Review

Recent Advances in Polybenzimidazole (PBI)-based Polymer Electrolyte Membranes for High Temperature Fuel Cell Applications

Vijayalekshmi Vijayakumar, Kihyun Kim, and Sang Yong Nam[†]

Department of Materials Engineering and Convergence Technology, Engineering Research Institute, Gyeongsang National University, Jinju 52828, Republic of Korea

Abstract

Polybenzimidazole (PBI), an engineering polymer with well-known excellent thermal, chemical and mechanical stabilities has been recognized as an alternative to high temperature polymer electrolyte membranes (HT-PEMs). This review focuses on recent advances made on the development of PBI-based HT-PEMs for fuel cell applications. PBI-based membranes discussed were prepared by various strategies such as structural modification, cross-linking, blending and organic-inorganic composites. In addition, intriguing properties of the PBI-based membranes as well as their fuel cell performances were highligted.

Keywords: Cross-linking, Fuel cell, Polybenzimidazole, Polymer electrolyte membrane, Structure modification

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have drawn a great deal of attention as clean energy generation devices due to their many attractive features, such as environmental friendliness, high efficiency, high power density and moderate operation conditions which provide their potential application in stationary, transportation and portable electronics[1-3]. Proton exchange membrane (PEM), facilitate the transport of protons from anode to cathode allow the completion of redox reaction in fuel cells, as well as function as barrier to avoid direct contact among fuel and oxidant[4]. Nafion, which consists of an aliphatic perfluorinated backbone with ether-linked side chains that end in sulfonated cation exchange sites with long-term stability in oxidative and reductive conditions are typically used as the electrolyte in PEMFCs because of their high proton conductivity, excellent mechanical properties and good chemical stability. However, the Nafion membranes have severe drawbacks of low conductivity at temperatures greater than 100 ℃ due to dehydration and high methanol permeation, which causes loss of fuel and reduction in cathode performance in PEMFCs limit its large scale applications[5]. PEMFCs operating at high temperatures (100~200 ℃) and low humidity conditions bring several distinct advantages including a high tolerance of the anode to CO poisoning, increased catalyst efficiency, easy water/thermal management and improved resistance to fuel impurities[6]. High temperature polymer electrolyte membranes, the essential components de-

termining efficiency of the fuel cell have become active field of research nowadays. Among the membrane materials for elevated temperatures, polybenzimidazoles (PBIs) owing to their high performance and low cost are considered to be promising candidates as high temperature polymer electrolytes[7].

Polybenzimidazole (PBI) is a rigid semi-crystalline polymer with good chemical resistance, high thermal stability and excellent mechanical strength[8]. Many types of polybenzimidazole based polymers, including poly(2,5 benzimidazole), phenylene based PBI, and pyridine based PBI polymers, owing to their high proton conductivity even at non-humidified conditions, as well as chemical, mechanical and thermal stabilities have been intensively studied and utilized in high temperature PEMFCs. Several different approaches such as doping, cross-linking, blending, copolymerization, hybridization with inorganic materials to improve applicability at high temperature have also been reported by several researchers[9]. In this review, the recent progress on PBI based high temperature PEMs is discussed.

2. Polybenzimidazole (PBI) Membranes

2.1. Acid-doped PBI membranes

Acid-base complex system formed by reacting polymer bearing basic sites with strong acids constitutes a new class of proton conducting polymer membranes. High acid contents result in high conductivity but sacrifice mechanical stability at high temperatures[5]. Wainright *et al.* firstly introduced acid doped PBI membranes for high temperature PEMFCs[10]. Various inorganic acids such as H_2SO_4, H_3PO_4, $HClO_4$, HNO_3, HBr, HCl, etc have been investigated as dopant in PBI based membranes[11,12]. From proton conducting mechanism points of view, phosphoric acids are interesting as they are more amphoteric, having both proton donor (acidic) and proton acceptor (basic) groups to form

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† Corresponding Author: Gyeongsang National University,
  Department of Materials Engineering and Convergence Technology, Engineering
  Research Institute, Jinju 52828, Republic of Korea
  Tel: +82-55-772-1657   e-mail: walden@gnu.ac.kr

dynamic hydrogen bond networks, in which protons can readily transfer by hydrogen bond breaking and forming processes. Savinell *et al.* were the first to dope PBI with PA, resulting membranes which exhibited significant proton conductivity in the temperature range above 100 ℃[13]. Phosphoric acid-doped polybenzimidazole membranes offer great potential for high temperature proton exchange membrane applications due to their high proton conductivity at elevated temperature and low humidity conditions. However, large amount of phosphoric acid doping tends to deteriorate mechanical and chemical stabilities of the membranes at high temperature and subsequently restricted its practical applications in HT-PEMFCs. Hence, the major challenge in fabricating high performance membranes is to maintain both high proton conductivity and good mechanical strength. Several strategies have been developed within the last decade to increase the stability as well as integrity and to reduce PA loss of the doped PBI membranes.

