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Chapter

Benzimidazole as Solid Electrolyte Material for Fuel Cells

Daniel Herranz and Pilar Ocón

Abstract

This chapter is focused in the application of benzimidazole, mainly in the form of poly[2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole] (PBI) and poly(2,5-benzimidazole) (ABPBI), in the fuel cell technology. A short introduction is given of the fuel cell principles, explaining both the theory and the high importance of this technology. PBI and ABPBI are used in a certain type of fuel cells: the polymer electrolyte fuel cells and are key materials in the composition of some of the electrolyte membranes used. Commercially available membranes composed of PBI are indicated in order to give an overview of their potential performance. The synthesis of the polymers is explained. Moreover, the preparation of the different kinds of membranes, both in proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs) is studied. A deep description is given about the properties that make this family of compounds so interesting for the fuel cell technology as well as an how these polymers have been characterized with the corresponding analysis. The comparison with other ion exchange membranes is also discussed. Special attention will be given to the state of the art of different kinds of PBI/ABPBI fuel cell electrolyte membranes, in which our group and others are working nowadays.

Keywords: polybenzimidazole, electrolyte, fuel cells, proton exchange membrane, anion exchange membrane

1. Introduction

Benzimidazole and its family can be used in the energy world easily in the form of polymers, since these materials have the possibility to create designed structures for many applications. The fuel cells and electrolyzers are emerging technologies with wonderful potential. In these technologies, an electrolyte is needed to separate two electrodes where electrochemical reactions occur. The separation must be physical and electrical, but the electrolyte allows the ionic conduction of ions in order to close the circuit (so the current goes through the external circuit and can be used) and to make possible the continuity of the reactions at the electrodes. Here is where benzimidazoles (in the form of polybenzimidazole, e.g.) play a key role, in the conformation of a solid polymer electrolyte membrane, alone or with other chemical materials.

But, what is a fuel cell? What do we understand for membranes in this field? Fuel cells are electrochemical devices that convert directly the chemical energy of the reagents into electrical energy and side-products via an electrochemical reaction. This process allows theoretical efficiencies as high as 80% [1], which is a wonderful advantage compared to the thermal machines limited thermodynamically by the Carnot cycle. There are many types of fuel cells, the most relevant are alkaline fuel cells (AFCs), polymer electrolyte membrane fuel cells (PEMFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs).

Polymer electrolyte membrane fuel cells have as principal characteristics the low operation temperature (<120°C), high power density, and easy scale-up, making them a promising technology for power generation. Their main application fields are backup power, portable power, distributed generation, and transportation [1]. It is relevant to note the role of transition energy technology, since they can play an important function in the near future in order to overcome the fossil fuel depletion and mitigate the climate change. The reason is that fuels like hydrogen or alcohols, which are produced by unsustainable ways, could be produced with renewable energies. An example of this is the actual production of hydrogen mainly from catalytic reforming of methane and just some from electrolysis [2]. The hydrogen can be produced from electrolysis powered with electricity coming from renewables. This should be done when production is higher than the demand, allowing to store chemically the energy and later use it when needed with a PEMFC; this is known as the "hydrogen economy system." It is also possible to accumulate energy in short-chain alcohols like methanol or ethanol and use them to power PEMFCs [3, 4], mainly used in the portable applications. A great advantage of this technology is the low pollution associated with the process. For example, when hydrogen is used as fuel, the only products are electricity and water. The potential of PEMFCs is really promising but still drawbacks as high cost (mainly from the expensive catalysts based in Pt) and low durability have to be overcome for a general commercialization [1].

In PEMFCs one of the most important components is the polymeric ion exchange membrane (IEM) that works as an electrolyte. It has to be an electrical insulator to force the produced electrons to go through the external circuit, it also has to avoid the mixture of the reagents supplied in anode and cathode, and it is responsible of the adequate ionic conductivity of the ions traveling through it. Depending on the ion movement, two types of IEMs can be distinguished: anion exchange membranes (AEMs), where the ionic charge carriers are the hydroxide ions (OH^-) that travel from cathode to anode, and cation exchange membranes (CEMs) where generally the proton ion (H^+) moves from anode to cathode in the fuel cell. For that reason, the last ones are also called proton exchange membranes (PEMs). The AEMs are used in alkaline media and the others in acid media. The proton exchange membrane fuel cells (PEMFCs) have been historically more used because of the discovery of the Nafion® membrane that has good ionic conductivity and durability and has been the standard so far [5]. The higher mobility of the H^+ ion compared to OH^- in aqueous media has also been a relevant factor [6]. The alkaline media in the other hand does not have a standard membrane and presents relevant advantages that have produced high interest in the last years. Some of them are the faster electrochemical kinetics in the alkaline media, possible absence of noble metals as catalysts, minimized corrosion problems, and cogeneration of electricity and valuable chemicals [7].

Independently of the media, membranes are expected to have good ionic conductivity, long-term chemical and electrochemical stability, adequate mechanical strength, good moisture control, low fuel or oxygen crossover, and production costs compatible with intended application [5, 6].

In the FCs, the active materials (fuel and oxidant) are continuously fed and extracted. The fuel cell, **Figure 1**, is made up of two electrodes: the anode, where the

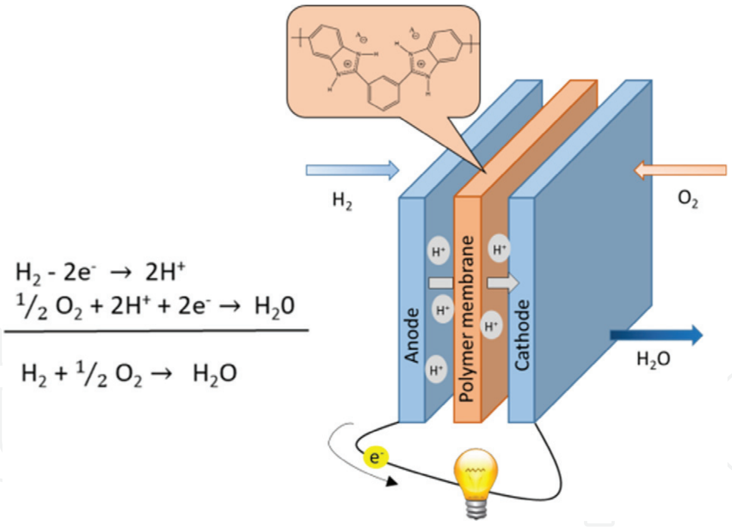

Figure 1.
Polymer exchange membrane fuel cell working with H_2 and O_2.

fuel is oxidized, and the cathode, where the oxidant (O_2) is reduced. It also involves an electrolyte, which acts as an ionic conductor and electrical insulator. The electrons obtained in the anode are addressed directly to the cathode through the external circuit, generating an electric current directly usable. In addition, the protons produced in the anode go through the electrolyte, up to the cathode to reduce O_2, generating water as the only product of the reaction. The reaction is exothermic and has a value of $\Delta H^0{}_r = -285.83$ kJ/mol for H_2O (l) and − 241.862 kJ/mol for H_2O (v). Although this is a spontaneous reaction, it needs to be catalyzed to be operational, since the kinetics of the process is too slow otherwise.

