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Recent Progress in the Development of PBI-Based Membranes for High Temperature PEM Fuel Cell Applications

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Abstract:

Proton exchange membranes fuel cells (PEMFCs) are a type of fuel cells applied with perfluorinated membranes, operating the design temperature of 80 °C, due to its low-temperature limitation and CO tolerance to fuel impurities, and high cost of Nafion® membrane, which made impeding the development of low-temperature commercialization. Nowadays many different types of membranes are studied for high temperature PEMFCs, especially in Polybenzimidazole (PBI) membrane. The development of PBI based membrane has been in progress for the last few decades, and as a good alternate membrane for high temperature fuel cell, operating at higher working temperatures (120~200 °C) and retaining membrane's physical properties and thermal stability, and high proton conductivity. However, both high temperature PEMs have faced considerable challenges for researchers, under high temperature conditions, degradation rate of proton exchange membranes, remaining high conductivity and mechanical stability. Moreover, the integration of plasticiser additives and filler additives, acid doping level will affect the advantages of PBI based membrane. The current research suggests that the application or integration such as additives and composite has proven potential to modify the properties of PBI membranes. The progress in the development of new composite materials was introduced on the basis of PBI membranes. More attention should pay to the promising and newly developed polymeric materials for high temperature PEMFCs.

Keywords:

High Temperature PEM Fuel Cell, Polybenzimidazole (PBI), Proton Conductivity, Phosphoric Acid, Acid Doping Level, Titanium

1. Introduction

Fuel cell is a kind of clean energy transition device that converting chemical energy into electrical energy, which has high efficiency and environment friendly. In fuel cell systems, the membrane and electrode applied in these devices to govern the reaction mechanisms, and the overall performance of the whole system [1]. Among the different types of fuel cells, proton exchange membrane fuel cells (PEMFCs) are the most common and promising one, the schematic flow of PEMFC is illustrated in Figure 1. According to variants of PEMFCs, it including low-temperature PEM fuel cells (LT-PEMFC), high temperature PEM fuel cells (HT-PEMFC) and direct alcohol fuel cells, including direct methanol fuel cells (DMFC) and direct ethanol fuel cells (DEFC) [2]. The Nafion® membrane is one of the most widely and common used PEM in PEMFCs, however it is limited to a design operating temperature 80 ℃, and requires water management to keep the membrane moist for suitable electrochemical conductivity [1,2,3]. Nafion® membrane impels proton transport across the membrane when hydrolysed with water, due to the membrane contains a sulfonic acid group pendant to the polytetraflfluoroethylene backbone. However, Nafion® membrane demonstrated severe drawbacks at temperatures above 100 ℃, which displayed poor proton conductivity at high temperatures due to the dehydration of water, and this will restrict the number of water-fifilled channels to transport the proton. To handle this issue, more and more researchers have developed different alternatives applying polymeric materials, or filler additives.

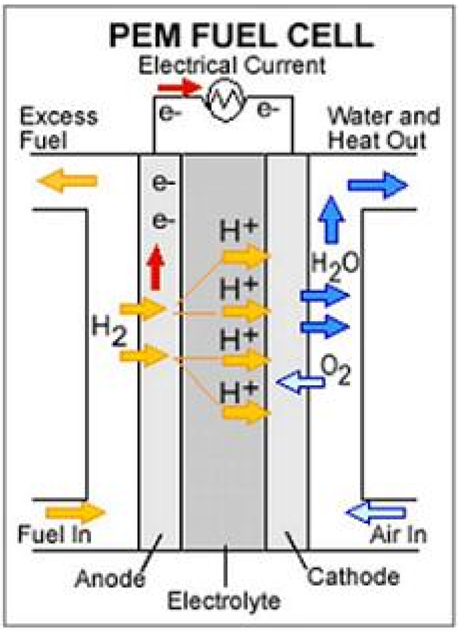

Figure 1. *The schematic principle of PEMFC-Reprinted from "Hydrogen Fuel Cells" by J. K. Harbeck, 2010, Stanford University.*

2. High Temperature Proton Exchange Membranes for PEMFCs

To developing alternative proton exchange membranes at temperatures > 100 ℃, the drawbacks of low-temperature PEMFCs should be avoided, proton conductive under high temperature conditions, requires more ion channels and proton transport capacity within the polymer electrolyte; a mixture of liquid-phase and gas-phase water co-exists during the operation and complicated electrode preparation techniques will be prepared; a low tolerance to the PPM of CO and the temperature limitations [1,2,3]. The intention of HT-PEMFC origins Phosphoric Acid Fuel Cell (Shorted in PAFC), phosphoric acid (PA) applied as electrolyte and operates at similar working temperatures, which happens in SiC matrix with thickness of 0.1 to 0.2 mm; at the other hand, in the case of phosphoric acid-doped PBI-based HT-PEMFCs, a solid polymer is used to mechanically and chemically retain PA [2,3].

