Progress of high temperature polybenzimidazole proton exchange membrane: a systematic review

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Abstract. Proton exchange membrane (PEM) is the core component of proton fuel cell. Generally speaking, ordinary PEM has the poor barrier to fuel (especially liquid fuel) and proton conduction has a strong dependence on water molecules. Compared with ordinary PEM, high temperature fuel cell works in high temperature non-water environment, which overcomes the above problems. Besides, the system is complex with low impurity and much simpler flow field design. Polybenzimidazole (PBI) not only meets the requirements of high temperature, but also has higher proton conductivity than ordinary PEM, i.e., is the best material for high temperature PEM. From this point of view, the properties and fabrication of PBI are systematically reviewed. Specifically, the factors influencing the performance of acid doped PBI high temperature PEM as well as existing problems (high temperature degradation as well as chemical oxidative degradation) are demonstrated. Furthermore, the corresponding solutions and future direction are put forward.

1. Introduction

PEM fuel cell (PEMFC) is the fifth-generation fuel cell developed after alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) [1, 2]. It has the advantages of simple structure, high energy conversion rate, low-temperature start-up, no electrolyte leakage and so on, i.e., become the preferred power source in many commercial fields. Therefore, the number of scholars in this field has gradually increased.

However, PEM has lots of defects, e.g., poor barrier to fuel (especially liquid fuel) and water molecules determined proton conduction [1, 2]. In this case, complex heat dissipation and humidification system are desired in the design of battery, which leads to various problems. Typically, high temperature PEMFC (HT-PEMFC) operates at high temperature (100-200 °C) without humidity [3]. Compared with traditional low temperature PEMFC, it has the advantages of low CO poisoning probability, high catalyst efficiency, simple water heat management and strong resistance to fuel impurities [3, 4]. As a matter of fact, polybenzimidazole (PBI) is one of the feasible approaches to realize the HT-PEMFC [5, 6]. It is a kind of aromatic heterocyclic polymerization containing benzimidazole group, which mainly plays the role of isolating both electrodes and transferring protons.

Contemporarily, lots of great progresses have been achieved in terms such the approach. Therefore, the recent developments and the gaps are reviewed in this perspective. In detail, this review is organized as follow: the properties as well as fabrication of PBI will be introduced in Sec. 2; the acid doping PBI for HT-PEMFC and its characteristic (proton transfer ability & thermal stability) will be discussed in Sec. 3; two issues (high temperature degradation and chemical oxidative degradation) needed to be addressed are demonstrated in Sec. 4 and Sec. 5, respectively; the future development suggestions are...
proposed in Sec. 6; finally, a brief summary is presented in Sec. 7.

2. Properties and fabrication of PBI

Figure 1 The two proton conduction mechanisms of PBI: (a) transport mechanism; (b) jump mechanism [8]

![Figure 1](image1.png)

Polybenzimidazole (PBI) is an aromatic heterocyclic polymer with benzimidazole repeating unit in the main chain of polymer [7]. The aromatic main chain exhibits the high mechanical stability and chemical stability, which satisfies the operating conditions of high temperature fuel cell. In order to provide proton transport channel to achieve effective proton transfer, HT-PEMFC should be doped with

Figure 2 Common types of PBI in HT-PEMFCs [9]

![Figure 2](image2.png)
PBI based on acid medium. Specifically, the basis of proton conduction is that the N atom in the imidazole ring of the substituent is easily protonated under acidic conditions, which forms a network like positive structure. The two major proton conduction mechanisms (transport mechanism and jump mechanism) are shown in Fig. 1 (collected from Ref. [8]). In terms of driving force of proton conduction, the two mechanisms both rely on the synergistic effects of the electric field force. The difference between the mechanisms is reflected in the microscopic process of conduction. Specifically, the proton is transferred with a carrier in the membrane (usually H2O) for transport mechanism while through the continuous formation and fracture of hydrogen bonds for jump mechanism. In high temperature fuel cells, PEMFC doped PBI with phosphoric acid not only plays the role of proton transfer, but also has excellent thermal stability at high operating temperature to ensure the continuous and stable operation of fuel cells [8]. The common structures of PBI polymers utilized in HT-PEMFCs are presented in Fig. 2, among which mPBI and abPBI are the most commonly types [9].