At atmospheric pressure, the maximum potential difference obtained by the fuel cell will be determined by the difference of energy between the initial and final state of the system. The Gibbs free energy variation of the process, ΔG, can be calculated from the operation temperature (T) and changes with both enthalpy (ΔH) and entropy (ΔS) of the reaction. Under standard conditions

$$\Delta G^0 = \Delta S^0 - T\,\Delta S^0 \tag{1}$$

and the maximum potential difference, obtained in the fuel cell, $E^0{}_{\text{theoric}}$, will be

$$E^0 = \frac{-\Delta G^0}{nF} = 1.23V \tag{2}$$

where n is the number of electrons exchanged and F is Faraday's constant. At 298 K and 1 atm, $\Delta G^0 = -237.340$ J/mol and therefore $E^0 = 1.23$ V. For an operating temperature of 80°C, the values of ΔH and ΔS change, but slightly, and the decrease in ΔG will be mainly due to the temperature, resulting in a theoretical potential difference of 1.18 V approximately. However, in practice this potential, called the open circuit potential, is significantly lower than this potential value, usually less than 1 V. This suggests that some losses appear in the fuel cell even when no external current is generated. The potential difference of the fuel cell in operation, that is, when the current is passing through the system, $E_{\text{fuel cell (I)}}$, will be given by the sum of thermodynamic or reversible value (I = 0), minus the anode and cathode activation overvoltage and the ohmic losses or overvoltage. The electrode kinetics was represented by the Butler-Volmer equation, the mass transport process was described by the multicomponent Stefan-Maxwell equations and Fick's law, and the ionic and electronic resistances are described by Ohm's law. The E $_{\text{fuel cell (I)}}$ value could be obtained by

$$E_{fuel\ cell\ (I)} = E_{Reversible\ (I=0)} - \eta_{activation} - \eta_{ohmic} \tag{3}$$

The losses considered are in relation to the activation overvoltages, and they are dependent on the kinetics of the processes involved and therefore directly related to the goodness of catalyst used for the process. Thus, $\eta_{\text{activation}}$ is related directed with both the oxidation kinetic reaction and the reduction kinetic reaction of the reagent involved in the catalysts surface materials. The $\eta_{\text{activation}}$ for an H_2/O_2 fed in PEMFC will come mainly determined by the slow kinetics of oxygen reduction reaction (ORR) on the catalyst material in comparison to H_2 oxidation, while $\eta_{\text{activation (transport)}}$ is the consequence of material transport. This overpotential considers the combination of the flow of reactants and products in the fuel cell. The polarization from concentration gradients occurs when a reactant is rapidly consumed at the electrode by the electrochemical reaction so that gradients are established. The η_{ohmic} = iR will be due to the combination of resistors provided by internal/external electrical contacts and ionic resistance due to ion motion through the membrane. Therefore, the fuel cell when current is not zero has an $E_{\text{fuel cell(I)}}$ expression like this:

$$E_{fuel\ cell\ (I)} = E_{rever\ (I=0)} - \frac{RT}{\alpha_c} ln\left(\frac{i}{i_{0,c}}\right) - \frac{RT}{\alpha_a} ln\left(\frac{i}{i_{0,a}}\right) - \frac{RT}{\alpha_c} ln\left(\frac{i_{I,c}}{i_{I,c} - i}\right) - \frac{RT}{\alpha_a} ln\left(\frac{i_{I,a}}{i_{I,a} - i}\right) \tag{4}$$

$$E_{rev\ (I=0)} = 1.229 - \left(8.5 \times 10^{-4}\right)(T - 298.15) + \left(4.308 \times 10^{-5}\right)T[\ln(P_{H2}) + 0.5\ln(P_{O2})] \tag{5}$$

being i_{oc}, α_c, i_{Lc} and i_{oa}, α_a, i_{La} the exchange current density, transfer coefficient, and limit current density of the cathodic and anodic processes, respectively [8]. The polarization curve of the device can be found in **Figure 2**, where the different losses mentioned above are indicated.

It was previously stated that the ion exchange polymer membrane is electrically insulator and practically impermeable to reactant gases, but some small amount of mainly H_2 will crossover from anode to cathode. Hydrogen that permeates through the membrane does not participate in the electrochemical reaction on the anode

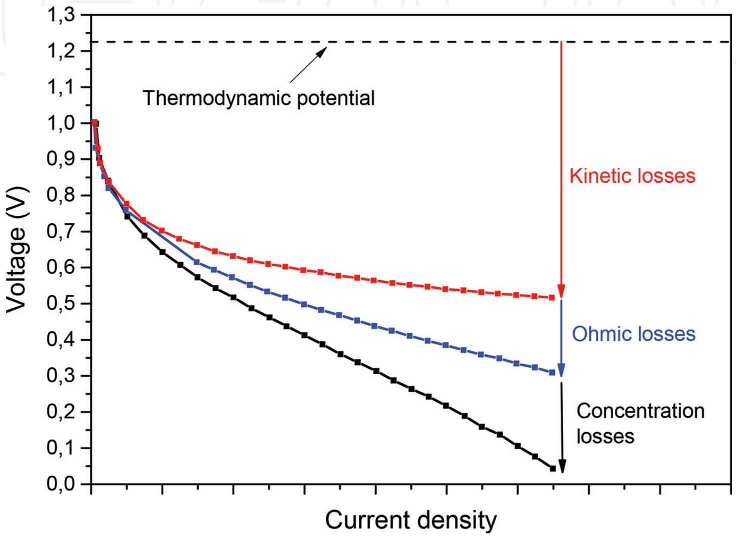

Figure 2.
Polarization curves with voltage losses of a fuel cell.

side. Each hydrogen molecule on the cathode side reacts with oxygen on the surface of the catalyst resulting in two fewer electrons in the generated current that travels through the external circuit and thus in a reduction of cathode and the overall fuel cell potential. These losses are not big in fuel cell operation, but when the fuel cell is at open circuit potential or at very low current densities, this situation may have a dramatic effect on fuel cell potential. At least, all these losses have to be taken into account when the device works and have a lot to do with good fuel cell performance.