2.1. Phosphoric Acid Dope Polybenzimidazole (PBI) Membrane

Nowadays, phosphoric acid doped polybenzimidazole (PBI) membrane has been repidly developed, which seen to be a promising alternative membrane proposed for high temperature PEMFC. The advantages of PBI-based polymers are as the followings: (1) Good protonic conductivity at elevated temperature; (2) Transports proton through membranes do not involve water transport, (3) Low gas permeability, (4) Low methanol crossover, and (5) Excellent oxidative and thermal-chemical stability and mechanical flexibility at elevated temperature (100-200 ℃) [3].

Unlike PAEK-, PI-, or PES-type polymers, phosphoric acid-doped PBI membranes didn't acquire functionalization to allow binding to PA molecules, benzimidazole rings play critical role in PBI backbone, which enabling proton conduction take place via both Vehicular mechanism and Grotthuss mechanism between water molecules and PA molecules. Among the properties of PBI-based membranes, the acid doping level (ADL) or percentage PA uptake (%PA), mechanical and thermal strengths, and proton conductivity, change with respective PBI types, on the other hand, the proton conductivity of PA-doped PBI membranes depends on the ADL, where more acid retained in the membrane leads to increased conductivity [4]. Li Q. et al. [5] demonstrated two alternative approaches to sulfonate the polymer backbone of the PBI membrane, one is post-polymerisation substitution of the polymer, another is synthetically modifying the benzimidazole monomers prior to polymerisation.

2.2. Challenges for PA Doped PBI Membrane

Bose et al. [6] studied recent challenges in the development of high temperature PEMs, e.g., the absence of humidification in high temperature PEMFCs will decrease proton conductivity, then causes large ohmic losses, where subsequently lower the efficiency of the PBI-based membrane. Hence the membrane will require water retention capacity, and offer a conducting path to ease the transport of protons crossover the membrane at lower relative humidity.

Proton conductivity increased subsequently at a high acid doping level (ADL), however, the membrane's tensile strength is lowered due to the plasticizing effect of PA [6]. Hence higher ADL means we have already jeopardised mechanical stability which significantly reduces PBI membrane performance and durability, ADL and membrane stability issue were remained as a challenge [7]. Moreover, due to PA remains in liquid-form embedded within the membrane's free volume, leaching occurs over the lifetime of usage [6].

Basis on the study of membrane electrode assembly (MEA), PA leaching appears on the cathode side of the membrane, in which water vapor produced from the cathode reaction can enhance the removal of PA. The more leakage rate occurs at a higher current density. Moreover, acid loss subsequently leads to higher cell resistance and conductivity drop [8].

Through researched several types of PBI, meta-PBI and ABPBI, dissolve poorly in common organic solvents, such as imethylformamide (DMF), dimethylacetamide (DMAc), and N-methyl-2-pyrollidone (NMP), affecting the process ability and membrane formation, which due to their rigid structure as well as high glass transition temperature. Nowadays, alternative acidic solvents have been utilized in improvement the effect of methane sulfonic acid (MSA), trifluoroacetic acid (TFA), formic acid (FA), and sulfuric acid (SA) as solvents for ABPBI was demonstrated by N. Ratikanta et al. group [9].

2.3. Improvements to PBI-based PEMs

Due to the PEM subjected to a faster rate of thermal and chemical degradation under high temperature conditions, PA loss while leaching and mechanical stress, more and more researchers have followed to improve the properties of PA-doped PBI, aiming to balance the acid uptake and proton conductivity with their physical properties, also overcome the solubility issue and slow down the acid leaching rate [6]. Researchers studied several PBI-based polymers with varying backbone structures have been synthesized in recent studies, such as utilized sulfonated PBI (SPBI), pyridine PBI (Py-PBI), PBI with ether bonds (OPBI), fluorinated PBI (F6-PBI), and branched PBI etc. Among these studies, crosslinking, introducing additional side-chains, blending, and filler additives have been applied and some of them have gotten a satisfied performance in stead.