2.2. Structurally modified PBI membranes

Exploring PBIs with novel chemical structures has been considered as an avenue to tailor the membrane properties and break the deficiencies of the established membrane systems based on PA-doped *m*-PBI for improving the overall desired properties of HT-PEMs. One promising method to potentially improve the acid doping level is to structurally design the PBI polymer with additional basic sites so that higher amounts of phosphoric acid can be loaded through acid-base interaction process. Introduction of pyridine ring to PBI (Bipy-PBI) remarkably improved the chemical interaction of phosphoric acid with the polymer backbone while retaining high thermal and mechanical stabilities. 146% increase in the membrane conductivity and 32% increase in the power density were recorded for the high molecular weight Bipy-PBI membrane at 120 ℃[7]. A series of polybenzimidazoles with increased imidazole groups were developed by incorporating some benzimidazole groups onto an aryl ether type polybenzimidazole backbone *via* a simple and efficient N-substituted reaction without catalyst. Those aryl ether type polybenzimidazole exhibited good solubility under extremely high molecular weight and the acid doped grafted membranes exhibited high mechanical strength even at high phosphoric acid doping levels. With an acid doping level of 22.1, the grafted membrane showed a high conductivity of 212 mS cm^{-1} at 200 ℃ without humidification and a H$_2$/O$_2$ fuel cell based on this membrane presented a peak power density of 443 mW cm^{-2} at 160 ℃[1].

Block copolymers have been reported as high temperature proton exchange membranes due to the nanophase separated structures and physico-chemical properties as a result of the combination of rigid and flexible segments in the copolymer, which results in continuous ion nano channels benefits proton transfer. PEMs based on block copolymers exhibit higher proton conductivity than Nafion within conditions of lower relative humidity. A series of PBI membranes with different block ratio of OPBI (poly(4,4'-diphenylether-5,5'-bibenzimidazole)) and *p*-PBI ((poly2,2'-(p-phenylene)-5,5'-bibenzimidazole)) structures prepared by Wang *et al.* (Figure 1) exhibited a maximum proton conductivity of 0.1 S cm^{-1} under anhydrous conditions at 180 ℃. Simultaneously, the membrane's mechanical and high temperature stability meet the prac-
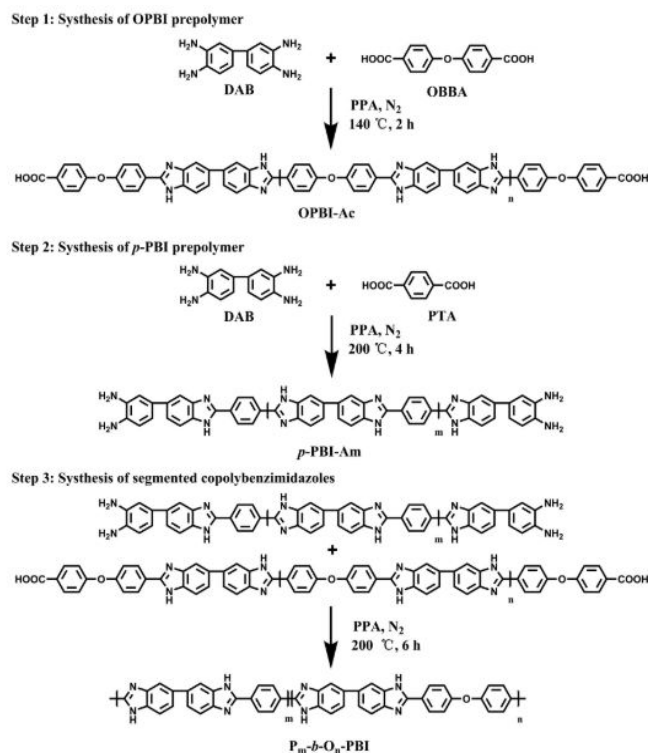

Figure 1. Synthesis of the segmented block copolybenzimidazoles[14].

tical application requirements for long term durability. The membrane electrode assembly (MEA) prepared using this membrane reached a maximum power density of 360 mW cm^{-2} at 160 ℃ under anhydrous conditions, which is much higher than that of MEAs containing single-structure OPBI or *p*-PBI and of traditional linear *m*-PBI or F6-PBI (Figure 2)[14]. The effects of pyrazole ring insertion into the polymer backbone as well as sulfonation on the membrane properties such as ionic conductivity, acid doping level and mechanical stability were investigated. Enhancement in mechanical strength with increasing butyl sulfonation level was reported, but mechanical stability deteriorated with acid doping. Proton conductivity of the prepared membranes was increased with increasing temperature and butyl sulfonation level[15].