2. Synthesis of polybenzimidazole materials

Polybenzimidazoles are synthesized by the repetitive reaction of aromatic amino groups with carboxyl groups using a 1:2 molar ratio by the process of step-grow polymerization [9]. Usually the monomer reagents are a diacid and a tetra-amine, like the example in **Figure 3**. There are many polybenzimidazoles but the ones that have presented better application and have been more studied are poly(2,2′-(*m*-phenylene)-5,5′-bibenzimidazole), known as PBI, and poly(2,5-benzimidazole), known as ABPBI. Both were first synthesized by Vogel and Marvel in 1961 [10]. For PBI the synthesis was a two-step process with an intermediate prepolymer that prevented the production of high molecular weight polymer. Cho et al. [11, 12] discovered a process with 3,3′,4,4′-tetraaminobiphenyl (TAB) and isophthalic acid (IPA) to do the synthesis in a single step obtaining high molecular weight, in the presence of catalyzers and at temperatures higher than 350°C. It is important to know the molecular weight of the polymer, which is obtained by the measurement of the inherent viscosity (IV, in dLg^{-1}) of the polymer dissolved in concentrated sulfuric acid. For membrane application, usually casted from solution, it is interesting to have high molecular weight in order to achieve mechanically stable membranes that can support higher doping and thus obtain better ionic conductivity. The previously described method of Vogel and Marvel and Cho et al. can be classified in the heterogeneous molten/solid state synthesis [13, 14]. The other synthesis method used is the homogeneous solution synthesis, using solvents as polyphosphoric acid (PPA) [15]; this method allows to use moderate temperature and more stable monomers and is excellent to synthesize linear high molecular weight polymers at laboratory or small batch scale. These advantages make this synthesis method the most commonly used. Another example of solvent is Eaton's reagent, a mixture of phosphorus pentoxide (P2O5) and methanesulfonic acid (MSA) proposed by Eaton et al. [16], which has low viscosity making it suitable for the homogeneous solution synthesis and the acid washing after it [17, 18]. A shorter reaction time with high molecular weight has been obtained using homogeneous solution microwave-assisted synthesis recently, both for PBI and ABPBI [14].

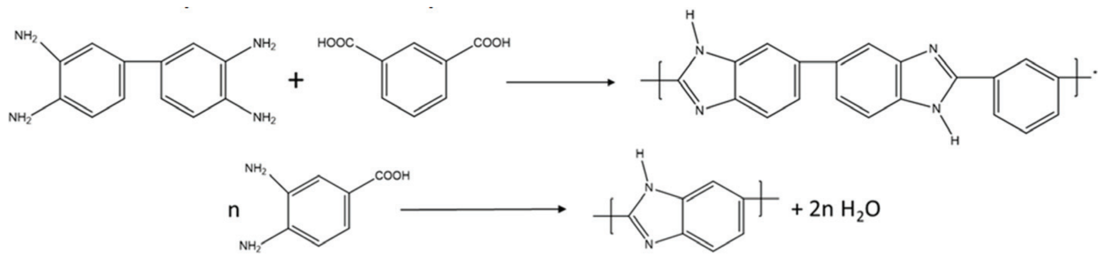

Figure 3.
Example synthesis of (top) poly(2,2′-(m-phenylene)-5,5′-bibenzimidazole), abbreviated as PBI, and (bottom) poly(2,5-benzimidazole) (ABPBI).

ABPBI is synthesized from a single monomer, (3,4-diaminobenzoic acid) (DABA), which as the advantages of being less expensive, commercially available, and non-carcinogenic. The scheme is shown in **Figure 3**. Different syntheses have been done by the homogeneous solution method in PPA or Eaton's reagent, and inherent viscosity values as high as 7.33 have been reached, as reported by Li et al. by using recrystallized DABA [19]. This is essential for the direct casting of ABPBI membranes since it has been suggested by Asensio and Gómez-Romero that values of at least 2.3 dL g^{-1} are necessary to cast good membranes [13].

In the case of ABPBI, since there is only a monomer, its purity is not as critical as in PBI; however, the use of high purity monomer produces polymers of high molecular weight [20]. Since polybenzimidazoles have to be doped in order to become ionic conductors, two methods are used to prepare the membranes: direct casting from the polymerization solution, as the work developed by Asensio et al. [21], or dissolving the previously synthesized polymer and then doing the casting of the membrane. The casting process consists in the formation of a thin film by the deposition of the polymer by evaporation of the solvent in the solution. To solubilize PBI or ABPBI, usually strong bases or acids are needed; only a few organic solvents can also do it; one of them is the N,N-dimethylacetamide (DMAc) [13, 22]. There is also an alternative way to cast ABPBI membranes from a mixture of NaOH and ethanol [23].

3. Properties of the materials and characterization

The structure of polybenzimidazoles has a good degree of flexibility and chemical and thermal resistance compared to other polymers with more single bonds in their main chain between aromatic units. The presence of aromatic units in the main chain to have higher thermal stability than the aliphatic analogs is also important [9]. In order to characterize polybenzimidazoles, one of the most important parameters is the molecular weight of the polymer, which will be highly related to the final membranes properties. The common way to obtain the molecular weight is by measurement of the intrinsic viscosity of the polymer (η_{IV}) at a certain temperature (normally 25–30°C). From the plotting of the specific viscosity (η_{sp}) as function of the polymer concentration, the intrinsic viscosity is calculated extrapolating to zero concentration. A simpler measurement process was proposed to do the calculation with a single-point method using Eq. (6), where C is the polymer concentration in a concentrated acid like 96 wt% H_2SO_4:

$$\eta_{IV} = (\eta_{SP} + 3\ln(1+\eta_{SP}))/4C \tag{6}$$

The protocol test is to calculate the η_{sp} of a polymer solution 5 g L^{-1} in concentrated sulfuric acid at 30°C using an Ubbelohde viscometer. From the η_{IV} value, the average molecular weight is calculated with the Mark-Houwink- Sakurada expression:

$$\eta_{IV} = K * M_W^{\alpha} \tag{7}$$

where the Mark-Houwink constants depend on the molecular weight range and distribution. Values often used for this constants are $K = 1.94 \times 10^{-4}$ dL g^{-1}, and $\alpha = 0.791$, obtained from Buckley et al. by light scattering measurements. Other solvents as formic acid or MSA can also be used to measure the viscosity of polybenzimidazoles [14].