3. Acid doping PBI for HT-PEMFC
Generally, the proton conductivity of PBI is only about 10-9ms·cm-1 [10], i.e., too low to be used as an independent solid electrolyte. Phosphoric acid is a good electrolyte with high thermal stability. To be specific, proton conductivity increases with the augment of temperature [11] and reaches 800ms·cm-1 at 200℃ [12]. In 1961, Vogel and Marvel synthesized PBI for the first time [13]. In 1995, Wayneright et al first applied phosphoric acid doped PBI membrane to HT-PEMFC and synthesized mPBI [14], which opened a new hot spot of PBI application research. Since then, phosphoric acid has become the first choice of acid dopants due to the high thermal stability and low vapor pressure at high temperature. The proton conductivity of PBI membrane doped with impurity acid was close to 0.1s/cm in the temperature range of 100 ~ 200℃. In this case, the requirements of high temperature fuel cell system are fulfilled. Besides, it is found that the order of proton conductivity of PBI doped HT-PEMFC with protonic acid is H2SO4 > H3PO4 > HClO4 > HNO3 > HCl [15]. In addition, the proton conductivity of phosphoric acid is the best at low humidity. Whereas, the maximum proton conductivity of sulfuric acid doped PBI membrane can exceed 0.2s/cm even under the condition that relative humidity is more than 50% [15]. In a word, phosphoric acid doped PBI HT-PEMFC combines the characteristics of low volatility and high proton conductivity of phosphoric acid with the excellent thermal stability of PBI materials. Thus, phosphoric acid is taken as an example to discuss the properties of phosphoric acid doped PBI for HT-PEMFC.

4. Proton transfer ability of phosphoric acid doped PBI for HT-PEMFC
Fig. 3 schematically illustrated the proton conduction mechanism of phosphoric acid doped PBI for HT-PEMFC [16]. According to the molecular structure of PBI, there are two N-H reaction sites in each repeating unit of benzimidazole. Therefore, it can adsorb two phosphate molecules to form unphosphate N=C transfer, which leads to low proton conductivity. In this case, the proton can pass through H2PO4-H+ H2PO4- and/or H2PO4-H+H2O, i.e., migrates freely in the membrane with high proton conductivity [15]. This mechanism was verified by the experimental results of proton conductivity of different molecular weight PBI membranes doped with phosphoric acid at different temperatures. The proton conductivity of PBI for HT-PEMFC with molecular weight of 3.7×104 is 0.046s/cm and 0.138s/cm at 180℃ with acid doping amount of 5.7 and 11.5 moles of phosphoric acid per mole of polymer repeating unit, respectively. Compared to the Nafion membrane, it is about a few orders of magnitude larger.
Figure 3 Proton conduction mechanism of (a) H3PO4 and (b) phosphoric acid doped polybenzimidazole membrane [16]

5. Thermal stability of phosphoric acid doped PBI for HT-PEMFC

Phosphoric acid doped PBI for HT-PEMFC has excellent thermal stability, which is able to work stably at higher temperature than 100˚C [15, 17]. In the TGA experiment [18], it lost the adsorbed water near 100˚C and dehydrated with phosphoric acid at 200-250˚C. Besides, the decomposition of the polymer itself occurred at about 600˚C. Additionally, the thermal decomposition behavior of the composite film at high temperature was tested. As given in Fig. 4(a), the initial thermal decomposition temperature of PBI film is about 580˚C. However, the initial thermal decomposition temperature decreases to about 180˚C; the first decomposition process lasts to 530˚C and the residual mass is close to 80% for PWA-LI composite film. The disappeared mass of 20% corresponds to the mass of PWA-LI in the composite film, which indicates that PWA-LI is mainly degraded during this period. The thermal stability of PBI/(PWA-LI) composite membrane is as high as 170˚C, which meets the requirements of fuel cell application (<100˚C). Furthermore, the DSC test of the composite membrane shows that the glass transition of PBI and PBI (PWA-LI) composite membrane does not occur in the temperature range of 100-300˚C. This conclusion can also be confirmed by nuclear magnetic resonance spectroscopy [18]. The 13C NMR spectra of the phosphate doped high temperature PEM were almost unchanged after heating at 250˚C for an hour, denoting that PBI still has good high temperature stability in the acid doped state. Moreover, the proton conduction is thermal sensitive, which increases with the increase of temperature, especially for carboxyl group [19].

