to membranes for alkaline fuel cells is focussing on preparation of high ionic conductivity membrane from crosslinked poly(arylene ether sulphones) [67].

Besides traditional methods for preparation of polymeric membranes with conductive polymers (phase inversion, lamination, irradiation, etc.), a new technique was recently developed—plasma techniques both for plasma polymerization and for plasma modification of membrane surfaces [68]. Proton exchange membrane for PEMFCs and membranes for alkaline fuel cells (AFCs) can be obtained using this technique.

3. Conclusions

Conductive polymers themselves are not forming membranes that can be used in various processes due to low mechanical strength, lack of elasticity and plasticity. For this reason, conductive polymer-based membranes are mainly composite membranes.

Preparation methods of composite membranes based on conductive polymers are similar to those used for simple membranes (sintering, lamination, irradiation, phase inversion, deposition on thin layers) for the formation of support polymer that confers mechanical strength and elasticity. Chemical oxidation polymerization and electrochemical polymerization are

used for the inclusion within the support structure of a polymer with conductive properties. There are three ways for preparation of composite membranes presented within the literature:

- Conductive polymer is formed at the same time with support membrane; in this case, the composite membrane contains the conductive polymer in all its structure;
- Conductive polymer is formed after support membrane preparation and its soaking in monomer solution followed by polymerization through chemical oxidation; in this case, composite membrane contains conductive polymer in all microporous structure;
- Conductive polymer is formed only after preparation of support membrane through deposition on its surface of conductive polymeric film; in this case, composite membrane contains in its structure two different layers—sandwich type.

Conductive properties of polymers that contain conjugated electrons systems (π - π or p - π) are low compared with metals, being at the level of semiconductors. In order to obtain polymers with better conductive properties, “doping” technique is used, through introduction within polymeric chain of atoms or groups of atoms that creates “defects” within macromolecule structure as a result having more rapid “jumping” of electrons between polar centres. Doping process takes place simultaneously with conductive polymer formation within the composite membrane structure, through dopants addition within monomer solution. Doping process takes place with conductive polymer preparation in some rare cases.

Conductive polymer-based composite membranes are used in membrane processes that generally use concentration gradient (pervaporation and gas separation) and electric potential gradient (electro-dialysis) as driving forces. There are also cases in which these membranes are used in processes that uses pressure gradient (MF, UF, RO). Many researches are focussed on conductive polymer-based composite membranes’ use for fuel cells.

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