There are various techniques in order to investigate the structure of polybenzimidazoles. Nuclear magnetic resonance is very powerful for pure organic compounds or the repeating unit of a polymer. Solvents that can be used include deuterated dimethyl sulfoxide (DMSO- d_6) and deuterated sulfuric acid (D_2SO_4). The most commonly used to record ^{1}H-NMR spectra is DMSO-d_6 because with D_2SO_4, the fast exchange interaction with the proton in the imine of the imidazole rings (-NH-) causes the chemical shift of that hydrogen to be often indiscernible [24]. ^{1}H-NMR PBI characteristic signals in DMSO-d_6 are at 13.2 (2H), 9.1 (1H), 8.3 (2H), and 8.0–7.6 (7H) ppm, the first of them attributed to the imidazole protons and the others to the aromatic protons [25, 26]. IR and Raman spectroscopy are also used, mainly to identify different functional groups and obtain or corroborate the chemical structure of the polymers [24, 27, 28]. In PBI, the IR spectrum region from 2000 to 4000 cm^{-1} is interesting since N–H stretching modes occur in this range, showing three typical bands at 3415, 3145, and 3063 cm^{-1}. The broad band around 3145 cm^{-1} has been attributed to the stretching vibrations of N–H groups self-associated by hydrogen bonds, and the peak at 3145 cm^{-1} is assigned to the N–H groups stretching vibration. In the region from 1630 to 1500 cm^{-1}, the peaks observed come from the vibration of C=C and C=N bonds [27]. In the Raman spectra of PBI, the most significant absorption band comes from the benzene ring vibration and is located around 1000 cm^{-1} [28]. For the measurement of the Raman spectra, it is relevant to use an excitation wavelength of 785 nm (red laser) since it gives much less fluorescence than the 532 nm (green laser) [29]. Because the structure and functional groups are the same, ABPBI presents the same IR peaks than PBI, as reported by Asensio et al. [30]. They also investigated the bands appearing when the polymer membrane is doped with phosphoric acid: in the N–H stretching zone, they found the evolution of nitrogen protonation by the acid, and in the medium and high doped samples, the broad band of N^+–H vibration becomes stronger, while the nonassociated imidazole protons decreases. In polybenzimidazoles doped with alkaline media for anion conductivity purposes, the structure changes are also clearly identified. Aili et al. [31] investigated PBI with different degrees of KOH doping and found that in the IR spectra, at KOH concentrations higher than 15 wt.%, the N–H stretching band at 3415 cm^{-1} disappear as well as the broad band around 3100 cm^{-1} of shelf-associated hydrogen bonded N–H groups. They concluded that the IR data indicated the predominance of the deprotonated form of PBI with KOH concentrations of the bulk solution around 15–20 wt.%. In the ^{1}H-NMR spectrum the signal at 13.3 ppm of the N–H proton disappeared at high bulk KOH concentration, and most signals from the aromatic protons showed upfield shift compared to pristine PBI, indicating complete ionization. This full ionization of the polymer releases the extensive intermolecular hydrogen bonding allowing for high swelling behavior and water and KOH uptake and therefore enhanced ion conductivity. This study corroborates the knowledge that the introduction of species that interact with imidazole groups by hydrogen bonding decreases the intermolecular polybenzimidazole cohesion, causing a strong plasticizing effect observed in the great decay of the tensile strength and enhanced elongation at break when the doping level increases, especially when full ionization of the polymer is reached. Using an even higher concentration doping solution, they found that a higher crystallinity structure was obtained, as observed by XRD, mechanical test, and swelling behavior measurements. X-ray photoelectron spectroscopy (XPS) is also a helpful technique for the characterization of polybenzimidazoles, concretely for the capacity to distinguish the oxidation states of the elements present and allow their quantification in the surface of the membrane [29]. Other fundamental measurements usually performed on the synthesized membranes are the determination of the ionic conductivity, the swelling behavior with water and in acidic/alkaline media, or the thermogravimetric analysis (TGA). In conclusion, a full set of characterization analysis have been studied and are used to identify and test the properties of the synthesized polybenzimidazoles and the membranes prepared with them.

4. Commercial availability

There have been different companies relevant in the fuel cell membrane field, probably the most known one is DuPont for developing the Nafion® membrane made of a sulfonated tetrafluoroethylene-based fluoropolymer-copolymer with excellent thermal and mechanical stability as well as high proton conductivity in low-temperature fuel cells. Companies like Solvay, Gore, and others have also commercialized membranes with this chemistry. This membrane has been the standard for fuel cells used in low-temperature and acidic media, but at temperatures higher than 100°C, Nafion® performance drops dramatically due to the lower hydration level. It is in these conditions where membranes made of polybenzimidazoles have shown good performance and promising applicability, and production for commercialization has occurred. BASF Fuel Cell (formerly PEMEAS Fuel Cell), a part of one of the larger chemistry industries, has developed a product line about a membrane electrode assembly (MEA) based in a PBI membrane, Celtec® [32, 33]. These MEAs optimal operation conditions are between 120 and 180°C, doped in phosphoric acid. They have shown relevant advantages working as high temperature PMFCs, like high tolerance to fuel gas impurities such as CO (up to 3%), H_2S (up to 10 ppm), NH_3, or methanol, no humidification required, far simpler system due to elimination of water, and a less complex reformer technology. In addition, several advantages can be obtained for the electrocatalysis, but it is necessary to be especially careful at the high stability toward corrosion needed to ensure long fuel cell lifetimes, apart from high activity for the oxidation of the fuels and the oxygen reduction reaction. Other companies that commercialize PBI- and PBI-based membranes are "PBI Performance Products" with their Celazole® PBI PEM [22, 34] and Danish Power Systems with their Dapozol® membranes and MEAs [35]. Membranes based on PBI are of high applicability as it can be observed, both for the fuel cell technology in development and also for other applications as carbon capture, pervaporation dehydration processes, or electrochemical hydrogen separation, among others.

5. Proton exchange membrane fuel cells (PEMFCs)

Polybenzimidazole (PBI) as ionic exchange membrane can be used as proton exchange if the material is doped with phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and nitric acid (HNO_3) solvent media. The PBI has benzimidazole units in the polymer chain and bears the pKa = 5.5 that is responsible for the weak acid character, and they have excellent oxidative and thermal stability [36]. The acid molecules penetrate the membranes during doping process, due to the acid-base interaction between them and gradually swelling of PBI membrane. Therefore, PBI can be easily doped with different types of strong acids, which act as predominant protonation through the PBI membranes.