X. Li et al. [10] studied additional benzimidazole groups onto the backbone of aryl-ether PBI (Ph-PBI) through an N-substituted reaction without catalysts, this polymer solubilities of Ph-PBI and grafted Ph-PBI were well demonstrated for most of the common solvents, ADL and proton conductivity have increased with a higher grafting degree. At 200 ℃, the conductivity of Ph-PBI with the maximum grafting degree reached 0.235S/cm.

H. Chen et al. [11] presented a dual proton transfer from a crosslinked membrane consisting of PBI with proton-donating and -accepting properties with polymeric ionic liquid (PIL) based on BuI-PBI and anion BF- as proton acceptors. This anionic part of PIL accept protons to enhance the PA capacity, and also accepting protons through electrostatic interaction. Hence, the anions of PIL facilitated proton transfer, the conductivity was increased.

Florian Mack et al. [12] attempted a novel acid-base blend membranes from the polybenzimidazoles F6PBI, PBIOO and PBI HOZOL for application in HT-PEMFCs. The synthesized blend membranes shows high thermal stability and drastically improved chemical stability compared to pure PBI and AB-PBI. After immersion for 144 hours, only slight changes in molecular weight distribution in Fenton's solution were detected with GPC. The review means these kind of acid-base blends are suitable as membranes for high temperature PEMFCs. However, the electrodes for the MEAs based on the blend membranes should be optimized to achieve higher cell performance than PBI or AB-PBI based MEAs, and pay attention to the development of novel catalyst layers containing the blend polymers, as binder to improve the three phase interlayer and the acid distribution in the electrodes [12].

Maya Staneva et al. [13] demonstrated PA doped para-PBI membranes, prepared with an easy and efficient procedure for reducing the doping. They start from a membrane with doping level 42.4 moles PA/PBI r.u. a series of membranes with reduced doping level (down to 17.2 moles PA/PBI r.u.) have been prepared, and the mechanical properties and proton-conductivity as function of the membranes doping level were studied. The proton conductivity has been performed at 160 °C and RH 10% and 15%, in the Figure 2 shows that decreasing the doping level does not affect considerably the proton conductivity. At RH 10% it remains practically unchanged (σ = 151 ÷ 155 mS·cm-1) for all doping levels [13].

Justo Lobato et al. [14] proposed a novel PBI based composite membrane with titanium dioxide and the results obtained and showed a high thermal stability. The sulphonated membrane and the composite membrane with 2% TiO_2 PBI reached the

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highest doping level at 15 mol H_3PO_4 per repeat unit of PBI and also showed the highest water uptake values under the same doping conditions. The result is that the sulphonated PBI membrane obtained the highest conductivity at 125 °C (0.18 S cm^{-1}), as shown in Figure 3 [14]. F. Javier Pinar et al. [15] also reported the composite membrane with 2% TiO_2 showed the highest cell performance at all operation temperatures as shown in Figure 4, better proton conductivity stability and also electrode stability over 150 h under our operating conditions. Furthermore, it has been demonstrated that reducing the acid leaching from the membranes by using inorganic fillers as micro-sized TiO_2, the degradation rate in the electrodes decreased. It means that a phosphoric acid doped 2% TiO_2 composite PBI based membrane is a promising candidate to operate as electrolyte in high temperature PEMs [15].

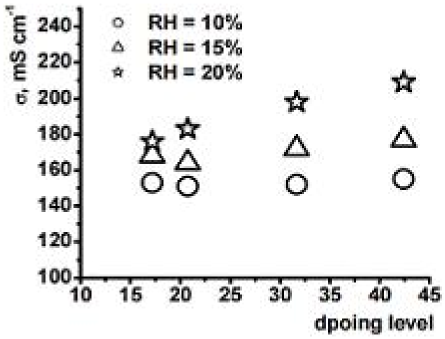

Figure 2. *Effect of doping level on proton conductivity at different relative humidity [13].*