A new class of copolymer formation by engrafting a thermosetting resin into a thermoplastic polymer reported by a leading company, BASF, resulting a threefold increase in the life time of the membrane. Phosphoric acid (PA) doped polybenzoxazine (PBOA)-*co*-PBI (or ABPBI) membranes synthesized through ring opening polymerization showed cross-linked structure and unprecedented results in terms of both long term durability and proton conductivity. It is noteworthy that the long term operation of PBOA-co-PBI (or ABPBI) membranes with large amount of PA exceeds 40,000 h at high temperature[16].

Ionic liquids due to their unique properties such as negative volatility, thermal stability, extensive electrochemical stability window and ionic conductivity, have aroused great concerns in the field of HT-PEMFC. However, leakage of ionic liquid when blended with polymer is a concern to be taken into account. Phosphoric acid doped composite membranes with cage like cross-linked structure (cPBI-IL-X)
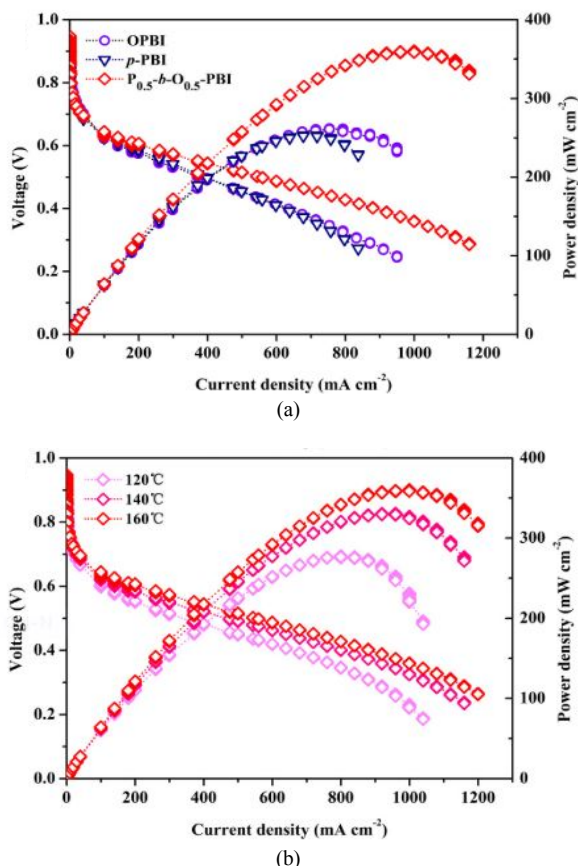
Figure 2. (a) Fuel cell performance of the OPBI, p-PBI and P$_{0.5}$-b-O$_{0.5}$-PBI membranes operating under anhydrous H$_2$/air at 160 ℃, (b) Fuel cell performance of the P$_{0.5}$-b-O$_{0.5}$-PBI membrane operating under anhydrous H$_2$/air at different temperatures[14].
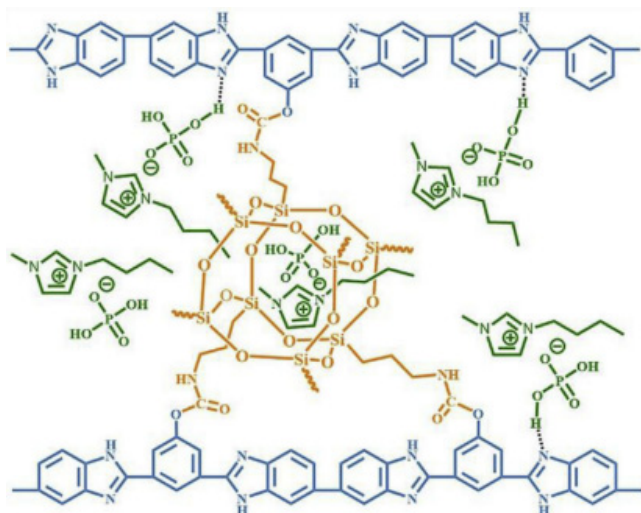

Figure 3 Schematic representation of the cPBI-IL-X membranes[17].

based on PBI containing hydroxyl groups, 3-(triethoxysilyl) propyl isocyanate and 1-butyl 3-methyl imidazolium dihydrogen phosphate (Figure 3) exhibited elevated proton conductivity. The cage like cross-linked structure strengthened the mechanical properties and improved the IL

retention of the membranes[17].

Asymmetric ether containing PBI with dense and porous structure facilitated improved PA doping level, almost twice as that of homogeneous dense poly[2,2'-(p-oxydiphenylene)-5,5'-benzimidazole] (OPBI) membrane. HT-PEMFC using this asymmetric OPBI membrane demonstrated an exceptional fuel cell functionality with a peak power density of 393 mW cm^{-2} at 160 ℃ under anhydrous conditions[18].