In these circumstances, the material can work as solid electrolyte in a fuel cell in temperature range between 100 and 200°C, overcoming the dehydration problem that the Nafion® membrane has in operation condition at around 100°C and in consequence the dramatically reduction of its proton conductivity, presenting a near zero electro-osmotic drag [37]. High temperature makes HT-PEMFC more tolerant to impurities in feed gases (CO, e.g.) and simplifies elimination of waste heat with a simpler cooling system. If the fuel cell is working with reformed natural gas as a power source, the device does not require humidification of reactants due to the simple water management; that is why all these features greatly simplify design of HT-PEMFC stack [38].

In the PBI/H_3PO_4 system, the polybenzimidazole acts not only as a matrix polymer but also as proton acceptor [39]. For HT-PEMFCs, PBI/H_3PO_4 is considered a reasonably successful solid electrolyte because the excellent conductivity and thermochemical stability. Phosphoric acid has been widely employed as an anhydrous proton conductor because of its high proton conductivity, low cost, and thermal stability. At temperatures above 150°C, the dehydration of the acid occurs and yields pyrophosphoric acid or higher oligomers, which exhibit worse proton conductivity. On the other hand, the long-running operation leads to the release and dilution of H_3PO_4 from the membranes, which results in a loss of the acid into the fuel cell gas/vapor exhaust streams, the decrease of membrane ionic conductivity, and thus a lower fuel cell performance occurs. The high proton conductivity of the membranes was proved only when the polymer holds a large excess of phosphoric acid [40]. The optimum doping level was around 5 moles H_3PO_4 per PBI repeat unit, where a compromise between conductivity and mechanical properties was achieved.

A thick membrane is not usually advantageous because it is mainly responsible for the large ohmic polarization and modest power performance of HT-MEA. However, approx. 100 μm has been implemented with the intention of improving their mechanical properties [41]. The acid doping is an essential process, but it softens the PBI membrane, causing membrane ripping in MEA fabrication. The mechanical stability of the doped PBI membrane can be improved by lowering the H_3PO_4 doping level; however, the proton conductivity is reduced [42].

The problems of HT-PEMFCs operating at temperatures up to 100°C are not solved yet and demonstrate the necessity of research on new and more satisfactory alternatives. In this context, the ionic liquids (ILs) have been used as nonaqueous and low-volatility proton carriers in replacement of aqueous electrolytes. The protic ILs for example are able to transport protons due to their acid-base character and their capability to form complex or intermolecular hydrogen bonds [43] even in nonaqueous conditions. This type of materials tries to overcome the formation of unstable materials in the operating conditions and then to improve the performance of the PEMFC at high temperatures. The first research team working in this subject was Watanabe and colleagues, who identified the potential electroactive use of ILs in fuel cell reactions [44]. Sometimes, polymer phase substrate and the IL result in nonhomogeneous and unmanageable membranes when both components are integrated together. In general, ILs and polymers dissolved in a common solvent and later are casted as a film. In this way hybrid membranes are obtained, and the materials may be studied once the solvent has been removed. PBI-based hybrid membranes holding ILs are examples of this methodology. Greenbaum et al. [45] demonstrated that the composite gel-type membranes obtained from H_3PO_4 and aprotic hydrophilic IL, namely, 1-propyl-3-methylimidazolium dihydrogen phosphate [PMI][H_2PO_4] and PBI, can be operated as ion exchange membrane up to 150°C in a PEMFC. The composite membranes were homogeneous and both chemically and thermally stable with wide temperature range. Nevertheless, phase separation occurred when mixing the 1-ethyl-3-methylimidazolium triflate [EMI][Tf] or 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [EMI][TFSI] ILs with H_3PO_4 and PBI, resulting in homogeneous membranes. Schauer et al. [46] investigated the use of aprotic ionic liquid 1-butyl-3-methylimidazoliumtrifluoromethanesulfonate [BMIM][TfO] and protic ionic liquid 1-ethylimidazoliumtrifluoromethanesulfonate [EIM][TfO] to prepare membranes with several different polymers: a polybenzimidazole derivative with benzofuranone (PBI-O-Ph), Udel®-type polysulfone (Udel® PSU), and poly(vinylidene fluoride-co-hexafluoropropene) fluoroelastomer. The proton conductivity of the membranes was a function of the temperature and the ionic liquid amount in the membrane and the polymeric matrix itself. For PBI-O-Ph-based membranes, the conductivity was very low up to 90°C. Wang et al. [47] studied the PBI/IL composite membranes where the IL was 1-hexyl-3-methylimidazolium trifluoromethanesulfonate [HMI][Tf], an organosoluble fluorine ionic liquid. The ionic conductivity reached a value as high as 1.6×10^{-2} S cm^{-1} at 250°C under anhydrous conditions, and the results depended on temperature and IL content. The IL [HMI][Tf] works simultaneously as plasticizer and ion carrier. On the other hand, the major drawback related to the IL addition is a loss of membranes' mechanical properties, resulting in a good solid electrolyte to carry out the functions of HT-PEMFC at temperature > 200°C.

In many cases imidazolium salts are the most investigated as ILs in these applications; composite membranes with good specific conductivity have been found for their application as electrolytes in PEMFCs; however low performances (maximum power densities of around 1 mW cm^{-2} [48]) have been obtained.

Another example of composite hybrid membranes is the use of PBI as matrix and the diethlyaminebisulfate/sulfate IL, [DE][SH], in different compositional ratios, PBI/[DE][SH$_x$], as was published by Ocón et al. [49]. In this case, the composite membranes were obtained using a solution casting method. The interaction between the IL and the PBI was analyzed by FTIR spectroscopy. The imine group from the imidazole ring of PBI composite membranes showed no evidence of protonation, and consequently, the interaction between the IL and PBI was weak, remaining free inside of the PBI structure and allowing for the ionic conduction. The mechanical properties and tensile stress of pristine PBI was deteriorated dramatically on increasing the IL content, despite the fact that the conductivity values were very acceptable for the described application. For demanding fuel cell operation conditions, such as 200°C, and low humidity conditions, the PBI/[DE][SH$_x$] membranes exhibited acceptable ionic conductivity values, higher than 0.01 S cm^{-1}. In addition to high proton conductivity in anhydrous environment, which is an indispensable condition for potential HT-PEMFC membrane candidates, other requisites must also be fulfilled: barrier to the reagent gases, thermal and dimensional stability under operating conditions, electrochemical stability under reducing and oxidizing potentials, and compatibility with the electrocatalyst. In this particular case, low open-circuit voltage (OCV) of the cell, 0.8 V, was obtained. This suggests a mixed potential, although no crossover was detected in the experiments. The authors suggested that kinetic complication could show up like additional oxidation and reduction reactions simultaneously with the corresponding oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR), respectively; furthermore, the poisoning effect of the H_2S generated at the anode should not be ignored.