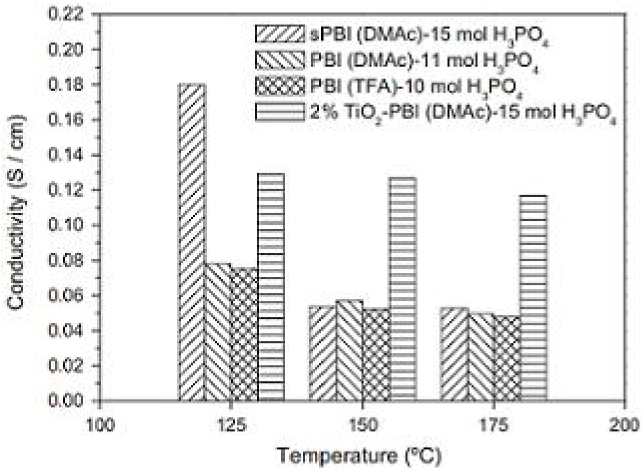

Figure 3. *Proton conductivity for PBI membranes at different temperatures [14].*

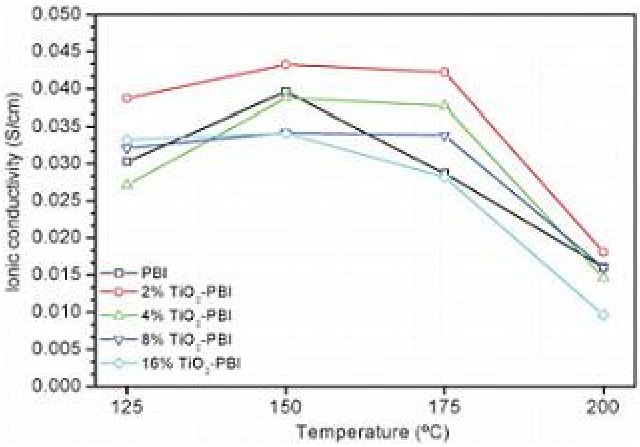

Figure 4. *Ionic conductivity values of the TiO2 composite membranes and the standard one at different temperatures. Acid bath = 75% wt [15].*

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Hooshyari et al. [16] demonstrated innovative composite membranes based on polybenzimidazole (PBI), they have proposed 2 membranes, PDC_3 containing dicationic ionic liquid 1,3-di (3-methylimidazolium) propane bis (trifluoromethylsulfonyl) imide, and PMC6 containing monocationic ionic liquid 1-hexyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide. These two types of composite membranes are as electrolyte for HT-PEMFCs applications under anhydrous conditions, which demonstrates high proton conductivity and thermal stability, and provide well-developed ionic channels which form facile pathways and thus considerably develop the anhydrous proton conductivity, due to the dicationic ionic liquid with a large number of charge carriers, this research for PA doped PDC_3 has attained proton conductivity of 81 mS/cm, which with PBI/IL mole ratio: 4 at 180 °C. Moreover, power density of 0.44 W/cm^2 is achieved at 180 °C for PA doped PDC_3 composite membranes, which shows these developed composite membranes can be considered as a promising candidates for HT-PEMFCs [16].

Chao Meng et al. [17] proposed a semi-interpenetrating network (semi-IPN) high-temperature proton exchange membrane based on polyethyleneimine (PEI), epoxy resin (ER), and polybenzimidazole (PBI), after characterized by thermogravimetric analysis (TGA) and tensile strength test, the prepared PEI-ER/PBI semi-IPN membranes shows excellent thermal stability and mechanical strength. After phosphoric acid (PA) doping treatment, the semi-IPN membranes show high proton conductivity. PA doping level and volume swelling ratio as well as proton conductivity of the semi-IPN membranes are found to be positively related to the PEI content. Their study has achieved high proton conductivity of 3:9 ∽ 7:8 × 10^{-2} S cm^{-1} at 160 °C for PA-doped PEI-ER/PBI series membranes. Figure 5 shows the polarization and power density curves of H_2/O_2 fuel cells obtained at 120 °C and 160 °C under anhydrous conditions [17].