2.3. PBI-based cross-linked membranes

Cross-linking is an effective strategy to enhance the performance of PA-doped PBI membranes. Typical methods such as excess PBI blending, thermal cross-linking and organic-inorganic composite are involved in the design of covalent or ionic cross-linking. Kim *et al.* reported highly durable and proton transportable phosphoric acid doped cross-linked benzoxazine - benzimidazole copolymer (P(pF-co-BI)) membranes. Benzoxazines are used as polymerizable cross-linking agents by forming the covalently bonded structure with the host material (PBI) during the thermal treatment. The cross-linked copolymer membranes were simply prepared by casting the solution mixture of poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI) with 6-fluoro-3-(pyridine-2-yl)-3,4-dihydro-2H-benzoxazine (pF) in N,N-dimethylacetamide, followed by subsequent stepwise heating to 220 ℃. A maximum conductivity of 0.09 S cm^{-1} at 150 ℃ under anhydrous conditions and the membrane electrode assembly using the same membrane with a high operating voltage of 0.71 V at 0.2 A cm^{-2} and durability of 1,077 cycles with slow life time loss rate of -0.4 mV h^{-1} on *in situ* accelerated mode were reported[9]. Cross-linked copolymer using PBI with 3-phenyl-3,4-dihydro-6-tert-butyl-2H-1,3-benzoxazine (pBUa) exhibited high proton conductivity of 0.12 S cm^{-1} at 150 ℃ and its MEA displayed operating voltage of 0.71 V at 0.2 A cm^{-2} and long-term durability up to 1,999 cycles with much slower performance decay, -0.03 mV h^{-1} [19]. A series of thermally cross-linked benzoxazine-benzimidazole copolymer, P(HFa-*co*-BI) prepared using poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (PBI), di-functional benzoxazine and 6,6'-(hexafluoroisopropylidene)bis(3-phenyl-3,4-dihydro-2H-benzoxazine) (HFa) heated at 250 ℃ was found to be thermally and mechanically stable. Even though the proton conductivity of P(HFa-*co*-BI) membranes was smaller than that of the PBI membrane, their cell performance (0.68 V at 0.2 A cm^{-2} at 150 ℃) was close to that of PBI membrane and their long-term durability (3,116 cycles on *in situ* accelerated lifetime mode of load cycling) was found to be far superior to the PBI membrane[20].

Small molecular cross-linking agents are always favoured by the researchers due to their well-defined structure and cross-linking mechanism. In order to overcome the drawbacks such as poor durability and mechanical property associated with traditional covalently crosslinked PBIs and branched PBIs after doping with PA due to large free volume and weak intermolecular force, a difunctional benzoxazine, namely, bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl) isopropane (BA-a), was used as the polymeric covalent cross-linker. Branched structure (Figure 4) within the host PBI polymer helped to enhance the stability and free volume, and the polymeric crosslinking structure prevented the dis-
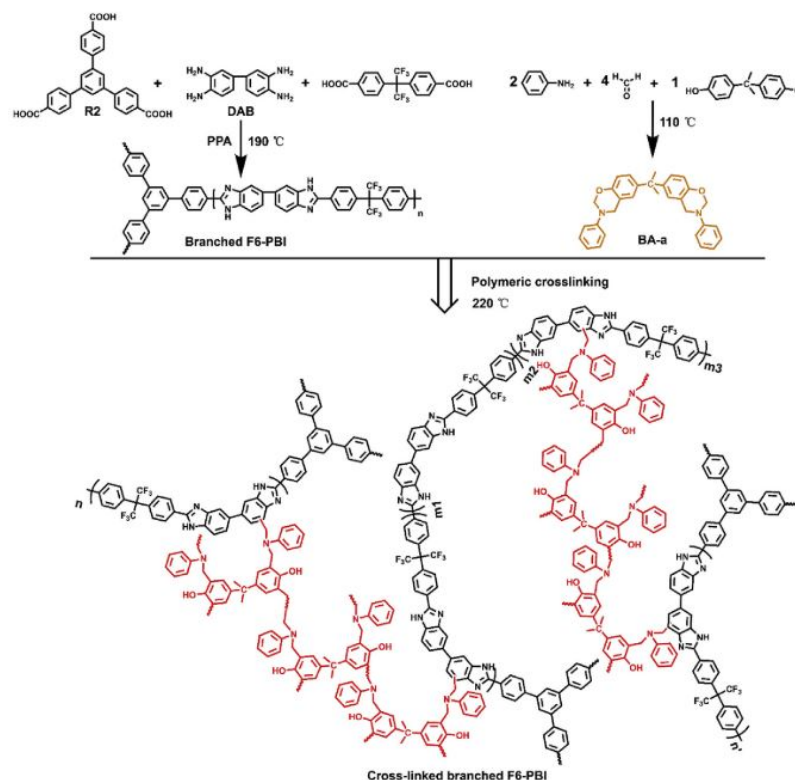
Figure 4. Synthesis of branched F6-PBI, BA-a and crosslinked branched F6-PBI[21].