On the other side, the beneficial effect on the decrease of the IL viscosity was observed in the performance of the fuel cell. The optimum performance was obtained with no limiting current, being the maximum current density ca. 70 mA cm^{-2} and 13.5 mW cm^{-2}, using 100% relative humidity at 80°C. At temperature higher than 80°C, the system starts to dehydrate, whereas the IL viscosity increases and the proton diffusion was hindered. The performance at 150°C wasn't good showing clear evidences of the system dehydration at temperatures beyond 80°C. The migration of the IL from anode to cathode was demonstrated in *postmortem* analysis of PBI/[DE][SH$_x$] composite-based electrodes. The IL went out of the composite membrane, and in consequence the cell resistivity increased by a factor of six times after polarization measurements.

It is necessary to keep in mind that the requirements of cell lifetime vary for different applications, that is, 5000 h for cars, 20,000 h for buses, and 40,000 h for stationary application with continuous operation [43]. This means that the development of ionic exchange membranes with a long operating life is a challenge to develop.

6. Anion exchange membrane fuel cells (AEMFCs)

Many electrochemical systems use ion exchange membranes, such as fuel cells, electrolyzers, or redox flow batteries. Traditionally cation exchange membranes have been used in these systems due to the idea that anion exchange membranes had too low conductivity and stability. However, in the last years, many advances have been made, and anion exchange membranes (AEMs) are demonstrating to have performances comparable to acid ones, showing promising application in several technologies [2]. These membranes conduct negatively charged ions like OH^- or Cl^- and usually have positive-charged groups in the polymer structure, which could be directly present in the polymer backbone or more commonly fixed to it by extended side chains of varying lengths and chemistries. Varcoe et al. [2] investigated a deep review about the different chemistries of polymer backbones and head groups and their current state of research. The use of alkaline media, compared to acid media, has some advantages like the better electrochemical kinetics of the oxygen reduction reaction (ORR). This allows the possibility of using non-noble metals in the electrocatalysts reducing the fuel cell system cost. Other advantages are the minimized corrosion problems and the cogeneration of electricity and valuable chemicals [7, 50]. Compared to classical alkaline fuel cells (AFCs) where the electrolyte is in aqueous phase, the use of AEMs solves the carbonation problems and the difficulties of the liquid electrolyte management. The fuels commonly used in anion exchange membrane fuel cells (AEMFCs) are hydrogen and alcohols. Hydrogen is the common fuel in commercialization and research and gives the higher power densities. On the other hand, alcohols like methanol or ethanol have the advantages of easier handle, store, and transport and can be acquired from abundant biomass, which is environmentally friendly considering the process is carbon-neutral.

Among all the polymers available and tested for AEMFCs, polybenzimidazoles have demonstrated good applicability, and the most commonly used and studied are PBI and ABPBI. Some of their advantages remain in the properties previously described, as excellent thermal stability, which allows to use them at higher temperatures, superior mechanical properties that can withstand the performance conditions, and the presence of amine and imine groups which form strong hydrogen bonding interactions and can be further functionalized. The great stability properties have also encouraged many studies combining polybenzimidazoles with other polymers, creating blend or crosslinked membranes with excellent performances. Membranes based on polybenzimidazoles alone or with other polymers have also demonstrated low alcohols crossover, making them adequate electrolytes in alcohol fuel cells. In the alkaline media, the pristine form of PBI can be equilibrated in aqueous solutions of alkali metal hydroxides forming homogeneous systems with the hydroxide salt and water dissolved in the polymer matrix. These materials have shown high ion conductivity and great chemical stability at low alkali concentrations and have been tested as anion-conducting electrolytes in fuel cells with hydrogen or alcohol and in water electrolyzers. In order to understand the physical and chemical properties of polybenzimidazoles in alkaline media, Aili et al. have made a study with thin films of PBI in aqueous KOH solution with concentrations from 0 to 50 wt.% [31]. They observed by the EDS cross-sectional maps that the dissolved KOH is evenly distributed in the electrolyte membrane. The polymer has strong water affinity through hydrogen bonding with the imidazole groups, absorbing around the water molecules per repeating unit (r.u.), and KOH forms various hydrated complexes when dissolved in water. The degree of ionization of the polymer is determined by the position of the acid-base equilibrium presented in **Figure 4**. They observed that it depends on the KOH concentration as was expected, increasing the KOH content per PBI r.u. with the higher concentration of the bulk solution, reaching 2.6 KOH molecules/r.u. at bulk concentration of 25 wt.%.

A similar trend was observed for the water molecules, reaching more than 20 H_2O molecules/r.u. at KOH concentration around 20–25 wt.% in the bulk solution. In the polymer phase, the number of water molecules per KOH decreased while increasing the bulk solution concentration, showing a concentrating effect of KOH in the polymer. They did the measurements by titration and gravimetrically, getting consistent results that corroborate previous knowledge. They also observed the anisotropic swelling behavior of the polymer at different KOH concentrations that had been previously reported and performed X-ray diffraction (XRD) measurements to explain it. The explanation they found was that the increasing of surface area and thickness up to 15 wt.% concentration was due to the uptake of water and KOH, but further increasing the concentration leads to full ionization of the polymer, breaking many of the hydrogen bonds and separating the layered structure. This separation is easier in the interlayer dimension than in the intra-layer one, causing high thickness increase and area decrease. When KOH bulk solution concentration reached 50 wt.%, sharp peaks appeared in the XRD and were attributed to a crystalline phase of a poly(potassiumbenzimidazolide) hydrate with a symmetric and highly regular structure with crystallite size in the range of 70–120 nm. These crystalline peaks were vanished after washing in water until neutral pH. They also observed that the previously described effect of the introduction of water and KOH that disturbs the polymer hydrogen bonding of imidazole groups affected the mechanical properties, causing great decay in the tensile strength and enhanced elongation at break. When full ionization of the polymer was reached, at 20–25 wt. %, more than 200% elongation at break and 0.3 GPa elastic modulus were obtained, which compared with the 80% elongation at break and 3.0 GPa in pure water, showing the great differences. The IR measurements showed clearly that the chemical environment of the benzimidazole moieties changed greatly from the