6. High temperature degradation of PBI-PEMFC

Although PBI-PEMFC has lots of advantages, there are some drawbacks should be mentioned. The first one is temperature degradation (also known as Thermal degradation) [3, 15]. It refers to the degradation of polymer materials caused by thermal action. Generally speaking, PBI membrane has good thermal...
stability. Nevertheless, the chemical bond between carbon and amine nitrogen (NH) (connected by imidazole ring and phenylene) on PBI molecular chain is easy to break after higher than 600 ℃. Thus, it results in the fracture of polymer skeleton and collapse of membrane structure [20]. Besides, it should be noted that the phosphoric acid in the membrane tends to dehydrate and condense to form polyphosphoric acid if the temperature is higher than 140 ℃ [18]. Furthermore, the self-dehydration phenomenon of 2H3PO4 = H4P2O7+H2O (g) will lead to the decrease of proton conductivity in the membrane and the change of membrane mechanical strength. In the high temperature conditions, the decrease of proton conductivity in the membrane will directly affect the performance of the battery. Moreover, the change of local membrane mechanical strength will also increase the possibility of mechanical damage to the membrane.

7. Chemical oxidative degradation of PBI-PEMFC

Another issue ought to be addressed is chemical oxidative degradation [3, 15, 21, 22], which has a significant effect on the battery life. It has been found that the low current density and high potential of the battery can affect the chemical oxidative degradation rate and mode of the PEM. One feasible solution is to using composite. According to Ref. [23-25], Fourier transform infrared spectroscopy is used to analyze the effect of electric field environment on the oxidative degradation of PBI molecular structure. As depicted in Fig. 5 [24], the mass loss of PBI-CeO2 composite membrane was lower than that of pure PBI membrane, indicating that the addition of CeO2 was beneficial to improve the oxidation resistance of the membrane. The molecular structure of PBI-CeO2 composite membrane before and after degradation was characterized by XPS and FTIR, which confirmed that the degradation of PBI followed the mechanism of intermediate chain break. Similar results are also reported in Ref with XRD techniques [26].

![Figure 5](image.png)

Oxidation degradation evolution for PBI and PBI-CeO2 [24]

8. Improvement direction of polybenzimidazole PEM

The proton conductivity of PBI membrane mainly depends on its phosphoric acid doping content [27]. With regard to HT-PEMFC, it is necessary to dope as much phosphoric acid as possible to ensure high proton conductivity [28]. However, as mentioned above, high phosphoric acid doping content will cause the rapid decline of mechanical strength. Thereby, it will increase the loss rate of phosphoric acid in the operation of the cell and affect the overall performance of the cell. In addition, the doped phosphoric acid is easy to be lost, which affects the working life [29]. In other words, the mechanical strength and dimensional stability of the film decrease after doping phosphoric acid. Therefore, it is necessary to improve the phosphoric acid doping level of PBI for HT-PEMFC on the premise of high mechanical strength. Moreover, reducing the loss rate of phosphoric acid is also urgent to ensure the high proton conductivity and stability of fuel cell.

Grafting is an effective method to improve the phosphoric acid doping level of PBI for HT-PEMFC [31, 32]. Grafting a large volume of side groups onto PBI molecular chain moderately will break the close packed structure of PBI molecular chain. By this mean, the free volume of PBI membrane is
increased, that is, the phosphoric acid doping level, proton conductivity and battery performance of PBI membrane are improved [32]. However, the existing PBI grafted modification generally has the problem that the grafted side chain does not participate in proton conduction, which affects the proton transport of PBI membrane. In addition, the loss rate of phosphoric acid increases with the increase of doping level, which greatly reduces the proton conduction stability of PBI membrane. On this occasion, further scenarios or approaches should be proposed for the sake of controlling the doping level.

9. Conclusion
In summary, the progress of HT-PEMFCs based on PBI has been discussed including its principals, performances, drawbacks as well as future directions. In detail, the basic descriptions and fabrication methods of PBI as PEMs have been introduced, which possess advantages in lots of aspects. Specifically, the performances on proton conductivity and thermal stability have been demonstrated. Besides, the shortcomings in degradation are evaluated from the perspective of thermal and chemical oxidative. Moreover, the suggestions for future research are given, that is, reducing the degradation rate and increasing the acid impurity rate. In this case, the performances of HT-PEMFCs will be improved, which will contribute to the practical application of clean energy. These results will offer a guideline for the PEMs development.

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