solution of the PBI matrix by PA and improved mechanical properties as well as excellent oxidative stability. Furthermore, the membrane electrode assembly fabricated with cross-linked membrane showed a peak power density of 690 mW cm^{-2} at 160 ℃, and maintained for 200 h under constant current discharge (200 mA cm^{-2}) without membrane degradation[21].

Benzimidazole grafted PBI prepared by nucleophilic substitution using 2-chloromethyl benzimidazole due to the presence of mobile imidazole ring on side chains provided additional alkaline site for acid-base interactions among the macromolecular chains. Cross-linking of these grafted polymer using 3-glycidoxy propyl trimethoxy silane and acid-base interactions maintained excellent thermal and chemical stability as well as sufficient mechanical strength to the membranes. In addition, the Si-O-Si cross-linked network led to higher PA levels and its stability as well as proton conductivity[6].

Chen *et al.* put forward to introduce cross-linked composite membranes with dual proton transfer channels based on polybenzimidazole (PBI) and polymeric ionic liquids (PILs) containing imidazole rings. Unlike ionic liquids (ILs), PILs tend to build continuous ionic channels as well as possess some of the unique features of the ionic liquids without IL leakage. The PIL ([PBI-BuI][BF$_4$]) membranes cross-linked with γ-(2,3-epoxypropoxy) propyltrimethoxysilane (Figure 5) exhibited a maximum conductivity of 0.117 S cm^{-1} at 170 ℃ and achieved balance between mechanical strength and PA uptake conveys that the composite membranes could be promising candidates as PEM at elevated temperature[22].

The degradation pathway of phosphoric acid doped polybenzimidazole

membranes in HT-PEMFCs depends on the acid content, and the main degradation pathways seems to be creep by the large amount of absorbed PA acting as a plasticizer of the membrane with cross-linked structure. Sulfonated para-polybenzimidazole membranes were stabilized by curing at 350 ℃. The conductivity of crosslinked sulfonated *p*-PBI and meta-PBI at 160 ℃ and 5% relative humidity reached 214 mS cm^{-1} and 147 mS cm^{-1}, respectively. Much lower voltage decay rate of about 16 μV h^{-1} at 600 mA cm^{-2} than commercial m-PBI (308 μV h^{-1}) was observed. Furthermore, the average voltage of these membrane at 600 mA cm^{-2} was 523 mV[23].

Ionically and covalently cross-linked PBI membranes by mixing with poly(tetrafluorostyrene-4-phosphonic acid) and halomethylated arylene polymers respectively as well as covalent-ionically cross-linked PBI blend membranes by mixing PBI with a sulfonated polymer and a halomethylated polymer resulted excellent chemical stabilities and conductivity in the range of 4~90 mS cm^{-1}[13].

2.4. PBI-based blend membranes

Polymer blending is a common and potentially versatile approach to enhancing the physico-chemical properties of one or more components. PBI membranes are highly impermeable to methanol with nearly zero water drag coefficient. On the other hand, low strain and brittleness has limited its wide usage. According to the Lewis acid - basic complexes polymer concept, interaction among Lewis acid -SO$_3$H groups bonded on the sulfonated polymers and Lewis base imidazole -NH and -N=C groups bonded on PBI impart the membranes suitable physico - mechanical and electrochemical properties. Blending of PBI-BS (two
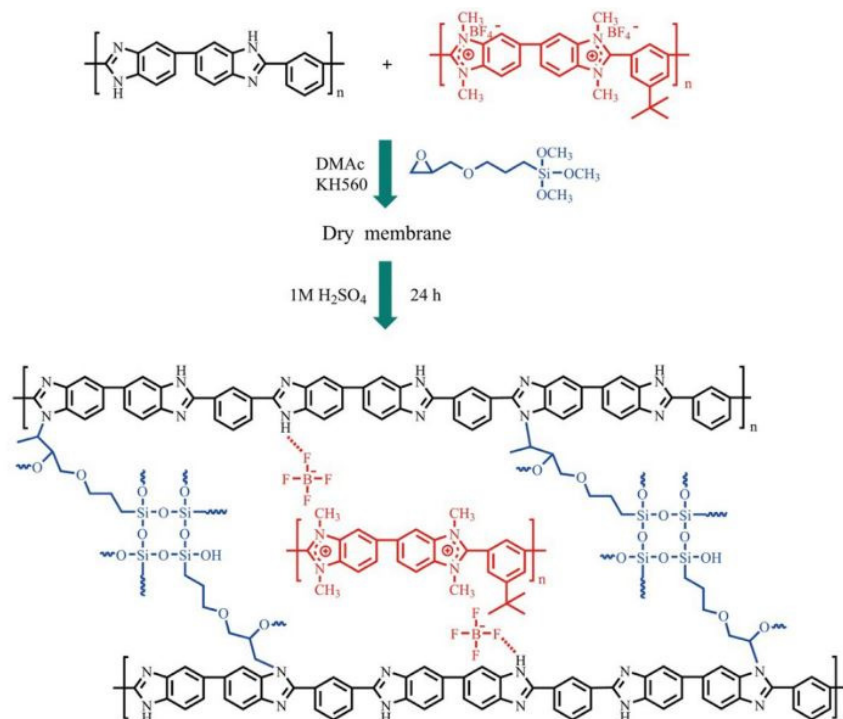
Figure 5. Synthetic process of cPBI-BF₄-X composite membranes[22].