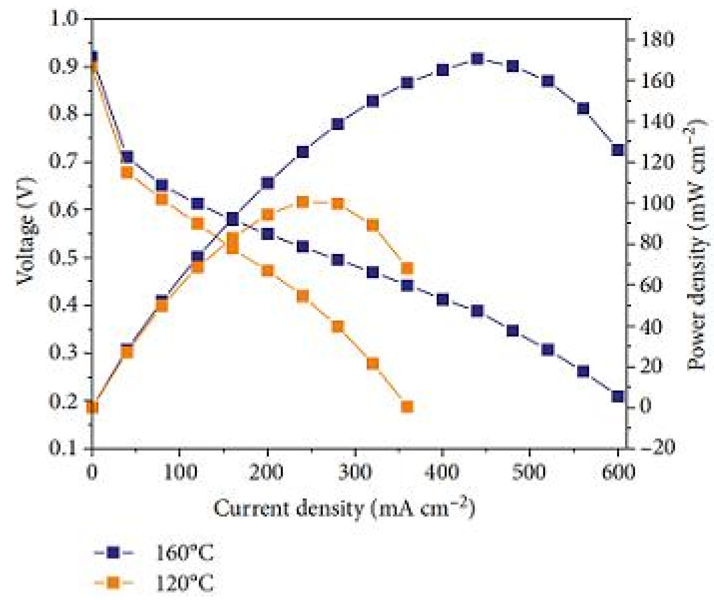

Figure 5. *Single cell performance of PA-doped PEI-ER(1 : 2)/PBI at 120 °C and 160 °C [17].*

3. Conclusions and Future Perspectives

In conclusion, as seen from the extensive review of PBI-based HT-PEMFCs conducted in recent years, developing PBI-based high temperature PEMs are able to overcome the shortcomings of low temperature PEMs like the Nafion® membrane, which shows high proton conductivity at high temperatures > 100 ℃, less depending on the water management control, ignored the evaporation of water, a wide tolerance to CO and other impurities.

Even though there are some challenges and issues at high temperature due to thermal and chemical degradation, mechanical stress and PA loss, PEMs derived from various composite polymers show multiple advantages. The different types of modification methods were addressed to enhance the performance of high temperature PEMs, which have observed improvements by electrochemical characteristics and durability tests. Their modified forms in long-term MEA tests at high temperatures, pressures, and fuel flows in actual working system of fuel cell stacks. The difficulty in commercializing PBI-based PEMs is due to the durability issues and mechanical and chemistry stability, still requires further research and continuous optimization.

The recent researchers studied the polymer solubilities of Ph-PBI and grafted Ph-PBI, which was demonstrated with high proton conductivity. A crosslinked membrane consisting of PBI with proton-donating and proton-accepting properties with polymeric ionic liquid (PIL) based on BuI-PBI and anion BF- as proton acceptors enhanced the PA capacity, and keep higher conductivity. Acid-base blend membranes from the polybenzimidazoles F6PBI, PBIOO and PBI HOZOL for application in HT-PEMFCs, which shows high thermal stability and drastically improved chemical stability after immersion for 144 hours. PA doped para-PBI membranes have been reported at 160 °C and RH 10% and 15%, the higher and stable proton conductivity has been performed. Composite membranes called PDC_3 and PMC_6 based on PBI, which shows high proton conductivity and thermal stability. PBI based titanium dioxide composite membrane obtained and showed a high thermal stability. The sulphonated membrane and the composite membrane with 2% TiO_2 PBI reached the highest doping level at 15 mol H3PO4 per repeat unit of PBI, this sulphonated PBI membrane obtained the highest conductivity at 125℃(0.18 S cm^{-1}), 2% TiO_2 showed the highest cell performance at all operation temperatures, better proton conductivity stability and electrode stability over 150 h. PA-doped PEI-ER/PBI membranes is also demonstrated as a promising alternative PEMs for HT-PEMFC application. The aforementioned studied methods shows their developed composite membranes can be considered as a promising candidates for high temperature PEM fuel cells.

Therefore, the above application and modification of commercial polymers through crosslinking, introducing additional side-chains, blending, and filler additives have been promoted. Furthermore, the filler additives still demand to play an important role to achieve and improve the mechanical stability as well as retaining the proton conductivity at high temperatures (120-200 ℃). The aforementioned additives form extensive interactions with polymer systems in PEMs, improving the polymer degradation and stability at high temperatures. These filler additives is better suited for high temperature PEMFCs due to their capability to improve the water retention capacity of the composite than pure membranes.

It is concluded that the properties of PBI and decreasing degradation rate can be improved and optimized by applying acid doping level techniques and suitable composites and additives, which can help developing a cost effective and commercializable PEMFCs. Therefore, PA doped PBI-based PEMs are considered as a very promising proton exchange membrane applied in high temperature fuel cells, especially in automotive industry and portable power supply.

Moreover, in future research of PBI-based PEMs at high temperatures, novel fillers such as SiO_2, CB, TiO_2, rGO and MWCNTs are recommended to be applied, and inherently forming extensive interactions to overcome the polymer degradation and leaching occurs over the lifetime of usage, thus maintain the mechanical and chemical stability while operating at high temperatures.

Conflicts of Interest

The author declares that there is no potential interest, and no conflict of interest regarding the publication of this article.

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