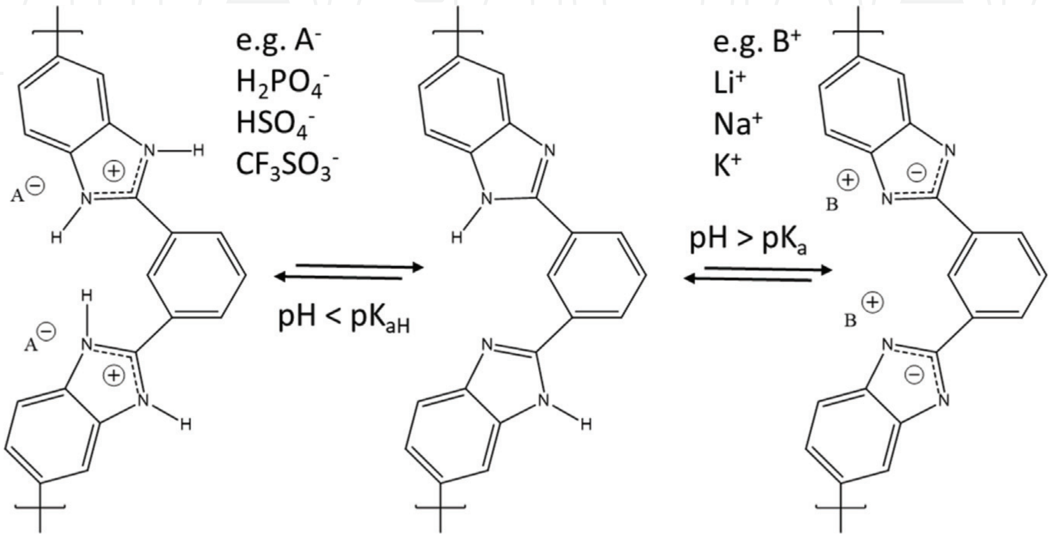

Figure 4.
Scheme showing the amphoteric nature of PBI in acidic (left) and alkaline (right) environments.

dissociation of the acidic proton. The result was that the deprotonated form of PBI predominates when the KOH concentration of the bulk solution is around 15–20%.

In order to discuss the different membranes based on polybenzimidazoles, the classification of anion exchange membranes made by Merle et al. will be useful [6]. Membranes are classified in three main groups: heterogeneous membranes, interpenetrating polymer networks, and homogeneous membranes. The heterogeneous membranes are composed by an anion exchange material embedded in an inert compound and can be divided in ion-solvating polymers if the inert compound is a salt or hybrid membranes in it is an inorganic segment. Polybenzimidazoles alone or blended with other polymers would fall into the category of ion-solvating polymers. The interpenetrating polymer network is a combination of two polymers in which one or both are synthesized or crosslinked in the presence of the other without any covalent bonds between them. The homogeneous membranes are composed only by the anion exchange material, forming a one-phase system, where the cationic charges are covalently bonded to the polymer backbone. Mobile counter ions are associated with the ionic sites to preserve the electroneutrality of the polymer. Examples of the cationic sites are the quaternary ammonium (QA) groups commonly used in AEMs. Depending on the production method and the starting materials, homogeneous membranes are divided into three types: (co) polymerization of monomers, modification into a polymer, and modification on a preformed film.

Alkali-doped PBI was investigated by Xing et al. for use in AEMFCs [51]. They obtained very interesting results, like conductivity as high as 9×10^{-2} S cm^{-1} at 25° C, higher than 2×10^{-2} S cm^{-1} of a H_2SO_4-doped PBI membrane, or the similar performance in hydrogen/oxygen fuel cells with alkali-doped PBI membrane and Nafion®117 membrane. Since that pioneering work, extensive attention has been paid to the alkali-doped PBI membranes, and thus great progress has been made. However, relevant issues are still remaining such as alkali leakage, fuel permeability, and mechanical stability. The single-cell performance of alkali-doped PBIs has been extensively studied with various fuels [52], such as hydrogen, methanol, ethanol, ethylene glycol, glycerol, formate, and borohydrides.

Using hydrogen as fuel, Zarrin et al. [53] have developed a stable and highly ion-conductive porous membrane doped with KOH. They found enhanced ionic conductivity by introducing the porosity in the membrane and obtained around twice better cell performance and conductivity compared with a commercial Fumapem® FAA membrane. Moreover, the KOH-doped PBI membrane maintained the ionic conductivity after 14 days of stability test, far more than the 3 h of the commercial one. The peak power density obtained with the porous PBI membrane of porosity 0.7 was 72 mW cm^{-2}, better than the 41 and 45 mW cm^{-2} obtained with a dense PBI membrane and the commercial FAA membrane, respectively. This better performance was demonstrated to be ascribed to the fact that the porous structure offered a higher ion transport rate through the membrane. One of the previously mentioned issues is the gradual alkali leakage during the cell operation. To solve it Zeng et al. [54] synthesized a sandwiched porous PBI membrane doped with KOH. The pore-forming method rendered numerous sponge-like walls and interconnected macropores, improving the interaction between the PBI and the doping alkali, indicating that both anionic conductivity and alkali retention could be enhanced by this method. Using this sandwiched porous PBI membrane doped with KOH in an AEMFC, they obtained an open-circuit voltage (OCV) of 1.0 V and a peak power density of 544 mW cm^{-2} at 90°C, which was higher than using the conventional membrane structure. They also investigated the durability of the fuel cell at a constant current density of 700 mW cm^{-2} and found that the conventional fuel cell had a dramatic voltage drop after short operation time, which was ascribed to the progressive release of the alkali solution. On the other hand, the sandwiched porous membranes performed with improved stability; the voltages reduced gradually to 0.1 V and remained there for another 25 h approximately. They explained that the performance enhancement was attributed to the retarding in the release of the alkali solution from the sponge-shaped wall, maintaining the high conductivity of the membrane. However, finally the leakage occurred, but as the authors indicated, the membrane could be reused after doping with KOH solution again.

Another approach was that used by Lu et al. [55]. They used PBI to react with poly(vinylbenzyl chloride) (PVBC), a polymer commonly used by other groups as for example Varcoe et al. in their grafted PTFE membranes [56, 57]. PVBC has the advantage of reacting with the imidazole rings of PBI creating a crosslinking connection with remaining -CH_2Cl groups unreacted that can be later functionalized as desired. For the functionalization of these groups, they decided to use the diamine 1,4-diazabicyclo (2.2.2) octane (DABCO), a very stable amine in alkaline media especially when only one of the two nitrogen is quaternized as previously reported [2, 6]. This method had the advantage that quaternization is done in the already casted membrane so it can be ensured that only one of the nitrogens react with PVBC obtaining the stability desired. Thanks to the good mechanical properties of PBI, they obtained membranes with good flexibility and strength both in dry conditions and saturated in water as well as high hydroxide conductivity (>25 mS cm^{-1} at room temperature) and superior chemical stability in alkaline environment. They tested the membrane in the H_2/O_2 fuel cell obtaining a peak power density of 230 mW cm^{-2} at 50°C and performed stability test, which showed high durability both in the constant current and continuous open-circuit voltage.