butyl sulfonate grafted PBI) into PBI introduced bulky butyl sulfonate side chains in the membranes, which produced higher strain to the membranes and more excess free volume to retain H_3PO_4. High molecular weight PBI (PBIh) (Mw: 1.60×10^5 g/mol) based membranes exhibited much better fuel cell performance and mechanical strength than medium molecular weight PBI (PBIm) (Mw: 9.16×10^4 g/mol) membranes[24]. The blending of the pendent piperidinium functionalized polyetheretherketone/polybenzimidazole system was intended to create strong interfacial interactions which resulted in well-connected ion transporting channels and high hydroxide conductivity (61.5~72.8 mS cm^{-1} at 80 ℃) as well as good tensile strength (42.8~58.9 MPa). Piperidinium functionalized membranes retained 95% of its original OH$^-$ conductivity when treated in 1 M KOH at 60 ℃ for 576 h[25].

Acid - base blending is an effective method to prepare high performance membranes. Blending PBI and SPEEK-Na followed by acidification resulted compact structure without any phase separation and improved mechanical, thermal and oxidative stability as well as a proton conductivity of 0.198 S cm^{-1} at 170 ℃ and 100% RH, and 0.099 S cm^{-1} at same temperature and 50% RH[26]. Ionically cross-linked system based on sulfonated poly(arylene ether sulfone) (sPES) and poly(p-benzimidazole) (p-PBI) exhibited good physico-chemical properties as well as a conductivity of 0.13 S cm^{-1} at 80 ℃ with only 5 wt% of PES[27]. Acid/base blend membranes of poly-[(1-(4,4'-diphenylether)-5-oxybenzimidazole)-benzimidazole] (PBI-OO), a PBI derivative and a sulfonated polysulfone can be covalently crosslinked through thermally induced Friedel-Crafts reaction between the sulfonic groups and electron rich phenyl groups without prior hydrolysis step. The resulting cross-linking moiety, aromatic sulfone bond (C-SO₂-C) is

chemically stable. The cross-linked blend membranes exhibited a stable performance for at least 1,000 h and the MEA prepared showed a peak power density of 452 mW cm^{-2}. Membrane with 20% polysulfone content remained flat and wrinkle free even after 34 days of phosphoric acid exposure[28].

2.5. PBI-based composite membranes

Reduction in conductivity above 160 ℃ due to the dehydration of the phosphoric acid, which turned into $H_4P_2O_7$ has been reported as a major challenge in PA doped membranes. Conductivity of Nafion 117 could not be measured at 160 ℃ as it lost proton migration ability above 100 ℃. Free PA leaching out the membrane not only reduce the mechanical strength and proton conductivity, but also cause fuel loss and short cuts due to membrane thinning and pin - hole formation. Organic - inorganic composites are one of the main focuses of recent attempts to develop polymer electrolyte membranes[29,30]. Ozdemir *et al.* investigated PBI based nanocomposite membranes (PBI/SiO₂, PBI/TiO₂, PBI/ZrP) for HT-PEMFCs and reported a maximum proton conductivity of 200 mS cm^{-1} at 180 ℃ for PBI/ZrP membrane with the highest doping level of H_3PO_4[31]. To broaden the operating temperature range of phosphoric acid (PA) doped PBI membrane based PEMFCs, a novel series of poly(2,5-benzimidazole)/sulfonated sepiolite composite membranes (ABPBI/S-Sep) with low PA doping levels were prepared via *in-situ* synthesis. Proton conductivity values above 0.01 S cm at 40~90 ℃/20~98% RH conditions and 90~180 ℃/anhydrous conditions as well as peak power density of 0.13 and 0.23 W cm^{-2} at 80 and 180 ℃ with 0% RH, respectively from the ABPBI/2S-Sep composite membrane reported are more beneficial compared to Nafion
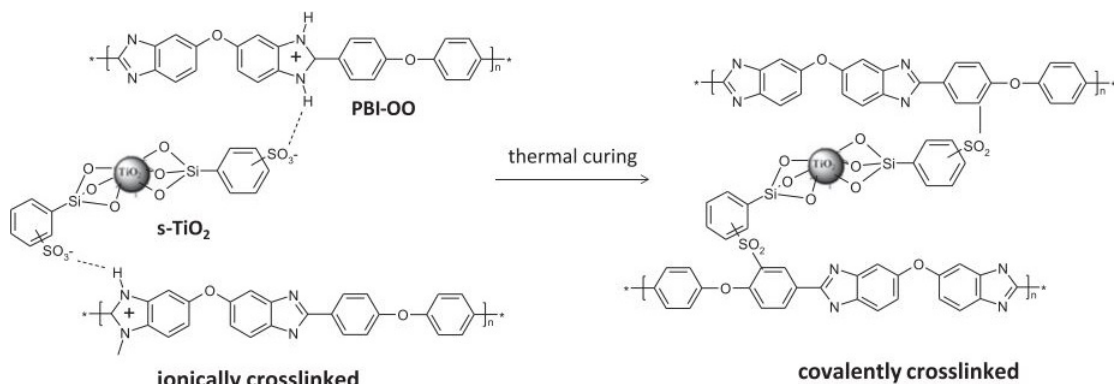
Figure 6. Synthesis of thermally cured membranes[40].

at low temperatures and PBI based membranes at high temperatures, respectively[32]. PA doped fluorine containing PBI/silica hybrid membranes using tetraethoxysilane (TEOS), a silica precursor, *via* sol-gel method in PBI solution, followed by solution casting exhibited enhanced mechanical properties and low methanol permeability[4]. Muthuraja *et al.* evaluated the conductivity and fuel cell performance of nano calcium titanate/PBI (nanoCTO/PBI) composites. The 15% nanoCTO-PBI composite membrane showed higher conductivity of 32.7 mS cm^{-1}. The membrane electrode assembly with the 10% nanoCTO-PBI composite membrane showed the current density of 419 mA cm^{-2} at 0.6 V and power density of 251.4 mW cm^{-2} at 160 ℃. This results indicated the possible application of the nanoCTO-PBI membrane for HT-PEMFCs[33].

Poly(4,4'-diophenylether-5,5'-bibenzimidazole) (OPBI), a diphenyl ether derivative of polybenzimidazole, is a promising alternative PEM material for high temperature (> 100 ℃) fuel cell because of their good solubility and processability, high thermal stability and desired mechanical strength. OPBI forms an acid-base complex when doped in strong acids like phosphoric acid and maintains high and stable conductivity at higher temperatures. The introduction of filler additives is an effective method to achieve membranes with improved water retention capacity, proton conductivity and controlled swelling[2]. Clays, owing to their high aspect ratio and strong interactions among siloxane oxygen atoms and polymer functional groups received much attention in nanocomposite PEM membranes. The effect of surfactants, dimethyl dihydrogenated ammonium chloride tallow (DDACT) contains two long alkyl chains and tributyl phosphonium molecule (TPB), a molecule containing short alkyl chains on OPBI/clay membrane properties were reported[34]. OPBI based membranes prepared *via* covalent cross-linking with chloromethylated polysulfone and doping with zirconium phytate (ZrPA) exhibit good thermal stability and proton conductivity up to 140 ℃[35]. Moradi *et al.* have recently prepared phosphoric acid doped PBI-Fe$_2$TiO$_5$ nanocomposite membranes for application in HT-PEMFCs and the effect of acid doping and filler mass fraction on proton conductivity was investigated experimentally and accounted in a model. The obtained proton conductivities by the model at various temperatures and PA doping levels were in good agreement with the experimental results indicating the reliability of the model[36].

Mustarelli and his co-workers proposed a new strategy to increase the acid retention capability of the membrane by increasing the polymer basicity. In their work, they had developed PBI based membranes by dispersing imidazole functionalized silica. Those membranes exhibited an outstanding improvement in the acid-retention properties and proton conductivity without degrading their film ability, allowing their use in PEMFCs at temperatures up to 150 ℃[37].