In addition to being used as an anion exchange membrane, alkali-doped PBI can work as ionomer, serving as ion-conductive pathway in the catalyst layer as well as a binder. Matsumoto et al. [58] developed a well-structured electrocatalyst for AEMFCs composed of carbon nanotubes (CNT), KOH-doped PBI ionomer, and platinum nanoparticles. This allowed them to obtain highly effective diffusivity and improved electrochemical activity, and they obtained a peak power density of 256 mW cm^{-2} at 50°C when tested in a H_2/O_2 fuel cell.

For fuel cells running on methanol, Hou et al. [59] tested a direct methanol fuel cell with a KOH-doped PBI membrane and observed that when a mixed solution of 2.0 M methanol and 2.0 M KOH was used as fuel, the OCV was around 1.0 V, and the peak power density was 31 mW cm^{-2} at 90°C. Wu et al. [60] prepared a membrane of KOH-doped PBI with CNT nanocomposites and obtained maximum power densities of 67 mW cm^{-2} and 104 mW cm^{-2} at 60 and 90°C, respectively, with a fuel composition of 2.0 M methanol + 6.0 M KOH and humidified oxygen. Li et al. [61] worked with pristine PBI membrane synthesized by solution casting method and treated it separately with 2.0 M H_3PO_4 and 6.0 M KOH to prepare a PEM and an AEM, respectively. They also studied several parameters of the structure design and operating parameters. They found that the conductivity of the KOH-doped PBI membrane was higher than the phosphoric acid membrane, 21.6 and 7.9 mS cm^{-1}, respectively. They also obtained a higher peak power density with the KOH-doped PBI membrane, 117.9 mW cm^{-2} at 90°C, than with the acid one, 46.5 mW cm^{-2}. They even reached a peak power density of 158.9 mW cm^{-2} at 90°C when using free-microporous layer electrodes and tripled the fuel flow rate.

In fuel cells running on ethanol, Hou et al. [62] developed a KOH-doped PBI membrane and found that with fuel composition of 2.0 M ethanol +2.0 M KOH, they obtained OCV of 0.92 V and maximum power density of 42.9 mW cm^{-2} at 75°C and 0.97 V and 60.9 mW cm^{-2} at 90°C. Modestov et al. [63] fabricated a membrane electrode assembly (MEA) employing non-platinum electrocatalysts and a KOH-doped membrane. In the anode they used a mixed solution of 3.0 M KOH

+2.0 M ethanol as fuel, while in the cathode they used air flow. With these conditions and at temperature of 80°C, a peak power density of 100 mW cm^{-2} was obtained at a voltage of 0.4 V. It was also found that by operating the fuel cell with pure oxygen, the current density was improved by 10%. Also using ethanol as fuel, recently Herranz et al. [29] tested the fuel cell performance of membranes synthesized with PBI and poly(vinyl alcohol) (PVA) with different weight ratios. PVA alcohol groups interacted with PBI by hydrogen bonding as well as allowing enhanced conductivity of the hydroxyl anion through the membranes. The increasing content in the PVA blend membrane leads to higher conductivities but if excessive could bring structural problems since PBI demonstrated to be essential for the membrane integrity. PVA:PBI 4:1 membrane obtained the best performance with a peak power density of 76 mW cm^{-2} at 90°C, 50% higher than a pristine KOH-doped PBI tested in the same conditions.

ABPBI has also been widely investigated for AEMs synthesis and application. Luo et al. [64] synthesized ABPBI and prepared the pristine membranes by the solution casting method. They studied the conductivity of the membranes at various alkali doping levels. They found high conductivity values for the membranes as 2.3×10^{-2} S cm^{-1} at 25°C and 7.3×10^{-2} S cm^{-1} at 100°C in the ABPBI membrane with alkali doping level of 0.37. They also founded the membranes have great thermal stability and excellent chemical stability, demonstrated by maintaining the conductivity values in alkaline media at 100°C for more than 1000 h.

Other alcohols and fuels have also been tested in AEMFCs using polybenzimidazoles in the membrane structure, showing promising results [65, 66]. Overall, the applicability and interest of benzimidazoles as AEMs are actual and will continue to increase due to their excellent properties.

7. Conclusions

Polybenzimidazoles have been deeply studied in the last decades, and great advancements have been done in their synthesis, making them economical materials with excellent thermal and mechanical properties as well as high chemical resistance in acidic and alkaline media. Their special structure with imidazole moieties and high intermolecular hydrogen bonding make them excellent materials to be used and ion exchange membranes for fuel cells. They can be used alone or in combination with other polymers or compounds, like the ionic liquids, as has been demonstrated many times. With them, it is possible to reach performances similar to other fuel cells and allow the application at higher temperatures, with all the benefits that implies. In the acidic media temperatures in the range of 120–200° C are used with good performances and easier water management, but still issues like structural stability with high doping level have to be solved. In order to help with the conductivity, ionic liquids have been investigated because of their nonaqueous and low-volatility properties as proton carriers. Interesting developments have been done but further research is necessary. In the alkaline media, their application has also attracted great interest. The ionization of the structure has been clearly identified at certain doping levels and the plasticizing effects it has. Pristine polybenzimidazole membranes have been directly doped with alkali solutions obtaining very good conductivity values, and other strategies like crosslinking with other polymers or synthesis of blend membranes have reported also promising results. The fuel cell performance is not yet as good as in the acidic media, but good results around 100 mW cm^{-2} have been obtained. Commercialization of membranes and MEAs based on PBI shows the potential they have, and research continues nowadays to develop them even more and better understand the possibilities of these wonderful materials in the fuel cell technology and the energy applications.

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Conflict of interest

The authors declare that they have no conflict of interest.

Nomenclature

PBI	Poly[2,2′-(*m*-phenylene)-5,5′-bisbenzimidazole]
ABPBI	Poly(2,5-benzimidazole)
PEMFCs	Proton exchange membrane fuel cells. Also used for general polymer electrolyte membrane fuel cells
AEMFCs	Anion exchange membrane fuel cells
IEM	Ion exchange membrane
AEMs/CEMs	Anion/cation exchange membranes
ORR	Oxygen reduction reaction
IV	Inherent viscosity
PPA	Polyphosphoric acid
MEA	Membrane electrode assembly
ILs	Ionic liquids
OCV	Open-circuit voltage
QA	Quaternary ammonium

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