As we have discussed earlier, the long term durability is one of the major challenges in commercialization of high temperature PEMs. Recently, second generation acid functionalized fillers have received much attention due to the mutual contribution to the proton transport. In addition, acid functionality provides better dispersion and improves polymer-filler compatibility which directly affects dimensional stability and mechanical integrity of the membranes. In this regard, various carbon based materials including graphene oxide, and silica functionalized with 3-propyl sulfonic acid were evaluated[11,38]. For example, highly durable 2,6-pyridine functionalized polybenzimidazole (Py-PBI) composite membranes prepared using highly dispersible phosphonic acid functionalized graphene oxide (PGO) exhibited a highest conductivity value of 76.4 × 10^{-3} S cm^{-1} compared to 19.6 × 10^{-3} S cm^{-1} for PA doped Py-PBI membrane at 140 ℃ and its fuel cell showed a maximum power density of 359 mW cm^{-2} at 120 ℃[39]. Composite membrane electrode assembly of poly-[(1-(4,4'-diphenylether)-5-oxybenzimidazole)-benzimidazole] (PBI-OO) and phenylsulfonated TiO$_2$ particles (s-TiO$_2$) transformed their ionically crosslinked system into a covalently crosslinked system after thermal curing via Friedel-Crafts sulfonylation (Figure 6). Those membranes after acid doping showed the highest PA uptake of about 392 wt%, and proton conductivity of 98 mS cm^{-1} at 160 ℃. A peak power density of 356 mW cm^{-2} was reported for membrane electrode assembly using the corresponding membrane, which is 76% higher than that of the pristine membrane based system (202 mW cm^{-2})[40].

3. Summary and Conclusions

PBI owing to their excellent thermal, mechanical and chemical stability has been recognized as an alternative for polymer electrolyte membranes for HT-PEMFCs and has made considerable progress in re-

Table 1 Summary of PBI Membranes

Membrane	Modification	Ion conductivity, σ (S cm^{-1})	Peak power density (mW cm^{-2})	Reference
g-PBI-20	Grafting benzimidazole pendant	0.212 (200 ℃, RH = 0%)	443 (160 ℃, Non-humidified)	[1]
P$_{0.5}$-b-O$_{0.5}$-PBI	Block copolymer	0.1 (180 ℃, RH = 0%)	360 (160 ℃ Non-humidified)	[14]
PPBI-BS-59%	Butyl sulfonation	0.011 (140 ℃, RH = 100%)	-	[15]
P(pF)-co-ABPBI-50	Copolymer	0.14 (150 ℃, RH = 0%)	450 (160 ℃, Non-humidified)	[16]
cPBI-IL-8	Cage-like, ionic liquid	0.13 (160 ℃, RH = 0%)	-	[17]
OPBI	Porous structure	0.07 (180 ℃, RH = 0%)	393 (160 ℃, Non-humidified)	[18]
C10F6-R2-6	Covalent cross-linking	0.07 (160 ℃, RH = 0%)	690 (160 ℃, Non-humidified)	[21]
cPBI-BF$_4$-40	Cross-linking, PIL	0.117 (170 ℃, RH = 0%)	-	[22]
c-MS-p-PBI	Thermal cross-linking, sulfonation	0.214 (160 ℃, RH = 5%)	447 (160 ℃)	[23]
SPEEK/PBI (20 wt%)	Acid-base ionic cross-linking	0.199 (170 ℃, RH = 100%)	-	[26]
c-BM-1	Covalent cross-linking	0.26 (160 ℃, RH = 5%)	452 (160 ℃, Non-humidified)	[28]
PBI/ZrP	Composite	0.2 (180 ℃)	-	[31]
10% nanoCTO-PBI	Composite	0.02 (160 ℃)	251.4 (160 ℃, Non-humidified)	[33]
Py-PBI-PGO	Composite	0.076 (140 ℃, RH = 0%)	359 (120 ℃, Non-humidified)	[39]
6-c-sTiO$_2$-PBI-OO (6 wt% sTiO$_2$)	Composite, thermal curing	0.098 (160 ℃, RH = 5%)	356 (160 ℃)	[40]

cent years. The use of PA doped PBI membranes offer high conductivity at elevated temperature and low humid conditions. However, large doping level deteriorate its stability and hence applicability in HT-PEMFCs. Many researchers have focused their attention to improve the performance properties and applicability of PBI based membranes for fuel cells. This article provide a review of up-to-date research on various efforts that has been made during the last ten years on PBI polymer electrolyte membranes for high temperature fuel cells. Table 1 shows a summarized report on membranes prepared by various approaches and their performances. Structurally modified membranes by inserting various functional groups, combining rigid and flexible segments, cage-like structures, etc demonstrated stability and conduction properties. Covalently cross-linked composite membranes with PILs exhibited dual proton conduction channels as well as balance between mechanical strength and PA uptake. Blending thermosetting resin with thermoplastic and composite membranes significantly affected the durability and performance of PEMFCs. We believe that the past investigations have laid a solid foundation for the basic understanding of how the various strategies affected the performances of PBI-based HT-PEMs.

Acknowledgment

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